# REVIEWS OF

# MODERN PHYSICS

# Multiple Scattering of Waves*

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(Received November 9, 1950)

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## I. INTRODUCTION: PREVIOUS WORK

### A. Particle Scattering

THE multiple scattering of particles by a distribution of scatterers has been studied extensively.†
Applications have been made to scattering of molecules in gases,[1] neutron diffusion,[2] radiative equilibrium in

stars,[3] charged particles,[4] gamma-rays,[5] cosmic-ray shower theory,[6] and resistivity of conductors.[7]

These problems have been treated by the Boltzman integro-differential equation for transport processes. The derivation of this equation requires the assumption of binary collisions and molecular chaos[8] (a lack of correlation between the positions of scatterers). In addition the treatment is classical in that the wave nature of the incident particles (or light) is neglected. Such a "ray" treatment of a wave problem will be valid for wavelengths small compared to the separation between scatterers. For larger wavelengths a wave treatment is desirable since the diffraction pattern will contain information concerning the correlation in scatterer positions.

The purpose of this paper is to develop a general, systematic treatment of the multiple scattering of waves. We shall assume that the properties of the individual scatterers are known—i.e., that the single scattering problem has been solved either experimentally or theoretically. We shall assume that the structure of the scattering system (gas, liquid, or solid) is given in the form of a many particle density function. Actually we shall use here only the one and two particle densities—i.e., the probability of finding a particle at a certain point, and the probability of finding a pair of particles at certain positions. Our problem is to relate

† References to this paper are not intended to be complete nor to indicate priority, but to serve, directly or indirectly, as a useful guide to the literature on multiple scattering.

[1] S. Chapman and T. C. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Teddington, 1939).
[2] R. E. Marshak, Revs. Modern Phys. 19, 185 (1947). O. Halpern and R. K. Luneburg, Phys. Rev. 76, 1811 (1949). Marshak, Brooks, and Hurwitz, Nucleonics 4, 10, 43 (1949); 5, 53, 59 (1949). See these papers for references to earlier work.
[3] E. Hopf, "Problems of radiative equilibrium," Cambridge Tract No. 31 (1934). S. Chandrasekhar, *Radiative Transfer* (Oxford University Press, London, 1950).
[4] H. S. Snyder and W. T. Scott, Phys. Rev. 76, 220 (1949).
[5] U. Fano, Phys. Rev. 76, 739 (1949). W. R. Faust, Phys. Rev. 77, 227 (1950).
[6] B. Rossi and K. Greisen, Revs. Modern Phys. 13, 240 (1941). H. S. Snyder, Phys. Rev. 76, 1563 (1949).
[7] E. Conwell and V. F. Weisskopf, Phys. Rev. 77, 388 (1950). A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Teddington, 1936).
[8] A more general theory of transport processes has been developed and applied to the theory of the liquid state. J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946); 15, 72 (1947). M. Born and H. S. Green, Proc. Roy. Soc. (London) A188, 10 (1946).

the density and directionality of the scattered waves to the properties of the individual scatterers and the structure of the system. In particular, we shall calculate the index of refraction and attenuation of the coherent beam.

## B. The Coherent Wave

The multiple scattering problem divides naturally into a consideration of the coherent and incoherent radiation. The solution of the coherent problem bridges the gap between molecular and continuum physics by proving that a collection of scattering molecules can be replaced by a medium with an index of refraction. Born[9] has calculated the index of refraction for light waves in an isotropic homogeneous medium consisting of dipole scatterers. Ewald[10] has considered the case of dipole scatterers distributed on a lattice for the x-ray as well as the optical case. The presence of Bragg reflections in the x-ray case means that the conventional medium point of view is not applicable unless the dielectric constant is treated as a periodic space function.[11]

Foldy[12] has treated the multiple scattering of scalar waves (e.g., sound) by isotropic, elastic scatterers (e.g., bubbles) that are distributed in a random fashion. He finds that the propagation constant in the medium $k'$ differs from its value $k$ when no scatterers are present according to the relation,

$$(k')^2 = k^2 + 4\pi n f, \tag{1B1}$$

where $n$ is the density of scatterers and $f$ is the scattering amplitude, which for his case is independent of direction.

We have followed Foldy's procedure and generalized it to include the following possibilities: (1) anisotropic scattering, (2) inelastic scattering, (3) scattering of quantized waves including photons, (4) creation and absorption of particles as in cosmic rays, (5) motion of the scatterers, and (6) scatterers that are randomly, partially, or completely ordered.

Our result for the index of refraction $k'/k$ is given by

$$(k')^2 = k^2 + 4\pi n c [f(a \leftarrow a)], \tag{1B2}$$

where $f(a \leftarrow a)$ is the elastic scattered amplitude in the forward direction (even if inelastic scattering is also present). The correction factor $c$ is defined by

$$c = (\text{effective field})/(\text{coherent field}) \tag{1B3}$$

where the effective field acting on a given scatterer depends on the correlation between scatterer positions. If the scatterers are distributed completely at random the constant $c$ will be essentially unity.

Actually scatterers cannot be distributed completely at random because they have finite size and are (approximately) impenetrable. However in the limit as size becomes small (compared to the separation) $c \rightarrow 1$. In the electromagnetic case, however, it is well known that the field inside a small cavity differs from the external field regardless of how small the cavity is. In the limiting case, using certain approximations[13] $c \rightarrow [\mathbf{E} + (4\pi/3)\mathbf{P}]/\mathbf{E} = (\epsilon + 2)/3$. Thus the equation analogous to (1B2) for the dielectric constant

$$\epsilon = 1 + 4\pi n c \alpha \tag{1B4}$$

reduces to the Lorentz-Lorenz law

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3) n \alpha, \tag{1B5}$$

where $\alpha$ is the polarizability of the atom.

The Lorentz treatment[13] of the effective field has been extensively applied by Debye and others to the problem of the dielectric constant of liquids.[14] Onsager[15] improved the Lorentz treatment for dipolar liquids by taking explicit account of the reaction field—i.e., the action of a molecule on itself through the polarization it induces in the surrounding medium. The Onsager viewpoint is frankly phenomenological in that he treats all but the chosen molecule as a medium. Kirkwood[16] has made an explicit attempt to take into account interactions between neighboring molecules, treating more distant molecules as a medium. Frenkel[17] gives an excellent summary of the various viewpoints.

The major generalization made by this paper is the treatment of anisotropic scatterers. The use of the effective field factor $c$ is no more rigorous than that of previous authors—except that in this paper it is a clearly stated approximation relating well-defined symbols. A more detailed discussion will be given in a paper devoted specifically to the effective field problem.[17a] We shall anticipate this paper by remarking that the use of such a constant $c$ (which may be wavelength dependent) is strictly legitimate for point scatterers: In the latter case one compares the effective field and the coherent field at a point. For non-point scatterers such a comparison must be made over a region comparable to the size of the scatterer (or the range of the interaction potential). In short, a detailed calculation of the spatial distribution of the effective field must be carried out. The way in which the equations of this paper may be applied to estimating the constant $c$ or the spatial distribution of the effective field will be discussed in the "effective field" paper.[17a] For the present, it seems

[9] M. Born, *Optik* (Verlag. Julius Springer, Berlin, 1933), pp. 313 ff.

[10] P. P. Ewald, Ann. Physik **49**, 4 (1916). M. Born and M. Goeppart-Mayer, Handbuch der Phys. 24/2, Chapter 4, Section 57. Reference 9, p. 327 ff.

[11] M. Von Laue, *Rontgenstrahlinterferenzen* (Akademische Verlagagesellschaft, Leipsig, 1941).

[12] L. L. Foldy, Phys. Rev. **67**, 107 (1945).

[13] H. A. Lorentz, *The Theory of Electrons* (B. G. Teubner, Leipzig, 1916), second edition, p. 137.

[14] P. Debye, *Polar Molecules* (Dover Publications, New York, 1945).

[15] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936). W. H. Rodebush and C. R. Eddy, J. Chem. Phys. **8**, 424 (1940).

[16] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939). See also G. Oster, J. Am. Chem. Soc. **68**, 2036 (1946).

[17] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), Chapter 5.

[17a] Phys. Rev. (to be published).

worthwhile to indicate how much progress can be made in treating anisotropic scatterers without improving on the effective field approximations of previous authors.

## C. Index of Refraction for Neutrons

The diffraction and refraction of neutrons in crystals, including polarization phenomena, were treated extensively by Halpern[18] and co-workers Hamermesh,[19] Johnson,[20] and Holstein.[21] Using the usual method of determining the phase shift introduced by a thin sheet of scatterers (see Sec. V) they calculated the index of refraction for neutrons in nonmagnetic crystals.[19] The same technique was also applied to ferromagnetic materials and a pair of indices of refraction were obtained corresponding to the two possible neutron spin states.[19] The difference between the two indices of refraction (corresponding to the neutron spin precession) was found proportional to the magnetization $M$. They point out[19] that their result must be corrected for the additional precession induced by $H$ and that the correct result is proportional to the magnetic field $B$.

H. Ekstein[22] has objected to the use of the thin sheet method in the presence of long range magnetic forces and has treated the ferromagnetic case by a rigorous method similar to that used by von Laue in the latter's theory of x-ray diffraction.[23] Ekstein verifies Halpern's result that the index of refraction contains a term proportional to $B$. He shows clearly that the index of refraction depends on the magnitude of $B$ and not on its orientation relative to the neutron propagation direction.

The ferromagnetic case is an interesting test of any general method of calculating indices of refraction because of an ambiguity that arises in evaluating the forward scattered amplitude.[22] The method used in this paper obtains unambiguous results by adding the contributions of the individual scatterers before passing to the forward direction.[24] Our result,[24] in agreement with previous authors, is that the index of refraction $(k'/k)$ is determined by

$$(k'/k)^2 = 1 - c[V_{Av} \pm |\mathbf{B}_{Av}|]/E, \qquad (1C1)$$

where $V_{Av}$ and $\mathbf{B}_{Av}$ are the macroscopic average nuclear potential and magnetic field; $E = (\hbar k)^2/(2m)$ is the neutron energy. Full agreement with the results of previous authors may be obtained by approximating the effective field factor $c$ by unity.

Experimental determinations of index of refraction have been made using critical angle measurements from neutron mirrors. A word of caution about comparison between theory and experiment: Magnetic fields will inevitably be present outside as well as inside the crystal. The relative index of refraction will then be determined by the jump in $B$ at the boundary—and the latter will depend on the orientation of $\mathbf{B}$ relative to the boundary. In fact for $\mathbf{B}$ normal to the boundary, there is no discontinuity in index of refraction (aside from nuclear effects) and hence no double refraction. For $\mathbf{B}$ tangential to the boundary, the discontinuity in $B$ is essentially $\mathbf{M}$. In the latter case, which is feasible experimentally there are several possible neutron propagation directions. The critical angle, according to the above theory, should be independent of these propagation directions.

Ekstein has suggested[23] that perhaps the correct neutron-electron interaction is of the form $\mu\boldsymbol{\sigma} \cdot (\mathbf{H} + 4\pi C\mathbf{M})$ rather than $\mu\boldsymbol{\sigma} \cdot \mathbf{B}$ where $C$ is a constant to be determined experimentally, and $\mathbf{H}$, $\mathbf{B}$, and $\mathbf{M}$ are the magnetic fields and the magnetization produced by the electrons. This is certainly a matter that can be settled by index of refraction measurements. This author personally favors the customary choice $C = 1$.

Goldberger and Seitz[25] have treated the neutron refraction in a crystal in which only nuclear (isotropic) scattering takes place. The virtue of their treatment is that they have taken proper account of the effective field in their formulation and in most of the stages of their calculation. Near the end, however, they neglect all terms of higher order than the first in the scattering amplitude. This approximation is exceedingly good for any reasonable experimental situation. Unfortunately, the effective field correction is in this case a *small* correction, and a more accurate treatment is necessary. More accurate results can be obtained directly from their equations. These results for the crystalline cases are mentioned briefly in Sec. V and the method used will be discussed in the "effective field" paper.[17a]

These authors and others dealing with neutron diffraction (references 48–52) describe the interaction between neutrons and nuclei by means of the Fermi pseudo-potential,[26] e.g., a square well shallow enough for low energy neutrons to be treated in Born approximation. They later replace the square well by a Dirac delta-function, chosen in such a manner as to preserve scattering amplitudes. These approximations are valid if

$$f \ll a \ll \lambda, \qquad (1C2)$$

where $f$ is the scattering amplitude, $a$ the well radius, and $\lambda$ the wavelength. These conditions can be satisfied in the desired experimental range.[27]

In the treatment of anisotropic as well as inelastic scattering, the introduction of a pseudo-potential is difficult if not impossible. It is far more convenient to work directly with the scattering amplitudes $f(b \leftarrow a)$ or

[18] O. Halpern, Phys. Rev. **76**, 1130 (1949).
[19] Halpern, Hamermesh, and Johnson, Phys. Rev. **59**, 981 (1941).
[20] O. Halpern and M. H. Johnson, Phys. Rev. **51**, 992 (1937); **52**, 52 (1937); **55**, 898 (1939).
[21] O. Halpern and T. Holstein, Phys. Rev. **55**, 601 (1939); **59**, 960 (1941).
[22] H. Ekstein, Phys. Rev. **78**, 731 (1950).
[23] H. Ekstein, Phys. Rev. **76**, 1328 (1949).
[24] M. Lax, Phys. Rev. **80**, 299 (1950).

[25] M. L. Goldberger and F. Seitz, Phys. Rev. **71**, 294 (1947).
[26] E. Fermi, Ricerca sci. **7**, Part 2, 13 (1936).
[27] H. Bethe, Revs. Modern Phys. **9**, 123 (1937).

with the corresponding transition matrix $T_{ba}$.[28,29] The transition matrix provides a direct relation between the incident and scattered state for any sort of collision. It is closely related to the Heisenberg scattering matrix and the collision matrix.[29]

## D. Coherence and Incoherence

Before proceeding to discuss the experimental and theoretical work on incoherent scattering it will be well to indicate clearly the distinction between coherent and incoherent scattering. The author begs the reader's indulgence at this point for reviewing well known material. It will appear later, however, that a comparison between the multiple scattering and the quantum-mechanical viewpoint toward incoherent scattering can be made the basis for understanding the limitations of a multiple scattering type of calculation.

We wish to discuss a system of scatterers whose centers are located at $r_1, r_2 \cdots r_n$. These scatterers need not be point scatterers, and may have a complex internal structure. If the initial states of these scatterers are different it will be convenient to describe this by a set of parameters $s_1, s_2, \cdots s_N$. The parameter $s_1$ can be used as a shorthand notation for all the quantum numbers that describe the state of scatterer 1. If several types of scatterers are present (as in an alloy $Cu_3Au$, or an isotopic mixture), it is convenient to regard them as several states of a single scatterer. In classical problems the parameter $s_1$ can be continuous: for example, it may represent the size of the scatterer. In general we shall have to deal with distributions of scatterer states as well as distributions in scatterer locations. Certain averages will have to be performed over these distributions. It is clear that the procedure followed in treating the parameter is identical to that followed in treating the location. Incoherence can be produced by parameter randomness just as it can by randomness in particle location. The treatment of short range order of spins in a paramagnetic crystal is analogous to the treatment of short range order of positions in a liquid. We can simplify the following discussion, therefore, by concentrating our attention on position.

It is rather obvious that waves scattered inelastically from two scatterers cannot interfere because of the different frequencies of the scattered waves. It is less obvious, but also well known, that incoherence between the two scattered waves will be produced if either scatterer changes its internal state, regardless of whether an energy change is involved. An excellent discussion of this point is given, for example, by G. Breit.[30] Whenever, a change in the internal state of a single scatterer is involved we may therefore describe the radiation as *strictly* incoherent. It is then permissible to

add intensities, and there is little difference between the particle and the wave point of view toward the problem.

Let us restrict our attention, therefore, to that portion of the scattering in which the internal states of the scatterers are unmodified. A diffraction pattern will now be produced because of the *relative coherence* of the scattered waves providing there is some order to the space arrangement of the scatterers.

For the purposes of the present paper, it is also useful to introduce the concept of *absolute coherence*. Scattering will be described as *absolutely coherent* if the scattered beam bears a definite phase relation to, and hence can be made to interfere with, the primary beam.

The complete solution of the scattering problem $\psi(r; r_1, \cdots r_N)$ is a function of the position of observation $r$ and an implicit function of the scatterer locations as well. The total density of radiation can be computed by squaring the wave function and averaging over the ensemble of scatterer distributions $\langle |\psi(r; r_1, \cdots r_N)|^2 \rangle$. If we were to perform an interference experiment with the incident wave $\phi(r)$ the total radiation density would have the form:

$$\langle |\phi(r) + \psi(r; r_1, \cdots r_N)|^2 \rangle$$
$$= |\phi + \langle \psi \rangle|^2 + \langle |\psi|^2 \rangle - |\langle \psi \rangle|^2. \quad (1D1)$$

This arrangement of terms indicates that $\langle \psi \rangle$ interferes with the main beam $\phi$ and may be regarded as absolutely coherent. $|\langle \psi \rangle|^2$ is the absolute coherent density, and $\langle |\psi|^2 \rangle - |\langle \psi \rangle|^2$ is the density of radiation that is not absolutely coherent.

