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Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

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A natural time-dependent generalization is given for the well-known pair distribution function $g(\mathbf{r})$ of systems of interacting particles. The pair distribution in space and time thus defined, denoted by $G(\mathbf{r},t)$, gives rise to a very simple and entirely general expression for the angular and energy distribution of Born approximation scattering by the system. This expression is the natural extension of the familiar Zernike-Prins formula to scattering in which the energy transfers are not negligible compared to the energy of the scattered particle. It is therefore of particular interest for scattering of slow neutrons by general systems of interacting particles: G is then the proper function in terms of which to analyze the scattering data.

After defining the G function and expressing the Born approximation scattering formula in terms of it, the paper studies its general properties and indicates its role for neutron scattering. The qualitative behavior of G for liquids and dense gases is then described and the long-range part exhibited by the function near the critical point is calculated. The explicit expression of G for crystals and for ideal quantum gases is briefly derived and discussed.

I. INTRODUCTION

IN two special cases, the first Born approximation for the scattering of x-rays or particles by a system S of interacting particles is known to express the differential cross section in terms of simple density distribution functions for the particles of S.

(i) If S is in a pure quantum state and if this state does not change in the scattering process, the latter is elastic and the differential cross section is expressible in terms of the density distribution $\rho(\mathbf{r})$ for one particle of the system (supposed for simplicity to be composed of identical particles). This applies for example to the elastic scattering of x-rays or electrons by the electrons of an atom.[1,2]

(ii) If the energy transfers occurring in the scattering process are negligible compared to the energy of the scattered photon or particle, the momentum transfer is essentially unique for each scattering angle and the differential cross section per unit angle is expressible in terms of the pair distribution function $g(\mathbf{r})$ of S, which describes the average density distribution as seen from a particle of the system. This is the so-called static approximation which applies, for example, to the sum of elastic and inelastic scattering of x-rays and electrons by the electrons of an atom,[3,4] as well as to that part of the scattering of x-rays by solids, liquids, and gases which leaves the atomic quantum states unchanged.[5,6]

The purpose of the present paper is to show that in Born approximation the scattering cross section is always expressible in terms of a suitably generalized pair distribution function $G(\mathbf{r},t)$ depending on a space vector $\mathbf{r}$ and a time interval t, and to study this function in some detail for a number of systems. For scattering theory this would be of rather academic interest in connection with x-ray scattering, for which the conditions of case (ii) above are usually well fulfilled. The same holds for electrons, for which, however, the Born approximation is of much more limited applicability than for x-rays. For slow neutrons, on the contrary, (wavelength $\gtrsim 1$A) now used in a rapidly growing variety of scattering experiments,[7] the energy transfers are usually comparable to or larger than the incident energy, whereas the first Born approximation holds quite well provided the neutron-nucleus interaction is described by means of the Fermi pseudopotential. The need has thus arisen for an improvement of the static approximation for scattering by general systems, and correction terms valid at relatively high neutron energies have been calculated by Placzek and by Wick.[8] We present here a general solution to this problem, applicable at all neutron energies, by describing the Born approximation scattering in terms of the time-dependent pair-distribution function G.

Furthermore, the fact that G has often, even for complicated systems, a number of qualitative properties which are easy to visualize, makes it in many cases a practical tool for the discussion of scattering experiments. Its use for the analysis and interpretation of experimental data has been illustrated elsewhere on the case of slow neutron scattering by ferromagnetic crystals.[9]

The generalized pair-distribution function $G(\mathbf{r},t)$, to which neutron scattering gives direct experimental access, turns out to be a very natural extension of the conventional $g(\mathbf{r})$ function. Independently of its use in scattering theory, it is of genuine interest from the general standpoint of statistical mechanics. Its physical

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[1] I. Waller, Z. Physik **51**, 213 (1928).

[2] N. F. Mott, Proc. Roy. Soc. (London) **A127**, 658 (1930).

[3] I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) **A124**, 119 (1929).

[4] P. M. Morse, Physik. Z. **33**, 443 (1932).

[5] I. Waller, dissertation, Uppsala, 1925 (unpublished).

[6] F. Zernike and J. Prins, Z. Physik **41**, 184 (1927); P. Debye and H. Memke, Ergeb. Tech. Röntgenk. **II** (1931).

[7] See, e.g., D. J. Hughes, *Pile Neutron Research* (Addison-Wesley Publishing Company, Cambridge, 1953).

[8] G. Placzek, Phys. Rev. **86**, 377 (1952); G. C. Wick, Phys. Rev. **94**, 1228 (1954).

[9] L. Van Hove, Phys. Rev. **93**, 268 (1954).

meaning is particularly simple in the absence of quantum effects: $G(\mathbf{r},t)$ is then, for the system under consideration, the average density distribution at a time $t'+t$ as seen from a point where a particle passed at time t'. This definition has to be slightly modified for a quantum system, in view of the noncommutativity of the operators representing particle positions at different times. In all cases $G(\mathbf{r},t)$ describes the correlation between the presence of a particle in position $\mathbf{r}'+\mathbf{r}$ at time $t'+t$ and the presence of a particle in position $\mathbf{r}'$ at time t', averaged over $\mathbf{r}'$. It essentially reduces to $g(\mathbf{r})$ for $t=0$.

The concept of time-dependent correlations has already been used in connection with neutron scattering by crystals in unpublished work by Glauber.[10]

The choice of a proper definition of the pair distribution $G(\mathbf{r},t)$ for general quantum-mechanical systems requires some care since it deals with correlations between noncommuting quantities. We will be led to it conveniently by starting from the Born scattering formula and following a natural extension of the well-known procedure to introduce the $g(\mathbf{r})$ function in the static approximation. This is done in the next section, where a number of general properties of $G(\mathbf{r},t)$ are also derived.

The use of the pair distribution G to describe neutron scattering data is indicated in Sec. III. This distribution is the proper function in terms of which to analyze the angular and energy distribution of neutrons scattered by general systems of nuclei, in exactly the same way as the $g(\mathbf{r})$ function is the proper function with which to analyze angular distributions in x-ray scattering. In full analogy with the x-ray case, it is expected to be useful mainly for systems too complicated to allow an explicit calculation of either the scattering or the pair distribution. Liquids and dense gases are clearly the principal examples of such systems.

The advantage of using pair distribution functions for the analysis of scattering data is their simple and intuitively clear physical meaning, which makes their qualitative behavior rather easy to visualize. It is therefore of importance to form as complete a picture of this behavior as possible, and, in absence of sufficient experimental data, it is indicated to discuss systems for which the pair distribution function can be entirely or partly calculated. In the present paper we treat mainly liquids and dense gases, for which the general shape of G is easy to guess and its long-range part near the critical point can be calculated (Sec. IV). We also consider more briefly crystals (Sec. V) and the ideal quantum gases (Sec. VI).

With the experimental data available so far, the best example of the usefulness of pair distributions in space and time for the analysis of scattering data is provided by the case of magnetic scattering of neutrons by ferromagnetic crystals.[11] A short account of the analysis has already been published.[9] The full discussion will appear as a separate paper.

II. THE PAIR DISTRIBUTION IN SPACE AND TIME

A. Definition

The correct definition of $G(\mathbf{r},t)$ for a general quantum-mechanical system is best inferred from the Born approximation scattering formula. The nature of the scattered particle and the details of the scattering law are, of course, largely irrelevant for this purpose. We will assume that the scattered particle is nonrelativistic and interacts with the particles of the system S through a potential $V(r)$ depending on distance only. For simplicity S is supposed to be composed of one single type of particle. The differential scattering cross section per unit solid angle and unit interval of outgoing energy ϵ of the scattered particle is given in the first Born approximation by

$$\frac{d^2\sigma}{d\Omega d\epsilon}=\frac{m^3}{2\pi^2\hbar^6}\frac{k}{k_0}W(\kappa)\sum_{n_0}p_{n_0}\sum_{n}\left|\left[\sum_{j=1}^{N}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)\right]_{n_0}^{n}\right|^2 \cdot\delta\left\{k^2-k_0^2+\frac{2m}{\hbar^2}(E_n-E_{n_0})\right\}, \qquad (1)$$

where m, $\mathbf{k}_0$, and $\mathbf{k}=\mathbf{k}_0-\boldsymbol{\kappa}$ are the mass and the initial and final wave vectors of the scattered particle. The operators $\mathbf{r}_j$ represent the position vectors of the N particles of the scattering system S, whose initial and final quantum states are labeled by n_0, n and have energies E_{n_0}, E_n, respectively. The bracket $[\cdots]_{n_0}{}^{n}$ denotes a matrix element and p_{n_0} is the statistical weight of the initial state n_0 (usually the Boltzmann factor divided by the sum of states). The function $W(\kappa)$ is defined by

$$W(\kappa)=\left\{\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})V(r)d\mathbf{r}\right\}^2.$$