If the scatterers have perfectly definite positions, e.g., a crystal at absolute zero, there will be no uncertainty in phase. In this situation it makes no difference whether we square first and then average, or reverse the procedure. All of the radiation can be regarded as absolutely coherent.

In the case of a liquid, the density of scatterers $n(r)$ can be regarded as a constant. The structure of the liquid expresses itself in the fact that the correlation density $n(r_1, r_2)$ for a pair of particles differs from the product of the individual densities $n(r_1)n(r_2)$. For a liquid $\langle \psi \rangle$ turns out to be the attenuating main beam. The difference $\langle |\psi|^2 \rangle - |\langle \psi \rangle|^2$ contains a term that corresponds to the addition of intensities, plus a term proportional to $n(r_1, r_2) - n(r_1)n(r_2)$. The latter term yields a diffraction pattern which corresponds to the *relative coherence* of scattering from a liquid molecule and its near neighbors. For a completely random distribution of scatterers $n(r_1 r_2) - n(r_1)n(r_2)$ vanishes and $\langle |\psi|^2 \rangle - |\langle \psi \rangle|^2$ contains only an intensity sum similar to that produced by the strictly incoherent addition of intensities from the individual scatterers.

## E. Multiple Scattering *versus* the Many Body Problem

The interaction of a wave with a many particle quantum-mechanical system can be treated from the many body viewpoint, i.e., interaction with the system

[28] Melvin Lax, Phys. Rev. 78, 306 (1950).
[29] B. A. Lippman and J. Schwinger, Phys. Rev. 79, 969 (1950).
[30] G. Breit, Revs. Modern Phys. 5, 91 (1933). See especially Sec. VII.

as a whole. This viewpoint is always permissible. On the other hand it is often desirable to use the multiple scattering viewpoint: the interaction is visualized in terms of a succession of scattering events. The multiple scattering viewpoint has the advantage of expressing a complex problem in terms of the properties of the individual scatterers. This important advantage has led to its use in a variety of problems involving sound, light, x-rays, and neutrons. The purpose of this section is to indicate qualitatively the assumptions that restrict the validity of the multiple scattering viewpoint.

One of the assumptions tacitly made in a multiple scattering problem is that the properties of the individual scatterer are unmodified by the fact that it is bound in a many particle system. This assumption can sometimes be removed if the modification in scatterer properties is properly accounted for. An example in which such a modification has been treated is the scattering of neutrons by a molecule of ortho or pera hydrogen.[31] This example is treated from the multiple scattering viewpoint in that scattering amplitudes are added from the two protons. The modification in scattering properties of the individual protons due to their bond is referred to as the chemical bond effect.

Another assumption tacitly made in a multiple scattering problem is that the scatterers move sufficiently slowly that their positions may be regarded as adiabatic parameters, i.e., that the scattered wave $\psi(\mathbf{r}; \mathbf{r}_1 \cdots \mathbf{r}_N)$ may be computed for a *fixed* set of scatterer position, and then the result averaged over the distribution of scatterer positions in time, or in configuration space. This assumption seems to be valid if the motion of a scatterer during one period of the radiation is small compared to the wavelength of the radiation, i.e., if the velocity of the scatterer is small compared to the velocity of the wave.

The multiple scattering viewpoint is a kinetic viewpoint and does not take into account adequately the energy-momentum considerations involved in a collision. To explain this point, it is necessary to make some comparison between the multiple scattering and the many-particle quantum-mechanical viewpoints. The simplest way to do this is to note that the coherent amplitude $\langle \psi(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) \rangle$ involves an average over the distribution of scatterer positions. This distribution is, in fact, described by the initial quantum mechanical state $|i\rangle$ of the scattering system. The coherent wave may therefore be denoted by $\langle i|\psi|i\rangle$, and the density of radiation by $\langle i|\psi^*\psi|i\rangle$. On the other hand, from the many body viewpoint the wave $\psi$ acts as a perturbation that induces transitions of the scattering system from its initial to all possible final states $|f\rangle$. The equality of the two results:

$$\langle i|\psi^*\psi|i\rangle = \sum_{all\ f} |\langle f|\psi|i\rangle|^2 \qquad (1E1)$$

is a closure theorem that follows directly from the rules of matrix multiplication.

The disagreement between the multiple scattering and the many body viewpoint follows from the fact that the closure theorem (1E1) is valid only if the sum is carried out over all final states. The many body perturbation calculation requires, however, that the sum be carried only over those final states that conserve energy.

It is now necessary to understand why the multiple scattering viewpoint works at all! If the momentum associated with the incident wave is large compared to the momentum of the individual scatterers, then it will turn out that the transition matrix elements will have a strong resonance for those final states that approximately obey energy conservation. Thus the sum over all final states will not differ appreciably from the sum over those that conserve energy—and the multiple scattering viewpoint becomes applicable. In the case of x-ray scattering by atoms, this approximate resonance manifests itself in a Compton line that is broadened by the momentum of the electrons within the atom.[32] The integrated intensity of the broadened Compton line is approximately the same as if it had not been broadened, i.e., the closure approximation is valid.[32] Thus it is permissible to treat the scattering of x-rays by an atom as a multiple scattering problem, i.e., by the addition of amplitudes appropriate to the individual electrons.[33]

If the momentum of the incident wave is small compared to the rms momentum of the scatterers, then the resonance line becomes very broad. So broad, in fact, that not all of the line is within the energetically permitted region. The decrease in integrated intensity of the line represents the failure of the closure approximation. A more detailed discussion of this decrease from closure is presented in Sec. VII. The condition that the incident photon momentum $h\nu/c$ be larger than the electron momentum $(2mE)^{\frac{1}{2}}$ for the usual electron kinetic energies within atoms $E$, is easily satisfied in the x-ray region, and completely invalid in the optical region.

In this section, in which we are discussing the limitations of the multiple scattering viewpoint, the author has deliberately chosen a system, such as an atom, in which the individual scatterers, the electrons, overlap each other considerably. In fact, the author and H. Feshbach[34] have applied a multiple scattering type of calculation to the production of mesons in a photonuclear collision—for which closure corrections are appreciable (see Sec. VII).

It is far more customary, however, to apply multiple

[31] See for example, H. Bethe, *Elementary Nuclear Theory* (John Wiley and Sons, Inc., New York, 1947), Chapter X.

[32] I. Waller, Phil. Mag. **4**, 1228 (1927); Z. Physik **79**, 370 (1932). I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) **A124**, 119 (1929).
[33] This has been done, for example, by W. H. Zachariesen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1944), pp. 91 ff.
[34] M. Lax and H. Feshbach, Phys. Rev. **81**, 189 (1951).

scattering methods to macroscopic systems (e.g., crystals) in which the individual scatterers are molecules rather than electrons, or nuclei rather than nucleons. In this way, a fairly large unit is treated by many body methods, avoiding closure corrections. And one has the advantage of dealing with scatterers that do not overlap greatly—whose properties may not be strongly modified by binding effects.

It is of interest to point out that the first term $f=i$ in the closure sum (1E1) is simply $|\langle i|\psi|i\rangle|^2$, the density of coherent radiation. This confirms the point stated in the previous section that the radiation $\langle i|\psi^*\psi|i\rangle - |\langle i|\psi|i\rangle|^2$ that is not *absolutely* coherent involves a change in the final state of the struck system. Part of this noncoherent radiation is *strictly* incoherent in that an individual scatterer has changed its state in the collision preventing any sort of interference. Such collisions involve primarily the properties of the individual scatterers, and a succession of them may certainly be treating from the (particle) multiple scattering point of view. Somewhat more interesting is the portion of the radiation that is elastic from the point of view of the individual scatterers but inelastic from the point of view of the system as a whole. Such collisions exhibit *relative* coherence and may display some sort of pattern depending on the correlation $n(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2)$. The more tightly bound the structure is, the greater correlation is to be expected. From a dynamic point of view, one might say that the larger the number of particles that share in absorbing the recoil momentum of the incident wave, the sharper will be the diffraction pattern. An ability of a group of particles (in, e.g., a liquid) to share the recoil depends on having some kind of bound structure. If the individual scatterers are free, there will be negligible correlation between them, and inelastic collisions will be strictly incoherent, because the recoil momentum will be absorbed by a single scatterer. Absolute coherence is always possible, however, in the forward direction, because elastic forward scattering does not require the absorption by the system of any recoil momentum.

## F. Inelastic X-Ray Scattering

The intensity of x-rays scattered by a crystal can be divided into three categories: (1) the strictly incoherent scattering due to a Compton collision, in which an individual atom is modified by the collision, (2) the Laue-Bragg diffraction in which the internal state of the crystal is unmodified by the scattering, (3) the temperature diffuse scattering that is elastic with respect to the individual atoms but inelastic with respect to the crystal as a whole (i.e., the relatively coherent scattering).

In this section we shall review from the multiple scattering point of view previous work on the influence of lattice vibrations on Laue-Bragg and temperature diffuse scattering.

The influence of thermal and zero-point motion on Laue-Bragg scattering has been shown both experimentally[35] and theoretically[36] to be accounted for simply by the replacement of the ideal atomic form factor $f_k$ of atom $k$ by $f_k \exp(-M_k)$. The Debye-Waller factor $\exp(-M)$ has a characteristic angular and temperature dependence that for monatomic cubic crystals may be approximated by

$$M = \frac{6\sin^2\theta}{\lambda^2}\frac{h^2 T}{m\kappa\Theta^2}Q(\Theta/T)$$

$$Q(x) = (x/4) + (1/x)\int_0^x xdx[\exp(x)-1]^{-1},$$

(1F1)

where $2\theta$ is the angle between incident and reflected x-ray beams, $\lambda$ is their wavelength, $h$ is Planck's constant, $\kappa$ is Boltzmann's constant, $m$ is the mass of the atom, $T$ is the absolute temperature, and $\Theta$ is the crystal Debye temperature. Since $Q$ does not differ appreciably from unity unless $\Theta/T>1$, we see that $M$ increases approximately proportionately to the temperature. At absolute zero, however, $M$ does not vanish because of the zero point vibrations of the lattice.

If the thermal vibrations were distributed in a random fashion, the temperature diffuse scattering should have no maxima. It should be distributed smoothly, increasing at large angles, where the coherent intensity is reduced. This in fact was the experimental situation before 1938. Some sort of pattern might be expected, however, due to relative coherence, if some correlation exists between the vibrations of the various atoms. Careful experimental work by Laval,[37] in fact, demonstrated the existence of strong, temperature-dependent diffuse spots in the neighborhood of the Laue directions. Detailed investigation by Laval, Preston,[38] and Lonsdale[39] confirmed the presence of regular patterns of diffuse spots. (These spots had not been discovered by previous investigators of diffuse radiation because the latter had avoided the Laue-Bragg directions.)

It was immediately recognized that the diffuse spots could be accounted for by the Faxen[40]-Waller[41] theory on the inelastic scattering of x-rays by thermally excited lattice vibrations. The theory has been treated in detail by Born and Sarginson,[42] Zachariesen,[43] Jahn,[44] and others. An excellent summary is given by Born.[45]

[35] F. C. Blake, Revs. Modern Phys. **5**, 169 (1933).
[36] I. Waller, dissertation, Upsala, 1925.
[37] J. Laval, Compt. rend. **208**, 1512 (1939).
[38] G. D. Preston, Proc. Roy. Soc. (London) **A172**, 116 (1939).
[39] K. Lonsdale, Rep. Prog. Phys. **9**, 256 (1943). Summary and bibliography of experimental work.
[40] H. Faxen, Z. Physik **17**, 266 (1923).
[41] I. Waller, Z. Physik **17**, 398 (1923).
[42] M. Born and K. Sarginson, Proc. Roy. Soc. (London) **A179**, 69 (1941).
[43] W. H. Zachariesen, Phys. Rev. **59**, 766, 860, 909 (1941). See also the interesting detailed discussion in Chapter X of Zachariesen's book, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945).
[44] H. A. Jahn, Proc. Roy. Soc. (London) **A179**, 320 (1942).
[45] M. Born, Rep. Prog. Phys. **9**, 294 (1943). Summary and bibliography of theoretical work.

In terms of the Born-Von Karman[46] normal coordinates, the lattice modes of vibration are elastic plane waves traveling with different orientations (and polarizations) in the crystal. The amplitudes associated with these waves obey (separated) harmonic oscillator equations. With the introduction of quantum mechanics, these waves acquire discrete energies and momenta. The term phonon is introduced, in analogy with the electromagnetic case, to describe the basic packet of energy and momentum carried by an elastic eigenwave.

Laue or Bragg reflection takes place whenever the change in propagation vector of the x-ray, $\mathbf{k}_b - \mathbf{k}_a$, can be set equal to a vector $K$ of the reciprocal lattice space (see Eq. (5.26)). In this case, the recoil momentum is absorbed by the crystal as a whole. Inelastic scattering corresponds to the absorption or creation of one (or more) phonons. If a phonon of propagation constant $q$ is absorbed conservation of momentum yields

$$\mathbf{k}_b - \mathbf{k}_a = \mathbf{K} + \mathbf{q}. \qquad (1F2)$$

This process leads, then, to a sharp diffraction spot in a direction differing from the usual Bragg direction by an amount determined by the phonon momentum. The incoherent superposition of spots produced by different phonons lead to the observed diffuse spots. The concentration of individual phonon spots in the neighborhood of the Bragg directions is based on the fact that the small momentum phonons are most effective in scattering.

The reason for the effectiveness of low energy phonons may be understood as follows: The intensity for inelastic scattering is proportional to the mean squared amplitude associated with the lattice wave producing the scattering:

$$\langle \xi_q^2 \rangle_{Av} = \frac{\langle E \rangle_{Av}}{\omega_q^2} = \frac{1}{\omega_q^2} \left[ \frac{\hbar \omega_q}{\exp(\hbar \omega_q / \kappa T) - 1} + \tfrac{1}{2} \hbar \omega_q \right]$$

$$\rightarrow \kappa T / \omega_q^2 \quad \text{for} \quad \hbar \omega_q \ll \kappa T. \quad (1F3)$$

The average is understood to be a mean over all possible initial states $|i\rangle$ weighted with the corresponding Boltzmann factor:

$$\langle \ \rangle_{Av} = \sum_i W_i \langle i| \quad |i\rangle$$
$$W_i = \exp[-E_i/\kappa T] / \sum_j \exp[-E_j/\kappa T]. \quad (1F4)$$

The mean square amplitude for the lattice wave of momentum $\hbar q$, treated as a harmonic oscillator varies inversely with the square of the oscillator frequency $\omega_q$. Thus the predominant inelastic scattering involves low frequency ("acoustic") Debye waves. Furthermore, the inelasticity is small, almost unmeasurable: $10^{13}$ sec$^{-1}$ compared to x-ray frequencies of $10^{18}$ sec$^{-1}$.

It may be worthwhile to present here an abridged version, in multiple scattering notation, of Born's

treatment of inelastic x-ray scattering—enough, at least, to see how the calculation produces the main features of the results. Born sums the transition probabilities over all possible final states and averages over all initial states. He immediately makes the closure ("multiple scattering") approximation to obtain the result:

$$d\sigma = d\sigma_0 \sum_f \sum_i |\langle f|\psi|i\rangle|^2 W_i \qquad (1F5)$$

$$= d\sigma_0 \langle |\psi|^2 \rangle_{Av} \qquad (1F6)$$

$$d\sigma_0 = \tfrac{1}{2}(e^2/mc^2)^2(1 + \cos^2 2\theta) d\Omega \qquad (1F7)$$

$$\psi = \sum_j f_j \exp[i(\mathbf{k}_a - \mathbf{k}_b)\cdot(\mathbf{r}_j + \mathbf{u}_j)] \qquad (1F8)$$

where $d\sigma$ is the radiation scattered into solid angle $d\Omega$ scattered per unit incident intensity, and $d\sigma_0$ is the corresponding quantity for Thomson scattering. The equilibrium lattice position is denoted by $\mathbf{r}_j$ and the deviation by $\mathbf{u}_j$. For simplicity of notation, we describe the monatomic case.