If, besides the momentum transfer $\hbar\boldsymbol{\kappa}$, we introduce the energy transfer

$$\hbar\omega=\hbar^2(k_0^2-k^2)/2m,$$

Eq. (1) can be written

$$\frac{d^2\sigma}{d\Omega d\epsilon}=A\,\mathcal{S}(\boldsymbol{\kappa},\omega), \qquad (2)$$

$$A=\frac{m^2}{4\pi^2\hbar^5}\frac{k}{k_0}W(\kappa), \qquad (3)$$

$$\mathcal{S}(\boldsymbol{\kappa},\omega)=\sum_{n_0}p_{n_0}\sum_{n}\left|\left[\sum_{j=1}^{N}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)\right]_{n_0}^{n}\right|^2 \cdot\delta\left\{\omega+\frac{E_{n_0}-E_n}{\hbar}\right\}, \qquad (4)$$

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[10] R. J. Glauber (private communication); Phys. Rev. **87**, 189 (1952); Phys. Rev. **94**, 751 (1954), and forthcoming paper.

[11] H. Palevsky and D. J. Hughes, Phys. Rev. **92**, 202 (1953); G. L. Squires (to be published). We are indebted to these authors for communication of their results before publication.

where, for given momentum and energy transfers, $\mathcal{S}(\boldsymbol{\kappa},\omega)$ is independent of the mass and energy of the scattered particle as well as of the interaction potential, whereas A depends only on the properties of the individual particles of S. This separation of two factors in the differential cross section is quite general; it is an immediate consequence of the use of momentum and energy transfers as independent variables.

It is now an easy matter to express in terms of a pair distribution the function $\mathcal{S}(\boldsymbol{\kappa},\omega)$ which, in the first Born approximation, contains the scattering properties of the system S. If it is remembered that in the static approximation [case (ii) of the introduction] the differential cross section per unit solid angle,

$$\frac{d\sigma}{d\Omega}=\int\frac{d^2\sigma}{d\Omega d\epsilon}d\epsilon, \tag{5}$$

is essentially, as a function of $\boldsymbol{\kappa}$, the Fourier transform over $\mathbf{r}$ of the $g(\mathbf{r})$ function, it is natural to expect $\mathcal{S}(\boldsymbol{\kappa},\omega)$ to be essentially the Fourier transform over $\mathbf{r}$ and t of the pair distribution in space and time $G(\mathbf{r},t)$. We therefore define the latter through the equivalent equations:

$$\mathcal{S}(\boldsymbol{\kappa},\omega)=(2\pi)^{-1}N\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G(\mathbf{r},t)d\mathbf{r}dt, \tag{6}$$

or

$$G(\mathbf{r},t)=(2\pi)^{-3}N^{-1}\int\exp[i(\omega t-\boldsymbol{\kappa}\cdot\mathbf{r})]\cdot\mathcal{S}(\boldsymbol{\kappa},\omega)d\boldsymbol{\kappa}d\omega. \tag{7}$$

The coefficient $(2\pi)^{-1}N$ in (6) is introduced for convenience. It makes $G(\mathbf{r},t)$ independent of N and asymptotically equal to the number density for the large systems of statistical mechanics, in which the limit $N\rightarrow\infty$ is to be taken. From Eqs. (4) and (7) one gets, successively,

$$\begin{aligned}G(\mathbf{r},t)=(2\pi)^{-3}N^{-1}\sum_{n_0}p_{n_0}\sum_{n}\sum_{l,j=1}^{N}\int d\boldsymbol{\kappa}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})\\ \cdot[\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_l)]_n{}^{n_0}\cdot\exp(iE_nt/\hbar)\\ \cdot[\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)]_{n_0}{}^{n}\cdot\exp(-iE_{n_0}t/\hbar),\end{aligned} \tag{8}$$

$$\begin{aligned}G(\mathbf{r},t)=(2\pi)^{-3}N^{-1}\sum_{l,j=1}^{N}\int d\boldsymbol{\kappa}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})\\ \cdot\langle\exp\{-i\boldsymbol{\kappa}\cdot\mathbf{r}_l(0)\}\cdot\exp\{i\boldsymbol{\kappa}\cdot\mathbf{r}_j(t)\}\rangle.\end{aligned}$$