To deal with averages of the form

$$\langle |\psi|^2 \rangle_{Av} = \sum_{jj'} A_j A_{j'}{}^* \langle \exp[i\Delta\mathbf{k}\cdot(\mathbf{u}_j - \mathbf{u}_{j'})]\rangle_{Av} \quad (1F9)$$
$$A_j = f_j \exp[i\Delta\mathbf{k}\cdot\mathbf{r}_j].$$

Born expresses the $\mathbf{u}_j$ in terms of the normalized lattice modes with amplitude $\xi_q$ and polarization $\mathbf{e}_q$:

$$\mathbf{u}_j = (mN)^{-\frac{1}{2}} \sum_q \mathbf{e}_q \xi_q \exp[i\mathbf{q}\cdot\mathbf{r}_j]. \qquad (1F10)$$

(Here $m$ is the mass of the atom, and $N$ the number of atoms in the crystal.) He then has to deal with averages of the form:

$$\langle \exp[i\mu\xi_q]\rangle \sim 1 - \tfrac{1}{2}\mu^2 \langle \xi_q^2 \rangle + \cdots \qquad (1F11)$$

$$\langle \exp[i\mu\xi_q]\rangle = \exp[-\tfrac{1}{2}\langle(\mu\xi_q)^2\rangle]. \qquad (1F12)$$

Equation (1F12), which is suggested by (1F11), since the mean value of all odd powers of $\xi_q$ vanishes, turns to be true exactly.[47] This equation is easily seen to be valid if $\mu\xi_q$ is replaced by a linear superposition of harmonic oscillator amplitudes $\sum \mu_q \xi_q$. Thus the theorem may be applied directly to (1F9) with the result

$$\langle \exp[i\Delta\mathbf{k}\cdot(\mathbf{u}_j - \mathbf{u}_{j'})]\rangle = \exp[M_{jj'} - M_j - M_{j'}] \quad (1F13)$$

$$M_j = \tfrac{1}{2}\langle(\Delta\mathbf{k}\cdot\mathbf{u}_j)^2\rangle \qquad (1F14)$$

$$M_{jj'} = \langle(\Delta\mathbf{k}\cdot\mathbf{u}_j)(\Delta\mathbf{k}\cdot\mathbf{u}_{j'})\rangle. \qquad (1F15)$$

Replacing $\exp(M_{jj'})$ by $1 + \exp(M_{jj'}) - 1$, the total intensity can be split into two terms:

$$d\sigma = d\sigma_1 + d\sigma_2$$
$$d\sigma_1 = d\sigma_0 |\sum_j f_j{}^T \exp[i\Delta\mathbf{k}\cdot\mathbf{r}_j]|^2 \qquad (1F16)$$

$$d\sigma_2 = d\sigma_0 \sum_{jj'} f_j{}^T f_{j'}{}^T \exp[i\Delta\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_{j'})]$$
$$\times (\exp M_{jj'} - 1), \quad (1F17)$$

where $f_j{}^T = f_j \exp(-M_j)$ is simply the atomic form factor corrected by the Debye-Waller factor. Thus $d\sigma_1$ is simply the coherent scattering using the temperature modified form factors.

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[46] M. Born and V. Karman, Physik. Z. 14, 15, 65 (1913). M. Blackman, Rep. Prog. Phys. 8, 11 (1941).

[47] H. Ott, Ann. phys., 23, 169 (1935). For a simpler proof see references 42 and 45.

Since $|\Delta\mathbf{k}| = 4\pi \sin\theta/\lambda$, the Debye-Waller factor can be given a simple interpretation:

$$M = (8\pi^2 \sin^2\theta/\lambda^2)\langle u^2_\perp \rangle, \qquad (1F18)$$

where $u_\perp$ is the displacement of the atom perpendicular to the Bragg plane involved in the scattering.

$d\sigma_2$ represents the temperature diffuse scattering. If we were to assume (incorrectly) that there is no correlation between scatterer displacements: $M_{jj'} = 0$, $M_{jj} = 2M_j$ we would obtain

$$d\sigma_2 = d\sigma_0 \sum_j |f_j|^2 [1 - \exp(-2M_j)] \qquad (1F19)$$

i.e., the diffuse scattering is strongest at large angles, where the Bragg intensity is greatly decreased because of the angular dependence of the Debye-Waller factor. It is much more reasonable to assume, however, that $M_{jj'}$ is a function of $j - j'$ that decreases smoothly (rather than abruptly) as the scatterer separation increases. $M_{jj'}/(M_j M_{j'})^{\frac{1}{2}}$ can for example remain appreciable for scatterers a hundred basic cells apart. In this case, the lattice sum (1F17) for $d\sigma_2$ is similar to the lattice sum for Bragg scattering for a crystal of about a hundred atomic layers. We might therefore expect the temperature diffuse scattering to exhibit broad maxima in the Bragg directions because of the small "effective crystal size."

An evaluation of $M_{jj'}$ may be made by inserting the normal mode expansion (1F10) into the expression (1F15) for $M_{jj'}$. After neglecting the dependence of $\omega_q$ on the polarization direction,‡ the result simplifies to:

$$M_{jj'} = (mN)^{-1}(\Delta\mathbf{k})^2 \sum_q \langle |\xi_q^2| \rangle \exp[i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_{j'})]. \quad (1F20)$$

Because of the periodicity condition at the edges of the crystal the components of $\mathbf{q}$ take the value $2\pi(\text{integer})/[a(N)^{\frac{1}{3}}]$. We have assumed here a cubic crystal, where $a$ is the lattice of the basic cube.‡ Thus sums may be replaced by integrals according to the recipe:

$$\sum_q \to N(a/2\pi)^3 \int d\mathbf{q}. \qquad (1F21)$$

If we approximate $\exp M_{jj'}$ by $1 + M_{jj'}$ and insert (1F20) into (1F17) we find that we have a lattice sum of the usual sort for Bragg reflections with $\Delta\mathbf{k}$ replaced by $\Delta\mathbf{k} + \mathbf{q}$ thus:

$$d\sigma_2 = (\Delta\mathbf{k})^2(a/2\pi)^3 m^{-1} \int [\langle |\xi_q|^2 \rangle d\sigma_1(\Delta\mathbf{k} + \mathbf{q})] d\mathbf{q}. \quad (1F22)$$

This formula justifies the earlier interpretive remarks: $d\sigma_1(\Delta\mathbf{k} + \mathbf{q})$ is a sharp diffraction spot in a direction differing from the usual Bragg direction because of the absorbed phonon momentum $\mathbf{q}$. The effectiveness of this phonon is determined by the mean squared amplitude $\langle |\xi_q|^2 \rangle$ which, according to (1F3), emphasizes low frequency phonons. The theory presented here corre-

sponds to the absorption (or emission) of *one* phonon because we have kept only terms linear in $M_{jj'}$. The term in $(M_{jj'})^n$ yields the $n$ phonon processes.

The Debye-Waller factor can be evaluated by noting that $M_j = \frac{1}{2}M_{jj}$ and converting the sum (1F20) to an integral:

$$2M_j = (\Delta\mathbf{k})^2(a/2\pi)^3 m^{-1} \int d\mathbf{q}\langle |\xi_q|^2 \rangle. \quad (1F23)$$

The evaluation of the integrals for $M$ and $d\sigma_2$ involve the mode frequencies $\omega_q$ through (1F3). The relationship between $\omega_q$ and $\mathbf{q}$ involves the interatomic forces and is rather difficult to evaluate explicitly.[45] Fortunately, the low frequency ("acoustic") modes are fairly important and these are essentially equivalent to the vibrations of the crystal regarded as a continuum. In other words, the relation between frequency $\omega_q$ and propagation constant $q$ is

$$\omega_q \simeq cq \qquad (1F24)$$

where $c$ is the velocity of sound in the crystal, which may depend on the direction of propagation and the polarization but is approximately independent of frequency.

It is also customary in evaluating $M$ to replace the cube of integration $(2\pi/a)^3$ by a sphere $4\pi q_m^3/3$ of equal volume. If the Debye temperature $\Theta$ is defined by:

$$\kappa\Theta = \hbar\omega_m = \hbar c q_m, \qquad (1F25)$$

(1F23) reduces to the result (1F1) previously quoted.

More accurate discussions of inelastic x-ray scattering without the assumptions of a monatomic, cubic lattice are presented in references 42–45.

## G. Inelastic Neutron Scattering

The inelastic scattering of neutrons by lattice vibrations is closely analogous to the corresponding x-ray case, and therefore shall be discussed briefly. The earliest contributions to this problem were made by Fermi,[26] Wick,[48] and Pomerantchuk.[49] Seeger and Teller[50] make an interesting comparison of the neutron and x-ray cases assuming that only one phonon is emitted or absorbed. Weinstock[51] calculates the inelastic cross section treating the crystal as a many-body problem and taking energetic restrictions into account properly. He proves that for moderate neutron energies, only elastic and first-order (i.e., one phonon) inelastic collisions are important.

The conclusions of these authors may be summarized in a way chosen to display the similarities and differences between neutron and x-ray scattering by crystals:

(1) The influence of thermal vibrations on elastic neutron scattering is accounted for, as in the x-ray case

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‡ These approximations are unnecessary, and made only to simplify the appearance of the final formulas.

[48] G. C. Wick, Physik. Z. **38**, 403 (1937).
[49] I. Pomerantchuk, Physik Z. Sowjetunion **13**, 65 (1938).
[50] R. J. Seeger and E. Teller, Phys. Rev. **62**, 37 (1942).
[51] R. Weinstock, Phys. Rev. **65**, 1 (1944).

(1F16) by the use of a Debye-Waller correction factor to the scattering amplitudes.

(2) The ratio of inelastic scattering of order $n$ to elastic scattering in both neutrons and x-ray cases is given roughly by $(M_{jj'})^n$ where $M_{jj'} \sim M \sim (\Delta \mathbf{k})^2 \langle u_\perp^2 \rangle$ and $u_\perp$ is the displacement of the atom perpendicular to the Bragg plane. Thus for moderate neutron energies and/or low temperatures, one-phonon processes will be small compared to elastic processes, and higher order (many phonon) processes will be small compared to the one-phonon processes.

(3) For neutron velocities greater than the velocity of sound in the crystal, inelastic scattering gives rise to diffuse spots similar to those found with x-rays. (Diffuse scattering takes place in all directions, but intensities are largest in the neighborhood of a Bragg direction.)

(4) Energy and momentum conditions play a larger role in neutron than in electron or x-ray scattering because of the large neutron mass. For neutron velocities less than the velocity of sound in the crystal, these conditions limit the possible directions of inelastic neutron scattering to sharply defined regions in the neighborhood of the Laue-Bragg directions. Seeger and Teller[50] give a simple graphical explanation of this point. Such restrictions may be expected because the adiabatic condition that the velocity of the scatterers be small compared to the velocity of the wave is violated. From another point of view, these energy-momentum restrictions indicate a failure of the closure approximation for low neutron velocities. On the other hand, x-rays of all energies travel with the velocity of light, and we might therefore expect the closure approximation to be better justified in the x-ray case.

(5) For sufficiently small neutron or x-ray energies, it is no longer possible to fulfill the Laue-Bragg conditions and the elastic cross section vanishes. The only reciprocal lattice vector on (or near) the Ewald sphere will be that corresponding to elastic forward scattering, which is always permissible. Inelastic scattering will therefore be possible only near the forward direction.

(6) Phonon emission by a neutron scattered near the forward direction is only possible if the neutron velocity is greater than the velocity of sound. (This momentum-energy condition is similar to the one for emission of Čerenkov radiation by a fast moving electron in a dielectric.) In the x-ray case, energy momentum restrictions always permit the emission of a phonon.

(7) At sufficiently low temperatures, phonon absorption is no longer possible in either the x-ray or neutron cases.

(8) Combining remarks (5), (6), (7), we may conclude that for low temperatures and low energy neutrons, the total neutron cross section vanishes whereas the corresponding x-ray cross section does not.

(9) For neutron energies sufficiently high that $(\Delta \mathbf{k})^2 \langle u_\perp^2 \rangle \cdot \gg 1$, inelastic collisions of all orders become important. The reason for this is that the neutron recoil momentum tends to be absorbed by a single struck nucleus—a result that would be expressed in a rather complicated way in terms of the normal modes of the crystal. Finkelstein[52] has therefore treated inelastic collisions of high energy neutrons using the Einstein model of a crystal in which the atoms are treated as independent harmonic oscillators. This approach provides a simpler description of large energy transfers, but as Finkelstein remarks is invalid for nearly elastic scattering because it predicts isotropic scattering rather than diffuse spots. The Einstein model can clearly produce no relatively coherent scattering since the motions of the scatterers are uncorrelated.

## H. Fluctuation Scattering

The Tyndall effect associated with light scattering by liquids and solutions was one of the earliest problems requiring a detailed study of incoherent scattering. The basic treatment of this problem was made by Smoluchowski[53] and Einstein.[54] Excellent summaries and comparisons with experiment have been given by Bhagavantum[55] and Cabannes.[56] The recent use of light scattering as a tool for investigating the structure of polymers in solution[57] has provoked new interest in the subject.

The scattering of light does not require a treatment formally different from that of x-rays or neutrons. However, the wavelength of light is so much greater than molecular separations that a simplified phenomenological treatment is possible. We may regard a liquid, for example, as having density fluctuations superimposed on a uniform density. The uniform density supplies the necessary scattering to propagate a coherent wave in the medium. The fluctuations in density cause incoherent scattering and an attenuation of the coherent wave.

In order to understand the assumptions involved in the Einstein-Smoluchowski treatment of the problem we shall present a simplified version of their calculation. We start by choosing a volume element $V$ whose dimensions are sufficiently small compared to the wavelength that the scattering from this volume can be regarded as simple dipole scattering. At the same time, the volume $V$ must be chosen sufficiently large that the correlation between density fluctuations in neighboring volume elements can be neglected. (This will permit the addition of intensities from these volume elements.) This requirement can usually be satisfied by using dimensions large compared to the molecular separations. Near the critical point, however, it may not be

[52] R. J. Finkelstein, Phys. Rev. **72**, 907 (1947).
[53] M. Smoluchowski, Ann. phys. **25**, 205 (1908).
[54] A. Einstein, Ann. phys. **33**, 1275 (1910).
[55] S. Bhagavantum, *Scattering of Light and the Raman Effect*, (Andhra University, Waltair, India; American edition-Chemical Publishing Company, Brooklyn, New York, 1942).
[56] J. Cabannes, *La Diffusion Moleculaire de la Lumiere* (Les Presses Universitaires de France, Paris, 1929).
[57] Outer, Carr, and Zimm, J. Chem. Phys. **18**, 830 (1950). Doty, Zimm, and Mark, J. Chem. Phys. **13**, 159 (1945).

possible to satisfy both of these assumptions simultaneously.

The fluctuation in density $\Delta n$ causes a fluctuation in dielectric constant $\Delta \epsilon$. As a result there is induced in the volume $V$ an electric moment

$$\mathbf{m} = V\Delta\mathbf{P} = V\Delta\epsilon\mathbf{E}/(4\pi). \tag{1H1}$$

The power radiated by a dipole $\omega^4 m^2/(3c^3)$ per unit incident flux $cE^2/8\pi$ is

$$\text{power/flux} = (8\pi/3)(2\pi/\lambda)^4(m/E)^2, \tag{1H2}$$

using $\omega/c = k = 2\pi/\lambda$. The turbidity $\tau$ is defined as the power scattered per unit volume per unit incident flux:[58]

$$\tau = \text{power}/(\text{volume} \times \text{flux}) = (8\pi^3/3)\lambda^{-4}V\langle(\Delta\epsilon)^2\rangle, \tag{1H3}$$

where $\langle(\Delta\epsilon)^2\rangle$ is the mean square fluctuation of the dielectric constant in the volume $V$. Of course, $\epsilon$ is the dielectric constant at the optical frequency used and is equal to the square of the index of refraction.

The mean square density fluctuation can be calculated by the methods of statistical mechanics and is given by:[59]

$$\langle(\Delta n)^2\rangle = -(n^2\kappa T/V^2)(\partial V/\partial P)_T. \tag{1H4}$$

The dielectric constant fluctuation is given by

$$\langle(\Delta\epsilon)^2\rangle = (\Delta\epsilon/\Delta n)^2\langle(\Delta n)^2\rangle \tag{1H5}$$

where $\Delta\epsilon$ is the change in dielectric constant in the volume $V$ associated with a density change $\Delta n$ in the same volume—assuming the remainder of the medium is unchanged in density. There is some controvery as to how $\Delta\epsilon$ should be computed. We may analyze the situation as follows: The additional polarization $\Delta\mathbf{P}$ has two contributions, (1) the increase in the number of dipoles, assuming the individual moments are unmodified, (2) the increase in the individual moments due to an increase in the effective field because the latter is density dependent.

Einstein assumed that the change in the effective field is the same as if the entire liquid (not merely the fluctuation volume) suffered the same density change. This yields the result

$$\Delta\epsilon/\Delta n = \partial\epsilon/\partial n \quad WKBJ, \tag{1H6}$$

because it is equivalent to associating a local dielectric constant with each density. This procedure is analogous to the Wentzel-Brillouin-Kramers-Jeffries approximation so frequently applied in quantum mechanics. Such an approximation would be valid, however, only if the density fluctuations were smooth and small over a dis-

tance of one wavelength—a condition not actually satisfied.