The last formula contains the Heisenberg operator $\mathbf{r}_j(t)$, defined for all j and t by

$$\mathbf{r}_j(t)=\exp(itH/\hbar)\mathbf{r}_j\exp(-itH/\hbar),$$

where H is the Hamiltonian of the system.[12] The bracket $\langle\cdots\rangle$ stands for the average of the expectation value of the enclosed operator:

$$\langle\cdots\rangle=\sum_{n_0}p_{n_0}[\cdots]_{n_0}{}^{n_0}. \tag{9}$$

With the help of the convolution formula for the Fourier transform of an (ordered) product, we obtain finally the expression

$$G(\mathbf{r},t)=N^{-1}\Big\langle\sum_{l,j=1}^{N}\int d\mathbf{r}'\cdot\delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}_j(t))\Big\rangle, \tag{10}$$

which defines $G(\mathbf{r},t)$ entirely in terms of space and time variables, with the proper ordering of the operators belonging to different times.

For $t=0$, all operators commute and the integration can be carried out, leading to

$$G(\mathbf{r},0)=N^{-1}\langle\sum_{l,j=1}^{N}\delta(\mathbf{r}+\mathbf{r}_l(0)-r_j(0))\rangle,$$

or

$$G(\mathbf{r},0)=\delta(\mathbf{r})+N^{-1}\sum_{l\neq j}\langle\delta(\mathbf{r}+\mathbf{r}_l-\mathbf{r}_j)\rangle=\delta(\mathbf{r})+g(\mathbf{r}), \tag{11}$$

according to the familiar definition of the conventional pair distribution $g(\mathbf{r})$. Similarly, in the scattering formula, if the incident energy is sufficiently large compared to the energy transfers, the momentum transfer for a given scattering angle is independent of the outgoing energy, and the differential cross section per unit solid angle becomes

$$\begin{aligned}\frac{d\sigma}{d\Omega}&=\int\frac{d^2\sigma}{d\Omega d\epsilon}d\epsilon=\hbar A\int\mathcal{S}(\boldsymbol{\kappa},\omega)d\omega\\ &=\hbar AN\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})\delta(t)G(\mathbf{r},t)d\mathbf{r}dt\\ &=[m/(2\pi\hbar^2)]^2NW(\kappa)\left\{1+\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})g(\mathbf{r})d\mathbf{r}\right\},\end{aligned}$$

the familiar formula in the static approximation. Just as measurement of $d\sigma/d\Omega$ provides an experimental determination of $g(\mathbf{r})$ in the latter approximation, the pair distribution in space and time $G(\mathbf{r},t)$ is experimentally accessible through measurements of $d^2\sigma/d\Omega d\epsilon$.

B. General Properties

We will now discuss a few immediate properties of the pair distribution in space and time. $G(\mathbf{r},t)$, which is in general complex, has the Hermitian symmetry,

$$G(-\mathbf{r},-t)=\{G(\mathbf{r},t)\}^*, \tag{12}$$

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[12] The introduction of a time variable to eliminate the δ function in Eq. (1) and the subsequent consideration of time-dependent operators have become familiar in scattering theory. See, e.g., A. Akhiezer and I. Pomeranchuk, J. Phys. (U.S.S.R.) **11**, 167 (1947); G. C. Wick, reference 8.