Since the fluctuations are small and localized a closer approximation to the correct answer may be obtained by neglecting any change in the effective field due to $\Delta n$ a procedure similar to the first Born approximation. The dielectric constant change due solely to the increase in the number of dipoles is

$$\Delta\epsilon/\Delta n = (\epsilon-1)/n \quad \text{Born.} \tag{1H7}$$

If the Clausius-Mosotti relation (1.5) is used

$$\partial\epsilon/\partial n = (\epsilon-1)(\epsilon+2)/(3n) \tag{1H8}$$

so that the Born approximation answer can be obtained from the W.K.B.J. result by dropping the sometimes appreciable effective field factor $(\epsilon+2)/3$. This was the procedure actually used by Bhagavantum[55] and Cabannes.[56]

In any case, the turbidity is given by

$$\tau = \frac{8\pi^3}{3} \frac{\kappa T}{\lambda^4}\left(-\frac{\partial \ln V}{\partial P}\right)_T\left(n\frac{\Delta\epsilon}{\Delta n}\right)^2 \tag{1H9}$$

pending a more accurate estimate of $\Delta\epsilon/\Delta n$ than (1H7).

Since density fluctuations are largest in gases, less in liquids and least in solids, the amount of light scattering observed *per molecule* will decrease in the same manner. To illustrate the order of magnitude of the effect, we mention that ether vapor is molecule for molecule seven times as effective as ether liquid in scattering light.[55]

Einstein in his original paper extended his treatment of light scattering to binary liquid mixtures. More recently Kirkwood and Goldberg,[60] and Stockmayer[61] have generalized Einstein's results to multicomponent systems. Briefly, we may describe their procedure as follows: the presence of more than one component increases the fluctuation $\langle(\Delta\epsilon)^2\rangle$ in the dielectric constant because of concentration fluctuations. The additional fluctuation can be written in the form:

$$\langle(\Delta\epsilon)^2\rangle_{\text{conc}} = \sum_{ij}(\Delta\epsilon/\Delta c_i)(\Delta\epsilon/\Delta c_j)\langle\Delta c_i\Delta c_j\rangle. \tag{1.20}$$

The concentration fluctuations $\langle\Delta c_i\Delta c_j\rangle$ are evaluated with the help of the grand partition function. Cross terms of the form $\langle\Delta n\Delta c_j\rangle$ are shown to vanish.

As in the one component case $\Delta\epsilon/\Delta c_j$ must be evaluated with care. The choice corresponding to Einstein's is $\partial\epsilon/\partial c_j$; Bhagavantum's choice, under Clausius-Mosotti assumptions, would be $3(\partial\epsilon/\partial c_j)/(\epsilon+2)$.

The theory discussed here breaks down near a critical point—the density fluctuations and the compressibility became infinite. Smoluchowski attempted (incorrectly) to remedy the difficulty by making a more accurate calculation of the density fluctuations—taking into account higher order terms in the expansion of the energy around its equilibrium value. However, the

[58] According to this definition, the power in the primary beam has an exponential attenuation $\exp(-\tau x)$. For a *random* distribution of scatterers $\tau$ would be equal to the density of the scatters $n$, times the cross section $\sigma$ of a single scatterer. The original definition includes the possibility of correlation in scatterer positions or states.

[59] L. Landau and S. Lifschitz, *Statistical Physics* (Oxford University Press, London, 1938), p. 117. See also references 41–44.

[60] J. G. Kirkwood and R. J. Goldberg, J. Chem. Phys. **18**, 54 (1950).

[61] W. H. Stockmayer, J. Chem. Phys. **18**, 58 (1950).

basic assumptions underlying (1H3) cannot be satisfied. Correlations became more important and extend over distances comparable to the wavelength. This must be taken into account in the scattering—and finite results will be obtained whether or not the density fluctuations diverge.

The importance of correlation in describing critical fluctuations was recognized by Ornstein and Zernicke,[62] and again more recently by Klein and Tisza.[63] Their treatments are in the main phenomenological. It is easiest to develop and understand the effects of correlation on scattering from a molecular point of view. We shall discuss the nature of critical scattering in more detail after developing our results from the molecular point of view (Sec. VI).

In this connection we must mention the important work of Zimm[64] in rederiving the Einstein formula from a molecular viewpoint. Our results are in complete agreement with Zimm when we specialize them to dipole scattering. We should mention of course that we obtain Zimm's results after solving our integral equation by the Born approximation—i.e., after neglecting the effects of multiple scattering. Multiple scattering effects may be important however in the critical region.[65]

## I. Approach to Scattering Problems

A variety of procedures have been devised for treating multiple scattering problems. The approximations involved in these procedures are determined primarily by the relation between the wavelength of the radiation and the average scatterer separation.

For wavelengths very short compared to scatterer separations ($\lambda \ll a$) the particle viewpoint is appropriate. The treatment is usually based on the Boltzmann integro-differential equation for transport processes. The latter is sometimes replaced by the simpler diffusion equation (see references 1–7). Another treatment is to calculate the scattering in successive orders: primary, secondary, tertiary, etc., taking into account attenuation for each order, but neglecting interference.[66]

For short wavelengths, the next stage of the approximation is the geometrical optics viewpoint. Propagation is considered from the ray viewpoint, diffraction is neglected but multiple refraction can be taken into account.[67] Huntington[68] has formulated the problem from the point of view of phase fluctuations. Bergmann[69] has given a consistent treatment of the effect of index of refraction fluctuations on the phase and intensity of radiation. His treatment is based on the eikonal equa-

tion. All of these treatments presuppose that appreciable index of refraction modifications or fluctuations occur only over distances large compared to a wavelength.

When the wavelength is large compared to the size of the scatterer ($\lambda \gg a$) simplifications occur: the single scattering angular distribution takes the simplest possible form, e.g., isotropic for neutrons and dipole for electromagnetic waves. (This is the region of Rayleigh $\lambda^{-4}$ scattering.) In addition the fluctuation volumes are small compared to the wavelength. Thus correlation effects can usually be neglected and the scattering due to these fluctuation volumes will have the same simple angular distribution as that of the single scatterers involved. These remarks are exemplified by the Einstein-Smoluchowski treatment of light scattering. The chief problem is to calculate the amount of the fluctuations.

For wavelengths comparable to the scatterer separation, correlation effects are important. A diffraction pattern can then be calculated from the Fourier transform of the correlation density (the "autocorrelation"). This is the usual liquid diffraction pattern for x-rays[70] or neutrons.[71] The same treatment can be applied to scattering by inhomogeneities provided the correlation between inhomogeneities at different places is known.[72] These wave treatments are usually calculated in Born approximation—i.e., neglecting multiple scattering effects.

A multiple scattering ("dynamical") theory of x-ray diffraction by crystals was devised by Darwin,[73] Ewald,[10] and von Laue.[11] The Darwin treatment considers the Fresnel diffraction of a plane of scatterers. The effects of a large number of parallel planes are handled by means of difference equations. The von Laue treatment is phenomenological, i.e., it makes use of the macroscopic Maxwell equations. The crystalline structure is represented by a periodic dielectric constant. A similar result has been obtained by Ekstein[23] in the case of neutron scattering. The most satisfactory dynamical treatment due to Ewald is based on the self-consistent field method. We shall describe this treatment in more detail since it is the basis of the approach used in this paper.

The method of the self-consistent field assumes that a wave is emitted by each scatterer of an amount and directionality determined by the radiation incident on that scatterer (the effective field). The latter is to be determined by adding to the incident beam the waves emitted by all *other* scatterers, and the waves emitted by those scatterers are in turn influenced by the radiation emitted by the scatterer in question. Attenuation need not be explicitly taken into account. It is automatically included in the forward "shadow" scattering of each scatterer.

[62] L. Ornstein and F. Zernicke, Proc. Amst. Akad. Sci. **17**, 793 (1914); **18**, 1520 (1916); **19**, 1321 (1917); Physik. Z. **19**, 134 (1918); **27**, 761 (1926).

[63] M. J. Klein and I. Tisza, Phys. Rev. **76**, 1861 (1949).

[64] B. H. Zimm, J. Chem. Phys. **13**, 144 (1945).

[65] H. A. Cataldi and H. G. Drickamer, J. Chem. Phys. **18**, 650 (1950); A. J. Babb and H. G. Drickamer, J. Chem. Phys. **18**, 655 (1950).

[66] D. L. Dexter and W. W. Beeman, Phys. Rev. **76**, 1782 (1949).

[67] R. von Nardroff, Phys. Rev. **28**, 240 (1926).

[68] H. B. Huntington, J. Acoust. Soc. Am. **22**, 362 (1950).

[69] P. G. Bergmann, Phys. Rev. **20**, 486 (1946).

[70] N. S. Gingrich, Revs. Modern Phys. **15**, 90 (1943).

[71] O. Chamberlain, Phys. Rev. **77**, 305 (1950).

[72] C. L. Pekeris, Phys. Rev. **71**, 2681 (1947).

[73] C. G. Darwin, Phil. Mag. **27**, 315, 675 (1914).

The self-consistent procedure is *not* an expansion in primary, secondary, tertiary waves, etc. The field acting on a given scatterer, or emitted by it includes the effects of all orders of scattering.

The work presented in this paper generalizes Ewald's work in two ways: the scattering system need not be a perfect crystal and the scatterers are not assumed to be point dipoles.

## II. SINGLE SCATTERING

In this section we wish to obtain the linear operator that relates the radiation emitted by a scatterer to that exciting it. Before finding an abstract expression for this linear operator we consider the case of elastic scattering, since the operators used in this example are well understood.

Scattering by a potential field obeys the differential equation

$$[\nabla^2 + k^2 - U(\mathbf{r})]\psi_a(\mathbf{r}) = 0 \tag{2.1}$$

and (treating the last term as an inhomogeneous term) the corresponding integral equation

$$\psi_a(\mathbf{r}) = \varphi_a(\mathbf{r}) - \int (4\pi R)^{-1} \exp(ikR) U(\mathbf{r}^1) \psi_a(\mathbf{r}^1) dV^1$$

$$\varphi_a(\mathbf{r}) = \exp(i\mathbf{k}_a \cdot \mathbf{r}) \quad R = |\mathbf{r} - \mathbf{r}^1|. \tag{2.2}$$

The subscript $a$ imples that $\psi_a(\mathbf{r})$ is that solution of (2.1) associated with an incident wave of propagation vector $\mathbf{k}_a$. This implication is automatically contained in (2.2) whose first term is the incident wave and whose second term is the scattered wave. Note that this second term describes the scattered wave at small as well as great distances. It will therefore be made the basis of our treatment of multiple scattering.

At large distances from the scatterer $kR \simeq kr - \mathbf{k}_b \cdot \mathbf{r}^1$; $\mathbf{k}_b = k\mathbf{r}/r$ so that the asymptotic solution takes the usual form:

$$\psi_a(\mathbf{r}) \rightarrow \varphi_a(\mathbf{r}) + f(b \leftarrow a) r^{-1} \exp(ikr) \tag{2.3}$$

where $f(b \leftarrow a)$ the scattering amplitude from direction $a$ to direction $b$ is given by:

$$f(b \leftarrow a) = -(4\pi)^{-1} \int \exp[-i\mathbf{k}_b \cdot \mathbf{r}^1] U(\mathbf{r}^1) \psi_a(\mathbf{r}^1) dV^1$$

$$f(b \leftarrow a) = -(4\pi)^{-1}(\phi_b, U\psi_a). \tag{2.4}$$

Equation (2.4) is an exact expression for the scattering amplitude. If the solution $\psi_a$ is replaced by the incident wave $\varphi_a$, (2.4) gives the scattering amplitude in first Born approximation. In our treatment of multiple scattering we shall assume that the solution $\psi_a$ of the single scattering problem is known, so that exact expressions for the scattering amplitude are available.

The generalized single scattering problem including inelastic scattering as well as the creation and destruction of particles can be described in terms of the

Schrodinger equation:

$$(E - H - V)\Psi = 0 \tag{2.5}$$

and the corresponding integral equation (see (2.2)):

$$\Psi_a = \Phi_a + \frac{1}{E - H} V \Psi_a. \tag{2.6}$$

States $\Phi_a$ and $\Phi_b$ are states of the unperturbed hamiltonian $H$. If creation and destruction of particles is involved, we should regard these states as abstract vectors in hilbert space. State $a$, for example can represent a photon of a certain momentum and state $b$ an electron pair with specified momenta. Equation (2.4) suggests that a transition amplitude from state to state $b$, $T_{ba}$, may be obtained by introducing a transition operator with the definition:

$$T\Phi_a = V\Psi_a$$

$$T_{ba} = (\Phi_b, T\Phi_a) = (\Phi_b, V\Psi_a). \tag{2.7}$$

In fact, it follows from time-dependent perturbation theory[28,29] that the transition probability from state $a$ to state $b$ is given by:

$$W_{ba} = \frac{2\pi}{\hbar} |T_{ba}|^2 \delta(E_b - E_a). \tag{2.8}$$

If the Born approximation $\Psi_a \simeq \Phi_a$ is introduced into (2.7), $T_{ba}$ is replaced by $V_{ba}$ and (2.8) becomes the usual Born approximation formula for the transition probability.

With the help of the transition operator, (2.6) may be rewritten in the form:

$$\Psi_a = \Phi_a + \frac{1}{E - H} T\Phi_a. \tag{2.9}$$

Since the last term in (2.9) represents the "scattered wave" and $\Phi_a$ represents the incident wave, we have obtained the desired relation:

$$(\text{scattered wave}) = (E - H)^{-1} T \text{ (incident wave).} \tag{2.10}$$

This relation will be made the basis of our treatment of the multiple scattering problem.

At large distances from the scatterer, where $V$ may be neglected, $\Psi_a$ must be a solution of the unperturbed equation, i.e., a superposition of states $\Phi_b$ for which $E_b = E_a$. This explains why the only observable transitions in (2.8) must conserve energy. On the other hand, near the scatterer, states with $E_b \neq E_a$ are important. The relation (2.10) between scattered and incident waves describes the local as well as the asymptotic behavior of the scattered wave since $T_{ba}$ has matrix elements to states $b$ that do not conserve energy.

If the single scattering problem cannot be solved exactly, $T_{ba}$ may be computed by a variational method.[28,29] The relationship between $T_{ba}$ and the scattering ampli-

tude $f(b\leftarrow a)$ of Eq. (2.3) is simply:

$$T_{ba} = -\frac{4\pi\hbar^2}{2m}f(b\rightarrow a) \qquad (2.11)$$

when the interaction energy $V$ is $\hbar^2 U(\mathbf{r})/(2m)$.

## III. MULTIPLE SCATTERING: BASIC EQUATIONS

We are now in a position to write down the basic equations describing multiple scattering in accord with the program stated in the introduction. If $\varphi(\mathbf{r})$ represents the incident wave, and $F(\mathbf{r}, \mathbf{r}_j)$ the wave scattered at $\mathbf{r}_j$ then the toal wave

$$\psi(\mathbf{r}) = \varphi(\mathbf{r}) + \sum_j F(\mathbf{r}, \mathbf{r}_j) \qquad (3.1)$$

represents the incident wave plus the sum of all scattered waves.[12]

The wave incident on scatterer $j$, denoted by $\psi^j(\mathbf{r})$, is given by the incident wave $\varphi$ plus the waves emitted by all scatterers other than $j$. Alternatively it may be written:

$$\psi^j(\mathbf{r}) = \psi(\mathbf{r}) - F(\mathbf{r}, \mathbf{r}_j). \qquad (3.2)$$

Since $\psi^j(\mathbf{r})$ is the *effective* field that *excites* scatterer $j$, the field emitted by scatterer $j$ must be given by:

$$F(\mathbf{r}, \mathbf{r}_j) = (E-H)^{-1}T(\mathbf{r}_j)\psi^j(\mathbf{r}) \qquad (3.3)$$

in accord with (2.10).

The transition amplitude $T_{ba}(\mathbf{r}_j)$ differs from the corresponding amplitude, $T_{ba}(0)$, for a scatterer located at the origin, by a phase factor. Using $\mathbf{r}_j$ as a temporary origin, we must have

$$(\varphi_b(\mathbf{r}-\mathbf{r}_j), T(\mathbf{r}_j)\varphi_a(\mathbf{r}-\mathbf{r}_j)) = (\varphi_b(\mathbf{r}), T(0)\varphi_a(r)). \quad (3.4)$$

The unperturbed states are plane waves§ quantized in a volume $V$:

$$\varphi_a(\mathbf{r}) = V^{-\frac{1}{2}}\exp(i\mathbf{k}_a\cdot\mathbf{r}) \qquad (3.5)$$

so that (3.4) yields the relationship:

$$T_{ba}(\mathbf{r}_j) = \exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}_j]T_{ba}(0). \qquad (3.6)$$

With this information about the phase relationships, Eqs. (3.1), (3.2), and (3.3) completely describe the multiple scattering problem. Eliminating $F(\mathbf{r}, \mathbf{r}_j)$, the total wave is given by:

$$\psi(\mathbf{r}) = \varphi(\mathbf{r}) + \sum_j(E-H)^{-1}T(\mathbf{r}_j)\psi^j(\mathbf{r}) \qquad (3.7)$$

in terms of the effective fields. The latter obey the system of linear integral equations:

$$\psi^s(\mathbf{r}) = \varphi(\mathbf{r}) + \sum_{j\neq s}(E-H)^{-1}T(\mathbf{r}_j)\psi^j(\mathbf{r}). \qquad (3.8)$$

If there are scatterers of various types present, $T(\mathbf{r}_j)$ must be replaced by $T(\mathbf{r}_j, s_j)$ where $s_j$ is a parameter (or set of parameters) describing the state of the

§ The normalization volume $V$ cancels out of observable physical quantities. Unless otherwise specified, we shall assume the normalization volume is unity.

scatterer. For scatterers of various elements, or various spins, $s_j$ takes on a set of discrete values. For scatterers of various sizes or velocities, $s_j$ takes on a continuous set of values. In this way we can treat Doppler shift and scattering by a substance partially ordered in space, spin, or alloy structure.