easily derived as follows: from (10),

$$\{G(\mathbf{r},t)\}^* = N^{-1}\left\langle \sum_{l,j} \int d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{r}_j(t))\delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}')\right\rangle$$

$$= N^{-1}\left\langle \sum_{l,j} \int d\mathbf{r}''\delta(\mathbf{r}-\mathbf{r}_j(t)+\mathbf{r}'')\delta(\mathbf{r}_l(0)-\mathbf{r}'')\right\rangle$$

$$= N^{-1}\left\langle \sum_{l,j} \int d\mathbf{r}''\delta(\mathbf{r}-\mathbf{r}_j(0)+\mathbf{r}'') \times\delta(\mathbf{r}_l(-t)-\mathbf{r}'')\right\rangle$$

$$= G(-\mathbf{r}, -t).$$

In the second step the integration variable is $\mathbf{r}''=\mathbf{r}'-\mathbf{r}$; the third step uses the invariance of the expectation value under the unitary transformation $\exp(itH/\hbar)$, whereas the last is based on the even character of the δ function. Property equation (12) is equivalent with the fact that $\mathcal{S}(\boldsymbol{\kappa},\omega)$ is a real-valued function.

Complex values of $G(\mathbf{r},t)$ reflect quantum properties of the system. Indeed, under classical conditions, the operators in (10) reduce to commuting c numbers and G takes the real, positive value:

$$G(\mathbf{r},t) = N^{-1}\langle \sum_{l,j} \delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}_j(t))\rangle.$$

As announced in the introduction, it is seen to describe the average density distribution at time $t'+t$ as seen from a point which was occupied by a particle at time t'; this distribution is independent of t', here given the value 0.

When quantum effects are present,—they are for any actual system in certain ranges of r and t values—, G is complex and the simple physical interpretation given above cannot hold in view of the noncommutativity of particle positions at different times. How this noncommutativity enters into the expression of G can best be seen by introducing suitable density operators. Let us consider in space a volume element ΔV centered at point $\mathbf{r}$ and define the Heisenberg operator $\Delta P(\mathbf{r},t)$ satisfying $\Delta P(\mathbf{r},t)\psi=\psi$ for all states ψ of the system for which, with probability one, at least one particle is in ΔV at time t, and $\Delta P(\mathbf{r},t)\psi=0$ for all states such that, with probability one, no particle is in ΔV at time t. One has, in the limit of infinitesimal ΔV,

$$\Delta P(\mathbf{r},t)/\Delta V = \sum_j \delta(\mathbf{r}-\mathbf{r}_j(t)),$$

and thus, taking identical volume elements around each point,

$$G(\mathbf{r},t) = N^{-1}\Delta V^{-2}\int d\mathbf{r}''\langle\Delta P(\mathbf{r}'',0)\cdot\Delta P(\mathbf{r}''+\mathbf{r}, t)\rangle. \quad (13)$$

For a system homogeneous in space (like a gas or a liquid), enclosed in a volume $V=N/\rho$, we get the very simple formula:

$$G(\mathbf{r},t) = \rho^{-1}\Delta V^{-2}\langle\Delta P(\mathbf{r}'',0)\cdot\Delta P(\mathbf{r}''+\mathbf{r}, t)\rangle, \quad (14)$$

where $\mathbf{r}''$ is an arbitrary point in V. From Eq. (13) or (14) follows immediately that the real part of G is related to the average value of the symmetrized product,

$$\tfrac{1}{2}\{\Delta P(\mathbf{r}'',0)\cdot\Delta P(\mathbf{r}''+\mathbf{r}, t)+\Delta P(\mathbf{r}''+\mathbf{r}, t)\cdot\Delta P(\mathbf{r}'',0)\},$$

and is therefore the natural extension to quantum systems of the classical, real-valued, pair distribution function in space and time, whereas the imaginary part reduces essentially to the average value of the commutator of $\Delta P(\mathbf{r}'',0)$ and $\Delta P(\mathbf{r}''+\mathbf{r}, t)$.

In the case of systems for which the symmetric or antisymmetric character of the wave function is of little importance, and which can thus be regarded as composed of distinguishable particles (Boltzmann statistics), the G function splits naturally into a part G_s describing the correlation between positions of one and the same particle at different times, and a part G_d referring to pairs of distinct particles (the subscripts stand for "self" and "distinct," respectively). They are defined as follows:

$$G_s(\mathbf{r},t) = N^{-1}\left\langle \sum_{j=1}^{N} \int d\mathbf{r}'\cdot\delta(\mathbf{r}+\mathbf{r}_j(0)-\mathbf{r}') \times\delta(\mathbf{r}'-\mathbf{r}_j(t))\right\rangle, \quad (15)$$

$$G_d(\mathbf{r},t) = N^{-1}\left\langle \sum_{j\neq l=1}^{N} \int d\mathbf{r}'\cdot\delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}') \times\delta(\mathbf{r}'-\mathbf{r}_j(t))\right\rangle. \quad (16)$$