## IV. STATISTICS OF SCATTERERS

The probability that the set of $N$ scatterers will be located in the volume elements $d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N$ with their states in the region $ds_1 \cdots ds_N$ is given by

$$p(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N; s_1s_2\cdots s_N)d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N ds_1 ds_2\cdots ds_N \quad (4.1)$$

a quantity whose integral is normalized to unity. The probability distribution for a single scatterer may be obtained by integrating over all other scatterers:

$$p(\mathbf{r}_1; s_1) = \int p(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N; s_1s_2\cdots s_N)$$
$$\times d\mathbf{r}_2\cdots d\mathbf{r}_N ds_2\cdots ds_N. \quad (4.2)$$

And the correlation probability for the simultaneous locations of a pair of scatterers is obtained by integrating over all but that pair of variables:

$$p(\mathbf{r}_1\mathbf{r}_2; s_1s_2) = \int p(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\cdots\mathbf{r}_N; s_1s_2s_3\cdots s_N)$$
$$\times d\mathbf{r}_3\cdots d\mathbf{r}_N ds_3\cdots ds_N. \quad (4.3)$$

If the distribution is random, the probabilities associated with a single particle are not influenced by information concerning other particles. In this case, the complete distribution factors:

$$p(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N; s_1s_2\cdots s_N)$$
$$= p_1(\mathbf{r}_1; s_1)p_2(\mathbf{r}_2; s_2)\cdots p_N(\mathbf{r}_N; s_N). \quad (4.4)$$

It is the difference

$$p(\mathbf{r}_1\mathbf{r}_2; s_1s_2) - p_1(\mathbf{r}_1; s_1)p_2(\mathbf{r}_2; s_2)$$

that is the true measure of correlation or nonrandomness between a pair of particles.

If the distribution is nonrandom it is possible to introduce a pseudo-factorization with the help of conditional probabilities:

$$p(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N; s_1s_2\cdots s_N)$$
$$= p_1(\mathbf{r}_1; s_1)p(\mathbf{r}_1 s_1|\mathbf{r}_2\cdots\mathbf{r}_N; s_2\cdots s_N) \quad (4.5)$$

where the last factor represents the distribution for particles 2, 3, $\cdots N$ knowing the values of $\mathbf{r}_1$ and $s_1$. Similarly

$$p(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N; s_1s_2\cdots s_N)$$
$$= p(\mathbf{r}_1\mathbf{r}_2; s_1s_2)p(\mathbf{r}_1\mathbf{r}_2; s_1s_2|\mathbf{r}_3\cdots\mathbf{r}_N; s_3\cdots s_N). \quad (4.6)$$

In this notation the average of the total wave over the ensemble of scatterers is given by:

$$\langle\psi(\mathbf{r})\rangle=\int \psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$$
$$\times p(\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)d\mathbf{r}_1\cdots d\mathbf{r}_N ds_1\cdots ds_N. \quad (4.7)$$

If the first scatterer is held fixed and all other scatterers are averaged over, this will be denoted by a subscript:

$$\langle\psi(\mathbf{r})\rangle_1=\int \psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$$
$$\times p(\mathbf{r}_1 s_1|\mathbf{r}_2\cdots\mathbf{r}_N;s_2\cdots s_N)d\mathbf{r}_2\cdots d\mathbf{r}_N ds_2\cdots ds_N. \quad (4.8)$$

If two scatterers are held fixed:

$$\langle\psi(\mathbf{r})\rangle_{12}=\int \psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$$
$$\times p(\mathbf{r}_1\mathbf{r}_2;s_1 s_2|\mathbf{r}_3\cdots\mathbf{r}_N;s_3\cdots s_N)$$
$$\times d\mathbf{r}_3\cdots d\mathbf{r}_N ds_3\cdots ds_N. \quad (4.9)$$

Probability distributions may be converted to density distributions or correlations by multiplying by some power of the number of scatterers:

$$n(\mathbf{r};s)=Np(\mathbf{r};s) \quad (4.10)$$

$$n(\mathbf{r}_1\mathbf{r}_2;s_1 s_2)=N^2 p(\mathbf{r}_1\mathbf{r}_2;s_1 s_2) \quad (4.11)$$

$n(\mathbf{r};s)$ is the density of scatterers of type $s$.

## V. THE COHERENT WAVE

The system of equations (3.8) has a solution $\psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$ for any particular choice of the locations and states of the $N$ scatterers. We are in general interested in an average of this solution over the probable distribution of scatterer locations and states. This average, $\langle\psi(\mathbf{r})\rangle$, is a function only of the position of observation $\mathbf{r}$ and is considerably simpler than the original solution $\psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$. The straightforward procedure of solving the system (3.8) for $\psi(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$ and then averaging, will not usually be practical. We shall instead take averages over Eqs. (3.7) and (3.8) in order to find an approximate equation obeyed by $\langle\psi(\mathbf{r})\rangle$. In this way, a system of equations (3.8) will be replaced by a single equation.

The average over (3.7) may be performed with the help of (4.7), (4.8), and (4.5):

$$\langle\psi(\mathbf{r})\rangle=\varphi(\mathbf{r})+(E-H)^{-1}\sum_j\int p(\mathbf{r}_j;s_j)$$
$$\times d\mathbf{r}_j ds_j T(\mathbf{r}_j s_j)\langle\psi^i(\mathbf{r})\rangle_j \quad (5.1)$$

where the *effective* field is defined by:

$$\langle\psi^1(\mathbf{r})\rangle_1=\int \psi^1(\mathbf{r};\mathbf{r}_1\cdots\mathbf{r}_N;s_1\cdots s_N)$$
$$\times p(\mathbf{r}_1 s_1|\mathbf{r}_2\cdots\mathbf{r}_N;s_2\cdots s_N)d\mathbf{r}_2\cdots d\mathbf{r}_N ds_2\cdots ds_N. \quad (5.2)$$

The effective field represents the field incident on a given scatterer whose position and state are known averaged over the distribution of all other scatterers relative to the known scatterer.

The effective field differs from the total field by the field emitted by one scatterer. If a sufficient degree of randomness is present the effective field is approximately equal to the coherent field

$$\langle\psi^i(\mathbf{r})\rangle_j\simeq\langle\psi(\mathbf{r})\rangle. \quad (5.3)$$

If correlations are present, the simplest approximation is

$$\langle\psi^i(\mathbf{r})\rangle_j\simeq c\langle\psi(\mathbf{r})\rangle \quad (5.4)$$

where $c$ is a constant depending on the correlation between pairs of scatterers. This approximation has been discussed in Sec. IA. A detailed treatment of the effective field is reserved for a future paper.[17a]

Inserting the exciting field approximation (5.4) into (5.1) and noting that the summation may now be replaced by a factor $N$, we obtain:

$$\langle\psi(\mathbf{r})\rangle=\varphi(\mathbf{r})+c(E-H)^{-1}\bar{T}\langle\psi(\mathbf{r})\rangle \quad (5.5)$$

or

$$(E-H-c\bar{T})\langle\psi(\mathbf{r})\rangle=0 \quad (5.6)$$

where

$$\bar{T}=\int n(\mathbf{r};s_j)T(\mathbf{r}_j s_j)d\mathbf{r}_j ds_j. \quad (5.7)$$

The significance and usefulness of the coherent wave equation (5.6) can best be illustrated by evaluating $\bar{T}$ for various distributions $n(\mathbf{r}_j s_j)$. Using (3.6) the space factors can be shown explicitly:

$$\bar{T}_{ba}=\int \exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}_j]d\mathbf{r}_j\int n(\mathbf{r}_j s_j)T_{ba}(0,s_j)ds_j. \quad (5.8)$$

For some problems there is no correlation between the state of the scatterer and its location:

$$n(\mathbf{r}_j s_j)=n(\mathbf{r}_j)\alpha(s_j) \quad (5.9)$$

and

$$\bar{T}_{ba}=\int n(\mathbf{r})\exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}]d\mathbf{r}\int \alpha(s)T_{ba}(0,s)ds \quad (5.10)$$

where subscript $j$ has been dropped. Since $n(\mathbf{r})$ represents the average density of scatterers (regardless of type) the first factor describes the addition of amplitudes from each of the scatterers with the appropriate phases taken into account. For a homogeneous scatterer $n(\mathbf{r})=n=a$ constant.

The space integration in (5.10) is to be carried over the (unit) volume of quantization. The orthogonality of the wave functions causes the integral to vanish unless $\mathbf{k}_a=\mathbf{k}_b$:

$$\bar{T}_{ba}=n\delta_{ba}\int \alpha(s)T_{ba}(0,s)ds. \quad (5.11)$$

The second factor is the appropriately weighted addition of the scattering amplitude of the various atoms present. For example, the alloy $Cu_3Au$ in the disordered state satisfies (5.9) and the coherent scattering amplitude is given by $f = \frac{3}{4}f_{Cu} + \frac{1}{4}f_{Au}$ with a similar relation among the $T$'s:

$$\int \alpha(s)T(0, s)ds = \frac{3}{4}T(0, Cu) + \frac{1}{4}T(0, Au). \quad (5.12)$$

For a homogeneous medium, the operator $\bar{T}$, according to (5.11), is diagonalized using plane waves as a base system. The solutions of the coherent wave equation (5.6) are simply plane waves. The index of refraction is therefore determined by

$$c\bar{T}_{aa} = cn \int \alpha(s)T_{aa}(0, s)ds,$$

i.e., by the elastic scattering amplitude in the forward direction (averaged over the kinds of scatterers) and by the density of scatterers. The correction factor $c$ represents the ratio between the effective field and the coherent wave. In the notation of the elastic scattering problem (2.1) and (2.3) the coherent wave equation can be written:

$$[\nabla^2 + k^2 + 4\pi nc f(a \leftarrow a)]\langle \psi_a(\mathbf{r}) \rangle = 0. \quad (5.13)$$

Thus the propagation vector $\mathbf{k}_a'$ in the *medium* of scatterers has a magnitude determined by:

$$(k')^2 = k^2 + 4\pi nc[f(a \leftarrow a)] \quad (5.14)$$

where the forward scattering amplitude $f(a \leftarrow a)$ is a weighted mean of the type (5.11) or (5.12). The forward scattered amplitude $f$ must have a positive imaginary part.[28] Thus the modified propagation vector $k'$ will be complex. In short, our coherent wave is the main beam, traveling in a medium with an effective index of refraction $(Rek')/k$, and a power attenuation coefficient $2Imk'$, both of which are determined by the scattering amplitude in the forward direction (5.14).

As long as the attenuation per wavelength is small $(Imk' \ll Rek')$ we have:

$$Rek' \simeq [k^2 + 4\pi nRe(cf)]^{\frac{1}{2}} \quad (5.15)$$

$$2Imk' = [4\pi nIm(cf)]/(Rek') \quad (5.16)$$

correct to order $(Imk'/Rek')^2$. From more elementary considerations we would expect a power law

$$Power \propto \exp[-n\sigma_t x], \quad (5.17)$$

where $\sigma_t$ is the total cross section. This expectation is consistent with (5.16) for $c = 1$ in view of the cross section theorem relating the total cross section to the scattering amplitude in the forward direction:[28]

$$\sigma_t(k') = (4\pi/k')Im[f_{aa}(k')]. \quad (5.18)$$

In all of the preceding calculation $\bar{T}$ and $f$ are operators acting on $\langle \psi_a(\mathbf{r}) \rangle$ and thus must be evaluated at the modified value $k'$. In other words, scattering amplitudes and cross sections must be evaluated for the wavelength appropriate to the medium.

For electrons or neutrons subject to the Schrödinger equation the change in index of refraction can be interpreted as a new relation between the energy and momentum of the wave appropriate to the medium:

$$E(p') = \frac{(p')^2}{2m} + c\bar{T}_{aa}(p'), \quad (5.19)$$

using (5.6) with the assumption that $H$ is the hamiltonian of a free particle. This sort of relation has been useful in treating Bloch waves in a crystal.[74]

We shall now discuss the coherent field for scatterers arranged in a perfect lattice. There are $N_1 \times N_2 \times N_3$ unit cells, described by the base vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Each unit cell contains scatterers of type $s_k$ at position $\mathbf{r}_k (k = 1, 2, \cdots \nu)$. Thus the atoms are located at

$$\mathbf{r}_j{}^k = \mathbf{r}_k + j_1\mathbf{a}_1 + j_2\mathbf{a}_2 + j_3\mathbf{a}_3, \quad (5.20)$$

where $j_1 j_2 j_3$ are integers. The scatterers are described by the density:

$$n(\mathbf{r}, s) = \sum_{k, j}\delta(\mathbf{r} - \mathbf{r}_j{}^k)\delta(s - s_k). \quad (5.21)$$

We shall assume our waves are quantized over a volume $V$ equal to the volume of the crystal. Insert (5.21) into (5.8) and integrate over the volume of the crystal:

$$\bar{T}_{ba} = I_{ba}F_{ba} \quad (5.22)$$

$$F_{ba} = \frac{1}{\nu}\sum_k \exp[i(\mathbf{k}_a - \mathbf{k}_b)\cdot\mathbf{r}_k]T_{ba}(0, s_k) \quad (5.23)$$

$$I_{ba} = \nu\sum_j[\exp\{i(\mathbf{k}_a - \mathbf{k}_b)\cdot(j_1\mathbf{a}_1 + j_2\mathbf{a}_2 + \nu_3\mathbf{a}_3)\}]. \quad (5.24)$$

The factor $F_{ba}$ is a weighted average of the scattering amplitudes of the various atoms, taking into account phases. Except for a numerical factor $F_{ba}$ is what is usually termed the form factor of the unit cell. The lattice sum $I_{ba}$ has the value:

$$I_{ba} = \nu e^{i\theta}\frac{\sin(N_1\mathbf{K}\cdot\mathbf{a}_1/2)}{\sin(\mathbf{K}\cdot\mathbf{a}_1/2)}\frac{\sin(N_2\mathbf{K}\cdot a_2/2)}{\sin(\mathbf{K}\cdot\mathbf{a}_2/2)}\frac{\sin(N_3\mathbf{K}\cdot\mathbf{a}_3/2)}{\sin(\mathbf{K}\cdot\mathbf{a}_3/2)}$$
$$(5.25)$$

$$\mathbf{K} = \mathbf{k}_a - \mathbf{k}_b$$

where the phase $\theta$ depends on the precise position of the crystal relative to the source and is essentially unknown.

Strong resonances of the lattice sum occur when the conditions for Bragg (or Laue) reflections are satisfied:

$$\mathbf{K} = \mathbf{k}_a - \mathbf{k}_b = 2\pi(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \quad (5.26)$$

where the triplet of integers, $h$, $k$, $l$ are the Miller indices of the reflection plane and the reciprocal vectors $\mathbf{b}_i$ are defined by:

$$\mathbf{b}_i = (\mathbf{a}_j \times \mathbf{a}_k)/(\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k). \quad (5.27)$$

[74] J. C. Slater, Phys. Rev. 76, 1592 (1949).

The forward direction $\mathbf{k}_a = \mathbf{k}_b$ always satisfies the Bragg conditions.

At these resonances the denominators of $I_{ba}$ vanish and $|I_{ba}|$ takes the maximum value $N = \nu N_1 N_2 N_3$. Thus the off-diagonal matrices $\bar{T}_{ba}$ are approximately as important as the diagonal $\bar{T}_{aa}$ if the incident direction $\mathbf{k}_a$ is at an appropriate Bragg angle. Away from a Bragg direction, only the diagonal matrix element $\bar{T}_{aa}$ is important—no scattering takes place, and the coherent wave is a plane wave whose index of refraction is determined by $c\bar{T}_{aa}$:

$$\bar{T}_{aa} = (\nu N_1 N_2 N_3)\left(\frac{1}{\nu}\sum_k T_{aa}(s_k)\right)$$

$$= nV\left(\frac{1}{\nu}\sum_k T_{aa}(s_k)\right). \quad (5.28)$$

If we note that because of our normalization procedure, $T_{aa}$ contains a factor $1/V$ we see that $\bar{T}_{aa}$ takes the same value as in the corresponding amorphous case (5.11). The index of refraction in the two cases—crystalline and random—will be approximately the same. However, the attenuation associated with the imaginary part of $T_{aa}$ does not apply to the crystalline case: since there is no scattering (away from the Bragg direction) there is no attenuation. The explanation of this paradox is that the correction factor $c$ for the effective field does not apply to the random case, but there is a correction in the crystalline case. And the correction is such that $c\bar{T}_{aa}$ is real. A detailed analysis of the crystalline effective field will be presented in another paper.[17a] We shall show that $c$ contains a small imaginary part with just the correct phase to cancel the imaginary part of $\bar{T}_{aa}$.