They verify separately the symmetry condition (12) and equations of type Eq. (13) with density operators $\Delta P_j/\Delta V$ defined for individual particles. For $t=0$, they reduce to

$$G_s(\mathbf{r},0)=\delta(\mathbf{r}), \quad G_d(\mathbf{r},0)=g(\mathbf{r}). \quad (17)$$

For the systems of large numbers of particles studied in statistical mechanics, solids, liquids, or gases, the pair distribution $G(\mathbf{r},t)$, in the definition [Eqs. (9) and (10)] of which the statistical weights p_{n0} must be given the Boltmann value

$$p_{n0}=Z^{-1}\exp(-\beta E_{n0}), \quad Z=\sum_{n0}\exp(-\beta E_{n0}) \quad (18)$$

(β^{-1} = temperature T multiplied by Boltzmann constant k_B), has especially simple asymptotic expressions for large r or $|t|$. For such systems, the particles in regions widely separated in space are statistically independent, and so are the properties of the system at two widely distant times. For sufficiently large r or large $|t|$, we can thus write asymptotically

$$\langle \sum_{l,j=1}^{N} \delta(\mathbf{r}+\mathbf{r}(0)-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}_j(t))\rangle \simeq \rho(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r}'),$$

where

$$\rho(\mathbf{r}')=\langle\sum_{j=1}^{N}\delta(\mathbf{r}'-\mathbf{r}_j(t))\rangle \tag{19}$$

is the average density at point $\mathbf{r}'$, independent of the time t. Hence, from Eq. (10), we can write the asymptotic formula

$$G(\mathbf{r},t)\simeq N^{-1}\int d\mathbf{r}'\cdot\rho(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r}'), \tag{20}$$

the right-hand side of which is the often considered autocorrelated density.[13] In particular, for an homogeneous system, $\rho(\mathbf{r}')$ is a constant, the number density $\rho=N/V$ (V volume of the system), and Eq. (20) reduces to

$$G(\mathbf{r},t)\simeq\rho. \tag{21}$$

It is the difference between G and its asymptotic value (20) which represents the correlation between pairs of particles. The instantaneous part of this correlation is contained in $G(\mathbf{r},0)=\delta(\mathbf{r})+g(\mathbf{r})$ and is well known from the study of the familiar $g(\mathbf{r})$ function. The interest of G for $t\neq 0$ is to describe in addition its time dependence: if we consider a given, fixed point of space through which a particle passes at time 0, the density distribution of the system is disturbed around this point not only at time 0, but before and afterwards. The average time variation of this disturbance is represented by the G function. As formally expressed by Eq. (20), the disturbance is negligible far from the fixed point at all times, and everywhere in the system long before and long after time 0. Except in the case of long-range order or under critical conditions, to be discussed later on, the size and duration of the disturbance are characterized by a length R_0 and a time T_0 of microscopic dimensions such that Eq. (20) holds for all t if $r\gg R_0$ and for all r if $|t|\gg T_0$. R_0 is the *range* of the pair correlation, T_0 its *relaxation time*. To establish from first principles the existence of R_0 and T_0, and, *a fortiori*, to calculate G in terms of intermolecular forces, are difficult problems of statistical mechanics, unsolved except in very special cases. The relaxation time T_0 in particular is obviously related to the irreversible return of a locally perturbed system to equilibrium, and thus depends on the ergodic properties of the system. Such problems will not be touched upon here. We hope to have shown, however, that quite apart from its interest for scattering theory, the pair distribution in space and time is an important extension of the conventional $g(\mathbf{r})$ function from the standpoint of general statistical mechanics.