Near a Bragg reflection, when $\mathbf{k}_a$ touches one of the Brillouin zones, one off-diagonal matrix element $\bar{T}_{ba}$ will be important. At a Brillouin zone corner, several matrix elements will be important. The coherent wave equation (5.6) must then be treated by the methods of degenerate perturbation theory. The large mixing of states represents a large reflection from the forward direction to the allowed Bragg directions. In this way the effectively large attenuation known as extinction is produced.

One word of caution should be added in the use of (5.14) to calculate the index of refraction. This equation may be rewritten in the form (see (2.11)):

$$(k')^2 = k^2 - \frac{2m}{\hbar^2}c(\bar{T})_{aa}. \quad (5.29)$$

By this notation we emphasize that the averaging process $\langle \sum_j T(\mathbf{r}_j)\rangle$ should be performed *before* taking the diagonal matrix element. Usually $(\bar{T})_{aa} = (T_{aa})_{Av}$, i.e., the scattering due to the combined potential is usually equal to the sum of the waves scattered by the individual scatterers. In the presence of long range forces, however, the scattering potential in the neighborhood

of a given scatterer may be appreciably modified by the presence of other scatterers and the order of calculation may be important.[24]

The method and results of our calculation of the coherent wave and its index of refraction may be compared with that of a more familiar technique.[75] The most common procedure is to take a thin infinite slab (of thickness $w$) and calculate the scattered radiation at a distance $L$ far from the slab. If $f(\theta)$ is the scattering amplitude from a point in the plane to the point $(0, 0, L)$, the total radiation is given by

$$e^{ikL} + \int f(\theta)\frac{\exp[ik(\rho^2+L^2)^{\frac{1}{2}}]}{(\rho^2+L^2)^{\frac{1}{2}}}nw2\pi\rho d\rho \quad (5.30)$$

where $\tan\theta = \rho/L$. If we integrate by parts and drop terms that vanish as $L\to\infty$, the total radiation is given by

$$e^{ikL}[1 + 2\pi inwf(a\leftarrow a)/k]. \quad (5.31)$$

In physical terms, only the *forward* scattering amplitude appears because only the first Fresnel zone contributes to the scattered radiation. The introduction of the slab can now be interpreted as having produced a small phase change:

$$\text{phase change} = 2\pi nwf(a\leftarrow a)/k. \quad (5.32)$$

If the propagation constant in the medium is $k'$ it is customary[75] to calculate the phase change according to

$$\text{phase change} = (k'-k)w \quad (5.33)$$

which leads to the relation

$$k' = k + 2\pi nf(a\leftarrow a)/k. \quad (5.34)$$

This result is approximately but not precisely in agreement with the one (5.14) obtained in this paper. The explanation of the discrepancy is that (5.33) is not a sufficiently precise calculation of the phase change. The slab should be considered a medium of propagation constant $k'$ embedded in a medium of constant $k$. If reflections are taken into account, the transmission coefficient of the slab is found to be

$$t = 1 + iw(k'^2 - k^2)/(2k). \quad (5.35)$$

Comparing with (5.31) we obtain a relation

$$w(k'^2 - k^2)/(2k) = 2\pi nwf(a\leftarrow a)/k \quad (5.36)$$

precisely equivalent to (5.14) provided effective field corrections can be neglected.

Is it legitimate, however, to treat the thin slab as a medium? The basic objection to the entire thin slab calculation is that it postulates rather than derives the existence of a medium. Additional objections have been raised to the thin slab calculation in the presence of long range forces.[22]

[75] See for example, E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1950), p. 201, revised edition (Notes by Orear, Rosenfeld, and Schluter). Also reference 19.

## VI. INCOHERENT SCATTERING

The density of incoherent radiation is given by $\langle|\psi(\mathbf{r})|^2\rangle-|\langle\psi(\mathbf{r})\rangle|^2$ and its directionality is determined by $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle-\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle$. The purpose of this section is to obtain an integral equation for $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle$. The coherent wave $\langle\psi(\mathbf{r})\rangle$ is presumed known by the methods of the preceding section.

From a naive point of view one might expect the incoherent radiation to be the sum of the incoherent contributions of each scatterer. This will be true for a random distribution of scatterers. In general, there will be an additional contribution if the scatterers exhibit some partial order. This "correlation contribution" can be studied to obtain information concerning the structure of the scattering system. X-rays[70] and neutrons[71] have been used in this manner to study the structure of liquids and glasses.

If we start from the basic equations,

$$\begin{aligned}\psi^*(\mathbf{r}_0)&=\varphi^*(\mathbf{r}_0)+\textstyle\sum_k F^*(\mathbf{r}_0,\ \mathbf{r}_k)\\ \psi(\mathbf{r})&=\varphi(\mathbf{r})+\textstyle\sum_j F(\mathbf{r},\ \mathbf{r}_j)\end{aligned}\qquad(6.1)$$

multiply and average over the configuration of scatterers, we obtain:

$$\begin{aligned}\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle&=\varphi^*(\mathbf{r}_0)\varphi(\mathbf{r})+\varphi^*(\mathbf{r}_0)\{\langle\psi(\mathbf{r})\rangle-\varphi(\mathbf{r})\}\\ &\quad+\{\langle\psi(\mathbf{r}_0)\rangle-\varphi(\mathbf{r}_0)\}^*\varphi(\mathbf{r})\\ &\quad+\textstyle\sum_{j,k}\langle F^*(\mathbf{r}_0,\ \mathbf{r}_k)F(\mathbf{r},\ \mathbf{r}_j)\rangle.\end{aligned}\qquad(6.2)$$

On the other hand, we can average Eqs. (6.1) and then cross-multiply. Only the last term on the right-hand side of (6.2) is modified by this change in the order of operations. If the new result is subtracted from (6.2) we obtain some cancellation

$$\begin{aligned}\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle&-\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle\\ &=\textstyle\sum_{j,k}[\langle F^*(\mathbf{r}_0,\ \mathbf{r}_k)F(\mathbf{r},\ \mathbf{r}_j)\rangle\\ &\quad-\langle F^*(\mathbf{r}_0,\ \mathbf{r}_k)\rangle\langle F(\mathbf{r},\ \mathbf{r}_j)\rangle].\end{aligned}\qquad(6.3)$$

If the scatterers are fixed in position (e.g., a perfect lattice) then there is no averaging process to perform, and the right-hand side of (6.3) vanishes. In other words, for fixed scatterers the operations of multiplication and averaging commute and there is no incoherent scattering.||

As in the coherent case

$$\langle F(\mathbf{r},\ \mathbf{r}_j)\rangle=\frac{1}{E-H}\int p(\mathbf{r}_j)d\mathbf{r}_j T(\mathbf{r}_j)\langle\psi^j(\mathbf{r})\rangle_j.\qquad(6.4)$$

The first term in (6.3) is a sum that should be broken into its diagonal $(j=k)$ and off-diagonal terms. In the diagonal case the average is given by:

$$\begin{aligned}\langle F^*(\mathbf{r}_0,\ \mathbf{r}_j)F(\mathbf{r},\ \mathbf{r}_j)\rangle&=\frac{1}{(E-H_0)^*}\frac{1}{E-H}\\ &\times\int T_0^*(\mathbf{r}_j)T(\mathbf{r}_j)p(\mathbf{r}_j)d\mathbf{r}_j\langle\psi^j(\mathbf{r}_0)^*\psi^j(\mathbf{r})\rangle_j.\end{aligned}\qquad(6.5)$$

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|| Except of course for inelastic scattering by the individual scatterers—whose effects are incoherent and whose intensities are additive.

A subscript zero has been placed on operators acting on the variable $\mathbf{r}_0$. These operators commute with operators (containing no subscript) that act on the variable $\mathbf{r}$. The corresponding average for the off-diagonal terms is

$$\begin{aligned}\langle F^*(\mathbf{r}_0,\ \mathbf{r}_k)F(\mathbf{r},\ \mathbf{r}_j)\rangle&=\frac{1}{(E-H_0)^*}\frac{1}{E-H}\\ &\times\int T_0^*(\mathbf{r}_k)T(\mathbf{r}_j)p(\mathbf{r}_k,\ \mathbf{r}_j)d\mathbf{r}_j d\mathbf{r}_k\langle\psi^k(\mathbf{r}_0)^*\psi^j(\mathbf{r})\rangle_{kj}.\end{aligned}\qquad(6.6)$$

Up to this point our treatment of incoherent scattering is exact. In order to simplify the problem it is now necessary to introduce assumptions relating the exciting field to the total radiation. The assumptions we make are similar to those introduced in the coherent case:

$$\begin{aligned}\langle\psi^j(\mathbf{r})\rangle_j&\approx c\langle\psi(\mathbf{r})\rangle\\ \langle\psi^j(\mathbf{r}_0)^*\psi^j(\mathbf{r})\rangle_j&\approx|c|^2\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle\\ \langle\psi^k(\mathbf{r}_0)^*\psi^j(\mathbf{r})\rangle_{jk}&\approx|c|^2\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle.\end{aligned}\qquad(6.7)$$

Equation (6.3) can now be simplified to the form:

$$\begin{aligned}\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle&-\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle\\ &=\frac{|c|^2}{(E-H_0)^*(E-H)}[(M+Q)\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle\\ &\quad-\bar{T}_0^*\bar{T}\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle]\end{aligned}\qquad(6.8)$$

$$\bar{T}_0^*=N\int T_0^*(\mathbf{r}_j)p(\mathbf{r}_j)d\mathbf{r}_j$$

$$M=N\int T_0^*(\mathbf{r}_j)T(\mathbf{r}_j)p(\mathbf{r}_j)d\mathbf{r}_j\qquad(6.9)$$

$$Q=N(N-1)\int T_0^*(\mathbf{r}_k)T(\mathbf{r}_j)p(\mathbf{r}_k,\ \mathbf{r}_j)d\mathbf{r}_k d\mathbf{r}_j.$$

After clearing of fractions (6.8) takes the form:

$$\begin{aligned}[(E-H_0)^*(E-H)-|c|^2\bar{T}_0^*\bar{T}]&\\ \times[\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle-\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle]&\\ =|c|^2(M+Q-\bar{T}_0^*\bar{T})\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle.&\end{aligned}\qquad(6.10)$$

Using the coherent wave equation (5.6) to annihilate the factor $\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle$, we obtain a homogeneous equation

$$\begin{aligned}[(E-H_0)^*(E-H)&\\ -|c|^2(M+Q)]\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle&=0.\end{aligned}\qquad(6.11)$$

Equation (6.10) can also be rewritten as an inhomogeneous integral equation:

$$\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle=\langle\psi^*(\mathbf{r}_0)\rangle\langle\psi(\mathbf{r})\rangle+L\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle\qquad(6.12)$$

$$L=\frac{1}{(E-H_0)^*(E-H)-|c|^2\bar{T}_0^*\bar{T}}|c|^2[M+Q-\bar{T}_0^*\bar{T}].\qquad(6.13)$$

In this form, we see that the coherent wave is the original source of the incoherent radiation. In fact to a first approximation (neglecting $L$) the total radiation is all coherent:

$$\langle \psi^*(r_0)\psi(r)\rangle \simeq \langle \psi^*(r_0)\rangle \langle \psi(r)\rangle. \qquad (6.14)$$

The higher approximations may be obtained from an iterated solution of (6.12):

$$\langle \psi^*(r_0)\psi(r)\rangle = (1+L+L^2+\cdots)\langle \psi^*(r_0)\rangle \langle \psi(r)\rangle. \qquad (6.15)$$

The operator $L$ generates only incoherent scattering. The effects of coherent scattering are already taken into account in the coherent density $\langle \psi^*(r_0)\rangle \langle \psi(r)\rangle$, in short, by the introduction of a medium. The successive terms $L, L^2\cdots$ represent radiation that has been incoherently scattered once, twice$\cdots$.

The term $M$ represents the purely incoherent addition of the intensities of the individual scatterers. To show this, we take the matrix element describing scattering from direction $\mathbf{k}_a$ to $\mathbf{k}_b$:

$$M_{ba;ba} = N|T_{ba}|^2. \qquad (6.16)$$

This term includes all processes inelastic (and elastic) with respect to an individual scatterer. The term $Q-\bar{T}_0^*\bar{T}$ represents scattering due to the correlation $p(\mathbf{r}_1, \mathbf{r}_2)-p(\mathbf{r}_1)p(\mathbf{r}_2)$ between scatterer locations:

$$(Q-\bar{T}_0^*\bar{T})_{ba;ba} = N^2|T_{ba}|^2 \int \exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}_{jk}]$$

$$\times [p(\mathbf{r}_j, \mathbf{r}_k)-p(\mathbf{r}_j)p(\mathbf{r}_k)]d\mathbf{r}_j d\mathbf{r}_k \quad (6.17)$$

where $\mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k$ is the separation of a pair of scatterers. This scattering, as we remarked in the introduction, is inelastic because recoil energy is absorbed by a group of scatterers. However, it is elastic with respect to the individual scatterers, i.e., the internal state of the scatterers is not modified since such modification would destroy all phase relations.

If we introduce relative coordinates $\mathbf{r}_{jk}$ and average coordinates $\mathbf{R}=(\mathbf{r}_j+\mathbf{r}_k)/2$, $p(\mathbf{r}_j\mathbf{r}_k)$ can, except for edge effects, be regarded as a function only of the separation. Integrating over $d\mathbf{R}$ and combining terms we get:

$$(M+Q-\bar{T}_0^*\bar{T})_{ba;ba} = N|T_{ba}^{el}|^2E+N|T_{ba}^{in}|^2 \quad (6.18)$$

$$E = \left[1+n\int \exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}_{jk}]g(\mathbf{r}_{jk})d\mathbf{r}_{jk}\right]$$
$$\qquad (6.19)$$
$$g(\mathbf{r}_{jk}) = \frac{p(\mathbf{r}_j\mathbf{r}_k)}{p^2}-1$$

where we have separated the terms elastic and inelastic with respect to the individual scatterers. Note that $\mathbf{k}_a$ and $\mathbf{k}_b$ are propagation vectors *in the medium*.

The turbidity $\tau$ of the medium, i.e., the attenuation constant of the coherent beam, may be obtained by solving the integral equation (6.12) in Born approximation (keeping only terms of order $|T|^2$). The result is

the same as if the scattering cross section of the individual scatterers were replaced by an effective cross section:

$$\tau = n\sigma_{\text{eff}}$$
$$d\sigma_{\text{eff}} = |c|^2 d\sigma^{el}E + |c|^2 d\sigma^{in}. \qquad (6.20)$$

The differential form is used here because $E$ modifies the angular distribution of the scattering. The choice $E=1$ is equivalent to a particle viewpoint since it neglects all correlations. $E-1$ is the usual liquid diffraction pattern.

Except near the critical point $g(\mathbf{r}_{jk})$ is appreciable only for distances of the order of the molecular separation. Thus for wavelengths large compared to the scatterer spacing, the exponential may be replaced by unity and

$$E = \left[1+n\int g(\mathbf{r})d\mathbf{r}\right] \qquad (6.21)$$

no longer modifies the angular distribution.

If we return to our original definitions (6.3) or (6.9) $E$ can be given a simple interpretation:

$$NE = \langle |\sum_j \exp[i(\mathbf{k}_a-\mathbf{k}_b)]\cdot\mathbf{r}_j|^2\rangle$$
$$\qquad - |\langle \sum_j \exp[i(\mathbf{k}_a-\mathbf{k}_b)\cdot\mathbf{r}_j]\rangle|^2. \quad (6.22)$$

In the long wave limit we obtain the result that $E$ is related to the density fluctuations:

$$NE = \langle N^2\rangle - |\langle N\rangle|^2 = \langle(\Delta N)^2\rangle. \qquad (6.23)$$

## A. Light Scattering

It may be of interest to compare these results with the phenomenological treatment of light scattering. The total cross section for scattering by a molecule of polarizability $\alpha$ is:

$$\sigma = \left(\frac{2\pi}{\lambda}\right)^4 \alpha^2 \int \frac{1+\cos^2\theta}{2}d\Omega \qquad (6.24)$$

so that

$$\sigma_{\text{eff}} = \left(\frac{2\pi}{\lambda}\right)^4 (\alpha c)^2 \int E\frac{1+\cos^2\theta}{2}d\Omega. \qquad (6.25)$$

The unknown constant $c$ can be eliminated since it also determines the index of refraction. Using (1B4):

$$\alpha c = (\epsilon-1)/4\pi n. \qquad (6.26)$$

Away from the critical point, $E$ is independent of angle and may be expressed in terms of the density fluctuations (6.23). Using (6.20) and (6.26) we have

$$\tau = 8\pi^3/3\lambda^4[(\epsilon-1)/n]^2(n/N)\langle(\Delta N)^2\rangle. \qquad (6.27)$$

This is in agreement with the phenomenological answer (1H3) and (1H5) if the choice $\Delta\epsilon/\Delta n = (\epsilon-1)/n$ is made. Agreement with the latter choice should be no surprise, since we have made use of the Born approximation.

Near the critical point, fluctuations, comparable to the wavelength may occur, and it is necessary to use

the original expression (6.19) for $E$. Although the correlation function $g(\mathbf{r})$ is unknown, its normalization is known through (6.21) and (6.23). Thus we may write the turbidity in the form:

$$\tau = \frac{\pi^2}{\lambda^4}\frac{(\epsilon-1)^2}{n}\int d\Omega \frac{1+\cos^2\theta}{2}\left[1+\left\{\frac{(\Delta N)^2}{N}-1\right\}\overline{\cos\mathbf{K}_{ab}\cdot\mathbf{r}}\right]$$

$$\overline{\cos\mathbf{K}_{ab}\cdot\mathbf{r}} = \int \cos\mathbf{K}_{ab}\cdot\mathbf{r}g(\mathbf{r})d\mathbf{r}\Big/\int g(\mathbf{r})d\mathbf{r}$$

$$\mathbf{K}_{ab}=\mathbf{k}_a-\mathbf{k}_b; \quad |\mathbf{K}_{ab}|=2k\sin\frac{\theta}{2}. \qquad (6.28)$$

Ornstein and Zernike[49] have investigated critical point fluctuations and concluded that the approximate form of the correlation function is $g(\mathbf{r})\sim r^{-1}\exp(-\kappa r)$ where $1/\kappa$ measures the "range" of the correlation. At the critical point itself $\kappa\to0$. With this choice of $g(\mathbf{r})$

$$\overline{\cos\mathbf{K}_{ab}\cdot\mathbf{r}} = \frac{\kappa^2}{\kappa^2+\mathbf{K}_{ab}^2}. \qquad (6.29)$$

Thus the scattering will have a forward maximum that becomes sharper and more pronounced as the critical point is approached. This peak corresponds to scattering by molecular clusters of size $\kappa^{-1}$. At a given angle, the frequency dependence of the scattering varies from $k^4$, away from the critical point ($\kappa\gg k$) to $k^2$ near the critical point ($\kappa\ll k$). The total attenuation is given by:

$$\tau = \frac{8\pi^3}{3\lambda^4}\frac{(\epsilon-1)^2}{n}\left[1+\left\{\frac{(\Delta N)^2}{N}-1\right\}\frac{\kappa^2}{\kappa^2+2k^2}I\right]$$

$$I = \frac{3}{8\pi}\int\frac{1+\cos^2\theta}{2}\frac{a}{a-\cos\theta}d\Omega$$

$$= \tfrac{3}{4}a\left[(a^2+1)\ln\frac{a+1}{a-1}-2a\right]$$

$$\simeq[1+\tfrac{9}{16}a^{-2}+\tfrac{2}{5}a^{-4}+\cdots]; \quad a-1=\frac{\kappa^2}{2k^2}. \qquad (6.30)$$

This formula diverges at the critical point, $\kappa=0$. However, the formula is not valid for fluctuation distances $1/\kappa$ comparable to the size of the macroscopic sample. In this case, the region of integration over $d\mathbf{r}$ is limited by the sample, and a finite attenuation dependent on the sample size is obtained. This point has been discussed in detail by Placzek.[76] However, the temperature region in which the fluctuation distance $1/\kappa$ is macroscopic in size is so close to the critical point as to be experimentally unrealizable. And, in fact, $\kappa/k$ is often large compared to unity, even near the critical point. The explanation for this is simply that fluctuation

[76] G. Placzek, Physik. Z. 31, 1052 (1930).

distances are usually of the order of intermolecular separations $10^{-8}$ cm. An increase by a factor $10^4$ is needed to make them comparable to the wavelength, and an additional factor of $10^4$ is needed to make them macroscopic in size.

The experimental work of Andant,[77] Battacharya,[78] Rousset,[79] and Drickamer[65] can be summarized briefly as follows: The frequency dependence of the scattering at a given angle for most substances changes from $k^4$ to $k^2$ as the critical point is approached. However, there are exceptions. A more detailed check on the angular and frequency dependence of the scattering under adequately controlled conditions seems advisable. Transmission measurements of the total attenuation may help to eliminate the effects of multiple scattering and absorption.

In any case a theory of the dependence of $\kappa$ on the thermodynamic state of the system is still lacking. Ornstein and Zernike show that $\kappa$ can be computed from:

$$\kappa^2 = \frac{6N}{\langle(\Delta N)^2\rangle\sigma^2} = \frac{6}{n(kT)\beta\sigma^2} \qquad (6.31)$$

$$\sigma^2 = \int r^2 f(\mathbf{r})d\mathbf{r} \qquad (6.32)$$

where $\beta$ is the compressibility, and $\sigma^2$ has the dimensions of an area. $f(\mathbf{r})$ represents the average fluctuations in density at $\mathbf{r}$ due to a unit fluctuation $\delta(\mathbf{r})$ at the origin, assuming that the density elsewhere is held at its average value. For comparison, $g(\mathbf{r})$ describes the mean density fluctuation at $\mathbf{r}$ induced by a fluctuation at the origin permitting the density at intermediate points to fluctuate. Thus $f(\mathbf{r})$ is a measure of the range at which molecular forces are directly effective—whereas $g(\mathbf{r})$ is a measure of the range at which they can be indirectly effective by means of "cooperative phenomena." Thus, we might expect $\kappa$ to depend strongly on the temperature, and $\sigma$ weakly. The experiments of Babb and Drickamer,[52] however, show that $\sigma$ itself depends fairly strongly on the temperature—the range of forces, or "size of molecular clusters" increasing to 1000 molecular diameters near the critical point. In addition there is a rapid decrease of scattering in the immediate neighborhood of the critical point that must be explained.

It should be emphasized that all of the results quoted here and applied to the light scattering situation are based on a Born approximation solution of the integral equation (6.12), i.e., these results neglect the effect of multiple incoherent scattering. We do not intend to solve this integral equation here, but it may be worthwhile to discuss its implications. Roughly speaking, we can say that the numerator of $L$: $|c|^2(M+Q-\bar{T}_0*\bar{T})$ describes the probability of a wave being scattered

[77] A. Andant, J. phys. et radium 5, 193 (1924).
[78] D. K. Battacharya, Proc. Ind. Assoc. Cultiv. Sci. 8, 277 (1923).
[79] A. Rousset, Ann. phys. 5, 5 (1936).

from one state (direction) to another. The denominator of $L$ then describes the spreading and attenuation that takes place between the point of scattering and the point of observation. This last remark can perhaps be best understood after introducing an approximation due to Foldy:[12]

$$(E-H_0)^*(E-H)-|c|^2\bar{T}_0^*\bar{T}$$
$$\equiv(E-H_0-c\bar{T}_0)^*(E-H-c\bar{T})$$
$$+(c\bar{T}_0)^*(E-H-c\bar{T})+(E-H_0-c\bar{T}_0)^*c\bar{T} \quad (6.33)$$

$$(E-H_0)^*(E-H)-|c|^2\bar{T}_0^*\bar{T}$$
$$\simeq(E-H_0-c\bar{T}_0)^*(E-H-c\bar{T}). \quad (6.34)$$

In the space representation:

$$\langle\mathbf{r}'|(E-H-c\bar{T})^{-1}|\mathbf{r}\rangle\sim\frac{\exp(ik'|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \quad (6.35)$$

where $k'$ is the propagation constant in the medium. The other factor has a similar form:

$$\langle\mathbf{r}_0'|(E-H_0-c\bar{T}_0)^{*-1}|\mathbf{r}_0\rangle\sim\left\{\frac{\exp(ik'|\mathbf{r}_0-\mathbf{r}_0'|)}{|\mathbf{r}_0-\mathbf{r}_0'|}\right\}^*. \quad (6.36)$$

The propagation from $\mathbf{r}$ to $\mathbf{r}'$ may be understood by setting $\mathbf{r}=\mathbf{r}_0$, $\mathbf{r}'=\mathbf{r}_0'$ so that the product of these two factors has the form $\exp[-2Imk'|\mathbf{r}-\mathbf{r}'|]/(\mathbf{r}-\mathbf{r}')^2$, i.e., an inverse square spreading factor times the appropriate exponential attenuation.

For the case of isotropic point scatterers¶ distributed at random, we obtain Foldy's integral equation:

$$\langle|\psi(\mathbf{r})|^2\rangle=|\langle\psi(\mathbf{r})\rangle|^2$$
$$+|f|^2\int\frac{\exp(-2Imk'|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^2}\langle|\psi(\mathbf{r}')|^2\rangle n(\mathbf{r}')d\mathbf{r}' \quad (6.37)$$

after making the approximation (6.34). This is precisely the integral equation one would write down from an intuitive "particle" point of view. Thus the error involved in Foldy's approximation (6.34) is a measure of the discrepancy between the wave and particle points of view. There will, of course, be additional differences if the scatterers are not distributed at random. These appear in the term $Q-\bar{T}_0^*\bar{T}$. All of these errors should be small if the wavelength $\lambda$ is small compared to the average scatterer separation $n^{-\frac{1}{3}}$, i.e., if $n\lambda^3\ll1$.

Point isotropic scatterers represent the only case for which an integral equation can be obtained for $\langle|\psi(\mathbf{r})|^2\rangle$ alone. Usually one must deal with the more general quantity $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle$, i.e., the scattering from a given region is determined not only by the density but also the directionality of the given radiation. In general we must make use of matrix elements of $L$ for which $\mathbf{r}_0\neq\mathbf{r}$. For point scatterers, only the values of $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle$

¶ Our results can be reduced to the case of isotropic point scatterers by choosing the form $T(\mathbf{r}_j)=-2\pi\hbar^2f\delta(\mathbf{q}-\mathbf{r}_j)$ where $\mathbf{q}$ is the $m$ position operator and $f$ the scattering amplitude, see (2.11).

in the immediate neighborhood $\mathbf{r}_0=\mathbf{r}$ are necessary. However point dipole scattering involves quantities of the form $\langle|\nabla\psi(\mathbf{r})|^2\rangle$ that can be computed from $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle$ but not from $\langle|\psi(\mathbf{r})|^2\rangle$ since the latter has lost all directionality information.

In a future paper we shall show that our integral equation for $\langle\psi^*(\mathbf{r}_0)\psi(\mathbf{r})\rangle$ can be transformed into an integral equation:

$$F(\mathbf{k}, \mathbf{r})=F_0(\mathbf{k}, \mathbf{r})$$
$$+\int K(\mathbf{k}, \mathbf{k}'; \mathbf{r}, \mathbf{r}')F(\mathbf{k}', \mathbf{r}')d\mathbf{k}'d\mathbf{r}' \quad (6.38)$$

for the density $F(\mathbf{k}, \mathbf{r})$ in phase space $d\mathbf{k}d\mathbf{r}$. This will facilitate a more detailed comparison with the particle point of view.

## VII. RELATION TO THE MANY BODY PROBLEM

In this paper we have attempted to describe the interaction of a wave with a system containing many particles using a multiple scattering point of view. In other words, we assume that the interaction of the wave with a single particle is known and that the interaction with the system is a combination of single particle scatterings. This point of view, however, does not provide a complete description of the possibilities associated with the many particle system. The purpose of this section is to indicate the sort of approximations implicit in the multiple scattering viewpoint in such a manner that the range of validity of the latter viewpoint can be understood.

It will be useful to consider first the calculation of the wave solution assuming the particle motion is known. Our procedure was to (1) obtain a solution $\psi(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2\cdots\mathbf{r}_N)$ for a fixed set of particle positions (2) permit these positions to vary with time, and average over time (3) replace the time average by an ensemble average. As far as the wave motion is concerned, the particle positions have been treated as *adiabatic parameters*.[80] This approximation is valid only if the particles are moving sufficiently slowly.

The description of the many-particle system enters only through the probability distribution $p(\mathbf{r}_1, \mathbf{r}_2\cdots\mathbf{r}_N)$. The influence of the wave on this distribution has been neglected. In other words, the many particle system is treated in Born approximation.

If *both* the wave and the particles are treated in Born approximation the complete wave function of wave plus system can be written in factored form $\psi(\mathbf{r})\Psi_i(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N)$. The Schrödinger equation of the wave plus system

$$[E-H-\sum_jV(\mathbf{r}-\mathbf{r}_j)]\psi(\mathbf{r})\Psi_i=0 \quad (7.1)$$

can be multiplied by $\Psi_i^*$ and integrated over the par-

[80] W. Pauli, *Handbuch der Physik*, Vol. 24/1, p. 161.

ticle variables to obtain a coherent wave equation:[23]

$$[E - H - \bar{V}]\psi(\mathbf{r}) = 0$$

$$\bar{V} = \int V(\mathbf{r} - \mathbf{r}_j) n(\mathbf{r}_j) d\mathbf{r}_j.$$

(7.2)

This is less satisfactory than the adiabatic treatment of the scattering since index of refraction now depends on $V_{aa}$ rather than on the forward scattered amplitude $T_{aa}$. The latter result is to be preferred from an intuitive point of view.

The errors involved in the adiabatic approximation are perhaps most serious for the incoherent scattering and it seems advisable to take into account (1) the momentum distribution of the scatterers and (2) the dependence of the matrix elements on the momentum of the scatterers. If the scattering system can be treated classically this can be done simply by introducing densities $n(\mathbf{r}_j, \mathbf{p}_j)$ in phase space and matrix elements $T_{ba}(\mathbf{r}_j, \mathbf{p}_j)$. In other words, the momentum $\mathbf{p}$ is treated as one of the parameters $s$ that describe the scatterer (see Sec. III).

If the scattering system must be treated quantum mechanically, however, a unique density in phase space does not exist. In addition, the recoil momentum absorbed by the scatterer must be taken into account. Thus we must use transition matrix elements of the form $T_{ba}{}^{\mathbf{p}'\mathbf{p}}(\mathbf{r}_j)$ where $\mathbf{p}'$ is the final momentum of the scatterer.

A closely related limitation of the multiple scattering approach is that it is based on a closure summation over all the final states of the scattering system (see Sec. IE). The closure approximation is valid only if one sums over *all* final states. On the other hand, it is only permissible to sum over those final states that conserve energy. Again, we see that corrections to the usual multiple scattering approach must be based on a consideration of the energetics of the problem.

In order to understand the nature of these corrections we shall consider a simplified problem: scattering by a finite system small enough to neglect multiple scattering effects. First of all, we shall state that for a single scatterer the exact transition probability per unit time $w_{ba}$ from direction $\mathbf{k}_a$ to direction $\mathbf{k}_b$ is given by:

$$w_{ba} = (2\pi)^{-2} \int d\mathbf{k}_b d\mathbf{p}' |T_{ba}{}^{\mathbf{p}'\mathbf{p}}|^2$$
$$\times \delta(\mathbf{k}_b + \mathbf{p}' - \mathbf{k}_a - \mathbf{p}) \delta(E_f - E_i). \quad (7.3)$$

The integration over $\mathbf{k}_b$ and $\mathbf{p}'$ arises from a summation over final states. The conservation of momentum condition arises from the integration over the initial and final states of the wave and the scatterer—all of which are represented by plane waves. The conservation of energy condition is part of the perturbation formula (2.8).

$$E_f = E_b + (p'^2/2M), \quad E_i = E_a + (p^2/2M). \quad (7.4)$$

Equation (7.4) indicates the form these energies take

if the scatterer is sufficiently heavy to be treated non-relativistically. This assumption is unnecessary to our general procedure. We have used units in which $\hbar = 1$ so that $k$ and $p$ both have the dimensions of momentum.

For a scattering system in the initial quantum-mechanical state $\Psi_i$ with the possible final states $\Psi_f$, the corresponding transition probability per unit time is given by:

$$w_{ba} = (2\pi)^{-2} \int d\mathbf{k}_b \sum_f |(\Psi_f, \sum_j T_{ba}(\mathbf{r}_j)\Psi_i)|^2$$

$$\times \delta(E_f - E_i). \quad (7.5)$$

This result can be reduced to the form obtained by the multiple scattering method, if we neglect energy restrictions on the sum over final states and apply closure:

$$\sum_{\text{all} f} |(\Psi_f, \sum_j T_{ba}(\mathbf{r}_j)\Psi_i)|^2 = (\Psi_i, |\sum_j T_{ba}(\mathbf{r}_j)|^2 \Psi_i) \quad (7.6)$$

$$= |T_{ba}|^2 (\Psi_i, |\sum_j \exp[i(\mathbf{k}_a - \mathbf{k}_b) \cdot \mathbf{r}_j]|^2 \Psi_i). \quad (7.7)$$

In going from (7.6) to (7.7) we have tacitly neglected the momentum dependence of the operator $T_{ba}{}^{\mathbf{p}'\mathbf{p}}$, i.e., the action of this operator on state $\Psi_i$.