The separation of G into its asymptotic value and a correlation term G',

$$G'(\mathbf{r},t)=G(\mathbf{r},t)-N^{-1}\int d\mathbf{r}'\cdot\rho(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r}'), \tag{22}$$

has also a simple significance for scattering. Insertion in (6) gives

$$\mathcal{S}(\boldsymbol{\kappa},\omega)=\delta(\omega)\cdot\left|\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})\cdot\rho(\mathbf{r})d\mathbf{r}\right|^2 +(2\pi)^{-1}N\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G'(\mathbf{r},t)d\mathbf{r}dt. \tag{23}$$

The first term of the right-hand side represents elastic scattering ($\omega=0$); for an homogeneous system of large dimensions it reduces to $N\rho\delta(\omega)\delta(\boldsymbol{\kappa})$, i.e., to forward elastic scattering, which in the first Born approximation is indistinguishable from the unscattered beam. The second term represents inelastic scattering: since G' tends to zero for r and $|t|\rightarrow\infty$, the energy distribution has no peak of form $\delta(\omega)$ in any scattering direction, nor has its angular distribution any peak of form $\delta(\boldsymbol{\kappa})$ in the forward direction. In some cases, however, the convergence of G' to zero may be slow. This will then produce, through the Fourier transform in the last term of (23), singularities of weaker type in the angular and energy distribution of inelastically scattered particles. A simple example of this situation is provided by slow neutron scattering in crystals and will be discussed in Sec. V.

The range R_0 and relaxation time T_0 determine the orders of magnitude $\hbar/R_0$, $\hbar/T_0$ of average momentum and energy transfers in those scattering processes which are appreciably affected by the collective properties of the system S. Let us consider incident particles with momentum of order $\hbar/R_0$, and let us determine under which condition the values of G for $|t|\sim T_0$ make an important contribution to the scattering. The condition is that the angle of scattering depends appreciably on both momentum and energy transfers [if it depends essentially on momentum transfer alone, the static approximation applies and the scattering depends on $G(\mathbf{r},0)$ only]. It requires that the spread $\hbar\Delta k$ in the length $\hbar k$ of the final momentum, due to energy transfers of order $\hbar/T_0$, is at least comparable to the momentum transfers $\hbar/R_0$. Since $\Delta k\sim(vR_0)^{-1}$, where v is the velocity of the incident particle, the condition is $v\lesssim R_0/T_0$ or $T_1\gtrsim T_0$, where T_1 is the time R_0/v in which the incident particle travels over a correlation range. In the latter form, the physical meaning of the condition is obvious: the time variation of G affects the total scattering and angular distribution only for a particle spending at least a time of order T_0 over a correlation length R_0. If on the contrary $T_1\ll T_0$, the scattering is not affected by the values of G for $|t|\sim T_0$. Apart from the distribution of outgoing energies, it is then entirely determined by the value of G for $|t|\ll T_0$, and the static approximation gives a good description of the

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[13] For large $|t|$, Eq. (20) is valid also for systems with a small number of particles if the initial state is a pure quantum state, nondegenerate in energy. The asymptotic convergence for $|t|\rightarrow\infty$ may then, however, hold only in the mean, as is the case for a harmonic oscillator.

effect of collective properties of S on the scattering, in the sense that $d\sigma/d\Omega$ can be calculated by replacing $G(\mathbf{r},t)$ by $G_{id}(\mathbf{r},t)+G(\mathbf{r},0)-G_{id}(\mathbf{r},0)$, where G_{id} is the pair distribution function for an ideal gas of same density and temperature as S.

For incident particles of wavelength $\sim R_0$, the ratio T_1/T_0 is essentially equal to the ratio of average energy transfer to incident energy. A very crude estimate of R_0 and T_0 for actual substances, solids or liquids at average temperatures, gives $R_0\sim 10^{-8}$ cm, $T_0\sim 10^{-13}$ sec, and thus $T_1/T_0\sim 10^5/v$ if the incident velocity v is measured in cm sec^{-1}. This gives $T_1/T_0\sim 10^{-6}$ for photons of arbitrary wavelength, and $T_1/T_0\sim 1$ for neutrons of wavelength around 1 A or somewhat larger, i.e., exactly of the right order R_0 for which collective effects on scattering are most conveniently observed. For electrons of wavelength around 1 A, one finds $T_1/T_0\sim 10^{-4}$.