In order to estimate the error involved in the closure approximation, we return to the original equation (7.5). If the states $\Psi_i$ and $\Psi_f$ are expressed in momentum space, the matrix element can be written in the form:

$$(\Psi_f, \sum_j T_{ba}(r_j)\Psi_i) = \int T_{ba}{}^{\mathbf{p}'\mathbf{p}} \delta(\mathbf{k}_b + \mathbf{p}' - \mathbf{k}_a - \mathbf{p})$$

$$\times \rho_{fi}(\mathbf{p}'; \mathbf{p}) d\mathbf{p}' d\mathbf{p} \quad (7.8)$$

where $\rho_{fi}(\mathbf{p}'; \mathbf{p})$ is the transition momentum density defined by:

$$\rho_{fi}(\mathbf{p}'; \mathbf{p}) = \sum_r \int \Psi_f{}^*(\mathbf{p}_1, \cdots \mathbf{p}_r = \mathbf{p}', \cdots \mathbf{p}_N)$$

$$\times \Psi_i(\mathbf{p}_1 \cdots \mathbf{p}_r = \mathbf{p}, \cdots \mathbf{p}_N) d\mathbf{p}_1 \cdots d\mathbf{p}_N / d\mathbf{p}_r. \quad (7.9)$$

The difficult part of the calculation of the squared matrix element is the evaluation of a sum of the form:

$$S = \sum_f \rho_{fi}{}^*(\mathbf{p}''', \mathbf{p}'') \rho_{fi}(\mathbf{p}', \mathbf{p}) \delta(E_f - E_i). \quad (7.10)$$

Unless one makes use of the complete closure approximation (7.6) the sum (7.10) cannot be evaluated without some assumption concerning the nature of the final state and its energy.

Suppose that the scattering system can be described in Hartree approximation:

$$\Psi_i(\mathbf{p}_1 \cdots \mathbf{p}_N) = \phi_1(\mathbf{p}_1) \cdots \phi_j(\mathbf{p}_j) \cdots \phi_N(\mathbf{p}_N)$$
$$\Psi_f(\mathbf{p}_1 \cdots \mathbf{p}_N) = \phi_1(\mathbf{p}_1) \cdots \phi_f(\mathbf{p}_j) \cdots \phi_N(\mathbf{p}_N). \quad (7.11)$$

Equation (7.11) describes a "one-particle" transition in which particle $j$ changes from state $j$ to state $f$. For this case, the transition momentum density is given by:

$$\rho_{fi}(\mathbf{p}', \mathbf{p}) = \phi_f{}^*(\mathbf{p}') \phi_j(\mathbf{p}) \quad (7.12)$$

and the sum $S$ takes the form:

$$S = \sum_{\text{all} f} \sum_{j=1}^{N} \phi_j{}^*(\mathbf{p}'')\phi_j(\mathbf{p})\phi_f{}^*(\mathbf{p}')\phi_f(\mathbf{p}''')\delta(E_f - E_i). \quad (7.13)$$

The energy difference can be written

$$E_f - E_i = E_b - E_a + \epsilon_f - \epsilon_j \quad (7.14)$$

where $E_b - E_a$ is the change in field energy and $\epsilon_f - \epsilon_j$ is the change in system energy associated with the transition of a particle from state $j$ to state $f$. The energies $\epsilon_j$ of the occupied states of the system will usually have a small spread compared to the possible final energies $\epsilon_f$. We shall therefore make the simplification of regarding $\epsilon_j \simeq \epsilon$ as being independent of $j$. In this way, the sum $S$ can be made to depend on the initial momentum distribution:

$$S \simeq \rho_{ii}(\mathbf{p}''; \mathbf{p})\sum_f \phi_f{}^*(\mathbf{p}''')\phi_f(\mathbf{p}')\delta(E_b - E_a + \epsilon_f - \epsilon)$$
$$\quad (7.15)$$
$$\rho_{ii}(\mathbf{p}''; \mathbf{p}) = \sum_{j=1}^{N} \phi_j{}^*(\mathbf{p}'')\phi_j(\mathbf{p}).$$

The one-particle contribution to the closure cross section can be obtained by neglecting all energetic restrictions i.e., regarding $\epsilon_f \simeq \epsilon'$ as independent of $f$ and extending the sum to all final states including those that violate conservation of energy:

$$\sum \phi_f{}^*(\mathbf{p}''')\phi_f(\mathbf{p}') = \delta(\mathbf{p}''' - \mathbf{p}'). \quad (7.16)$$

If this result is inserted into the preceding equations, (7.5) takes the form:

$$w_{ba} = (2\pi)^{-2} \int d\mathbf{k}_b \delta(E_b - E_a + \epsilon' - \epsilon) \int |T_{ba}{}^{\mathbf{p}'\mathbf{p}}|^2$$

$$\times \rho_{ii}(\mathbf{p}; \mathbf{p})\delta(\mathbf{p}' + \mathbf{k}_b - \mathbf{p} - \mathbf{k}_a)d\mathbf{p}'d\mathbf{p}. \quad (7.17)$$

Equation (7.17) is very suggestive of a simple superposition of the contributions of scatterers of various momenta:

$$w_{ba} = \int w_{ba}(\mathbf{p})\rho_{ii}(\mathbf{p}; \mathbf{p})d\mathbf{p}. \quad (7.18)$$

Equations (7.17) and (7.18) are equivalent, however, only if $\epsilon' - \epsilon$ is set equal to a function of $\mathbf{k}_a - \mathbf{k}_b$ appropriate to the single scattering problem.

Equations (7.17) or (7.18), based on the closure approximation (7.16), in general, overestimate the correct answer because they include contributions from final states that are excluded by energy conservation. In order to indicate when this overestimate is serious we shall attempt a calculation not based on the closure sum (7.16). For this purpose, it will be necessary to make some explicit assumption concerning the final state $\phi_f(p')$. The simplest assumption, valid in a large number of cases, is that the recoil particle may be described by a plane wave of definite momentum:

$$\phi_f(\mathbf{p}') = \delta(\mathbf{p}' - \mathbf{p}_f); \quad \epsilon' = (p_f{}^2/2M). \quad (7.19)$$

Using (7.15) and (7.5), we find for the transition probability

$$w_{ba} = (2\pi)^{-2} \int d\mathbf{k}_b \int |T_{ba}{}^{\mathbf{p}'\mathbf{p}}|^2 \rho_{ii}(\mathbf{p}; \mathbf{p})$$

$$\delta(\mathbf{p}' - \mathbf{p} + \mathbf{k}_b - \mathbf{k}_a)\delta\left(E_b - E_a + \frac{p'^2}{2M} - \epsilon\right)d\mathbf{p}'d\mathbf{p}, \quad (7.20)$$

a result similar to (7.17), except that the domain of integration is limited by the energy conservation delta function.

In order to compare the transition probability for the system (7.20) with the corresponding probability for a single scatterer (7.3) we note that the phase space density has the normalization:

$$\int \rho_{ii}(\mathbf{p}; \mathbf{p})d\mathbf{p} = N \quad (7.21)$$

and that the choice

$$\rho_{ii}(\mathbf{p}; \mathbf{p}) = \delta(\mathbf{p}) \quad (7.22)$$

together with $\epsilon = 0$ would reduce (7.20) to the corresponding result (7.3) for a single scatterer. To a first approximation then, the system cross section will be $N$ times the single scatterer cross section. Actually, this first approximation is an overestimate because the retion of integration over $\mathbf{p}$ does not completely cover the density function $\rho_{ii}(\mathbf{p}; \mathbf{p})$ because of energy momentum considerations. To determine the extent of this overestimate, we must determine the region of integration over $\mathbf{p}$ and compare it to the region in which $\rho_{ii}(\mathbf{p}; \mathbf{p})$ is important.

By integrating first over $\mathbf{p}'$ and $\mathbf{k}_b$, (7.20) can be written approximately in the form:

$$w_{ba}(\text{system}) = \int w_{ba}(\mathbf{p})\rho_{ii}(\mathbf{p}; \mathbf{p})d\mathbf{p}$$
over $\quad (7.23)$
$$|\mathbf{p} + \mathbf{k}_a| \leqslant d$$

where $w_{ba}(\mathbf{p})$ is the transition probability for a single scatterer of momentum $\mathbf{p}$. The limits of integration are determined by the energy conservation condition

$$E_b - E_a + \frac{(\mathbf{p} + \mathbf{k}_a - \mathbf{k}_b)^2}{2M} - \epsilon = 0 \quad (7.24)$$

after $\mathbf{k}_b$ has been allowed to take the extreme values permitted to it. The most favorable direction for $\mathbf{k}_b$ is parallel to $\mathbf{p} + \mathbf{k}_a$ since there the scattered wave is best able to absorb the incident momentum. The region of integration is then

$$|\mathbf{p} + \mathbf{k}_a| \leqslant d \quad (7.25)$$

where $d$ is the maximum with respect to $\mathbf{k}_b$ of the expression

$$d = \{[2M(E_a - E_b + \epsilon)]^{\frac{1}{2}} + k_b\}_{\max}. \qquad (7.26)$$

For simplicity, let us assume that the relation between $E_b$ and $k_b$ is the nonrelativistic relation between total energy (kinetic+rest) and momentum:

$$E_b \sim m_b c^2 + k_b^2 / 2m_b. \qquad (7.27)$$

In this case, the value of $d$ is:

$$\begin{aligned} d &= [2(M + m_b)(E_a - E_t)]^{\frac{1}{2}} \\ E_t &= m_b c^2 - \epsilon, \end{aligned} \qquad (7.28)$$

where $E_t$ can be interpreted as the threshold energy for the reaction.
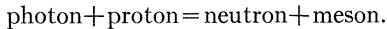
The region covered by the momentum space density can be described by the root-mean-square momentum $(\Delta p)$:

$$(\Delta p)^2 = \int \mathbf{p}^2 \rho_{ii}(\mathbf{p}; \mathbf{p}) d\mathbf{p} / N. \qquad (7.29)$$

We are now in a position to state the condition under which the one-particle closure contribution (7.18) is a good approximation to the correct transition probability. The condition is that the sphere of integration $|\mathbf{p} + \mathbf{k}_a| \leqslant d$ of radius $d$ about $-\mathbf{k}_a$ should enclose the sphere $\mathbf{p} \leqslant (\Delta p)$ near the origin in which the momentum density $\rho_{ii}(\mathbf{p}; \mathbf{p})$ is important. This condition will be satisfied if:

$$d > k_a + \Delta p. \qquad (7.30)$$

The analysis presented here has been applied to the production of mesons in a collision of a photon with a nucleus.[34] For this application $\mathbf{k}_a$ and $E_a$ can be interpreted as momentum and energy of the incident photon; $\mathbf{k}_b$ and $E_b$ are the momentum and energy of the produced meson. The scattering system is a nucleus, and the individual scatterers are nucleons. For positive meson production the basic reaction is of the form:

photon+proton = neutron+meson.

The cross section for photoproduction by a nucleus is related to the corresponding cross section for a free proton by a formula essentially the same as (7.23) except that only the density in momentum space of the protons appears.

The significance of the limitation (7.25) is that only a certain portion of the proton momentum distribution is energetically capable of interacting with the photon to produce a meson. Near threshold only protons moving with momenta nearly opposite to the photon can participate in the collision. In this case, a minimum of energy is used to satisfy momentum restrictions and a maximum is available for the reaction itself. At high photon energies there is energy to waste on momentum requirements, and the photon can interact even with protons moving away from it. At sufficiently high ener-

gies, the closure condition (7.30) will be fulfilled when the photon can interact with the major portion of the protons (the latter are concentrated in a sphere of approximate radius $\Delta p$).

The closure approximation is then rather successful at high energies. The dynamical reason for this is that at high energies the binding of the scatterers into a system is unimportant—the scatterers can be treated as if they were free. This treatment will be valid when the recoil momentum that would be acquired by a single scatterer is large compared to the rms momentum it had before the collision—a condition described mathematically by (7.30). Under these circumstances, the wavelength $h/|\mathbf{k}_a - \mathbf{k}_b|$ associated with the momentum transfer $|\mathbf{k}_a - \mathbf{k}_b|$ will usually be small compared to the scatterer separations, and interference effects from the various scatterers can be neglected. These interference terms have been neglected in our discussion of the one-particle transitions (7.11). However, the closure approximation (1.8) includes contributions from all two-particle and higher order transitions—i.e., it includes interference effects.

The success of the closure approximation at high energies can also be explained from the kinematical point of view. The closure approximation is equivalent to the multiple scattering viewpoint adopted in this paper. The chief assumption inherent in this viewpoint is the adiabatic treatment of the scatterer positions. The higher the energy of the incident radiation, the more permissible is it to regard the scatterer motion as adiabatic.

## VIII. SUMMARY

After summarizing previous work on the multiple scattering of light, x-rays, and neutrons, a general theory of the multiple scattering of waves is developed. Foldy's procedure for isotropic, elastic scattering is generalized to include (1) anisotropic scattering, (2) inelastic scattering, (3) scattering of quantized waves, including photons, (4) creation and absorption of particles as in cosmic rays, (5) Doppler shift due to motion of the scatterers, (6) scatterers that are randomly, partially, or completely ordered.

The problem of the effective field is avoided (for the present) by setting the effective field equal to a wavelength dependent factor $c$ times the coherent field. The propagation constant in the medium of scatterers $k'$ is found to be related to its value $k$ when no scatterers are present by

$$(k')^2 = k^2 + 4\pi nc[f(a \leftarrow a)], \qquad (8.1)$$

where $n$ is the density of scatterers and $f(a \leftarrow a)$ is the (complex) elastic scattered amplitude in the forward direction. The index of refraction of the medium is $k'/k$.

The total radiation, coherent plus incoherent, is found to obey an integral equation whose inhomogeneous term is the coherent radiation. The rate at which

the coherent beam attenuates (due to incoherent scattering) is determined by the Born approximation solution of this integral equation. The corresponding differential cross section for a medium of volume $V$ is the cross section for a single scatterer $|f(b\leftarrow a)|^2 d\Omega$ multiplied by the average number of scatterers $\langle N \rangle$, by a correction $|c|^2$ for the effective field, and by a correlation correction

$$E = \left\{ 1 + n \int \exp[i(\mathbf{k}_a - \mathbf{k}_b) \cdot (\mathbf{r}_j - \mathbf{r}_k)] \right.$$

$$\left. \times \left[ \frac{p(\mathbf{r}_j, \mathbf{r}_k)}{p^2} - 1 \right] d(\mathbf{r}_j - \mathbf{r}_k) \right\} \quad (8.2)$$

where $p(\mathbf{r}_j, \mathbf{r}_k)/p^2$ is the probability of finding two particles at a separation $|\mathbf{r}_j - \mathbf{r}_k|$ normalized to unity at large separations. For wavelengths comparable to the particle separation, $E$ describes the liquid type diffraction pattern produced by the short range order in particle separations. For long wavelengths $E$ reduces to the Einstein factor measuring the fluctuation in the number particles in volume $V$:

$$E = (\langle N^2 \rangle - |\langle N \rangle|^2)/\langle N \rangle. \quad (8.3)$$

The question of coherence and incoherence is discussed in detail. A well-known theorem is verified: that scattered radiation is coherent only if the internal state of the scattering system is unmodified by the collision.

Another problem considered is the extent to which a collision with a many particle system can be treated as a multiple scattering problem. The equivalence between the two approaches is shown to be based on a closure approximation. When the closure approximation is satisfied the scattering can be described completely using only a knowledge of the initial (but not the final) state of the scattering system. In fact, only the one- and two-particle densities of the initial state need be used.

The error involved in the closure approximation is shown to depend on the momentum distribution in the initial state and to become negligible at high energies.

There are a number of problems that require further consideration and a more detailed treatment than was possible in this paper. The most important of these is an evaluation of the relation between the "effective field" and the coherent field. The solution of this problem is fundamental to any prediction of an index of refraction—and its relation to the structure of the system. The effective field problem is a chestnut that dates back to Lorentz. Its solution will not be easy. Under the simplest assumptions, the relation between the effective and coherent fields will be described by an integral equation. The present paper makes the most elementary contribution toward the solution of the effective field problem: it provides a notation that adequately describes the problem.

A second problem is the transformation of the space integral equation (6.12) describing the incoherent radiation into an integral equation in phase space of the form (6.38). Such a transformation will not simplify materially the problem of solving the incoherent integral equation—but it places the solution in a form both customary and easy to visualize.

A third problem is the comparison of our integral equation (probably in phase space form) with the corresponding equation obtained from a particle viewpoint, the Boltzmann transport equation. Since most particles should be described by waves in quantum mechanics, the solution of the third problem provides an estimate of the error involved in using a particle—or classical—viewpoint in transport problems.