Before closing this section, we mention an extension of the $G(\mathbf{r},t)$ function to systems of identical particles with spin, to be used later in connection with spin-dependent scattering. If a_j is an operator depending on the spin of the jth particle, the same for each particle, a spin-dependent pair correlation is defined by

$$\Gamma(\mathbf{r},t)=N^{-1}\Big\langle\sum_{l,j=1}^{N}\int d\mathbf{r}'\cdot a_l(0)\delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}') \times a_j(t)\delta(\mathbf{r}'-\mathbf{r}_j(t))\Big\rangle, \quad (24)$$

in terms of the Heisenberg operators,

$$a_j(t)=\exp(itH/\hbar)a_j\exp(-itH/\hbar).$$

For a system of Boltzmann particles with spin-independent Hamiltonian H and for the thermal distribution (18), there is no correlation between spins nor between spins and positions. Using the definitions (15) and (16) we then find

$$\Gamma(\mathbf{r},t)=\langle a^2\rangle_{\text{Av}}G_s(\mathbf{r},t)+\langle a\rangle_{\text{Av}}{}^2G_d(\mathbf{r},t), \quad (25)$$

where a is any of the a_j's and $\langle\cdots\rangle_{\text{Av}}$ denotes an average over the spin states of the corresponding particle. Correlations involving the spins can be produced either by the symmetry requirements of the wave functions (Bose-Einstein and Fermi-Dirac particles) or by spin interactions. The first case is illustrated in Sec. VI. The second case occurs in ferromagnetic substances and will be discussed in a separate paper.

The extension of the foregoing considerations to systems composed of different types of particles is straightforward and will not be given here.

III. NUCLEAR SCATTERING OF SLOW NEUTRONS

As mentioned before, it is for the scattering of slow neutrons that use of the pair distributions in space and time is of most practical interest. We consider in the present section scattering due to the nuclear interaction between neutrons and the nuclei of the scattering system S. If the true interaction is replaced by the corresponding Fermi pseudopotential,

$$V(r)=(2\pi a\hbar^2/m)\delta(r),$$

where m is the neutron mass and a the scattering length of the nuclei assumed all identical, the Born approximation formula can be applied.[14] Equations (2), (3), and (6) give then, for the cross section of S,

$$\frac{d^2\sigma}{d\Omega d\epsilon}=\frac{a^2N}{2\pi\hbar}\frac{k}{k_0}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G(\mathbf{r},t)d\mathbf{r}dt. \quad (26)$$

If the nuclei of S have a nonvanishing spin, this equation assumes a to be spin independent. For nuclei with a spin-dependent scattering length, or for nuclei belonging to different isotopes (the mass differences being neglected), Eq. (26) is simply replaced by

$$\frac{d^2\sigma}{d\Omega d\epsilon}=\frac{N}{2\pi\hbar}\cdot\frac{k}{k_0}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot\Gamma(\mathbf{r},t)d\mathbf{r}dt,$$

with the spin- or isotope-dependent scattering lengths a_j to be used in the definition (24) of Γ.[14] In most cases the nuclei can be treated as Boltzmann particles and the spin or isotope disorder can be considered perfect, so that Eq. (25) applies, and, remembering $G=G_s+G_d$, we obtain

$$\frac{d^2\sigma}{d\Omega d\epsilon}=\frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon}+\frac{d^2\sigma_{\text{inc}}}{d\Omega d\epsilon}, \quad (27)$$

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon}=\frac{\langle a\rangle_{\text{Av}}{}^2N}{2\pi\hbar}\frac{k}{k_0}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G(\mathbf{r},t)d\mathbf{r}dt, \quad (28)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d\epsilon}=\frac{\{\langle a^2\rangle_{\text{Av}}-\langle a\rangle_{\text{Av}}{}^2\}N}{2\pi\hbar}\frac{k}{k_0}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)] \cdot G_s(\mathbf{r},t)d\mathbf{r}dt. \quad (29)$$

Equations (28) and (29) are the so-called coherent and incoherent scattering cross sections.

The separation Eq. (23) of elastic and inelastic scattering applies to Eq. (28). A similar separation can be performed for Eq. (29) by considering the limit of G_s for $|t|\to\infty$. In the static approximation we get, as in Sec. II,

$$d\sigma_{\text{coh}}/d\Omega=\langle a\rangle_{\text{Av}}{}^2N\left\{1+\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})g(\mathbf{r})d\mathbf{r}\right\}, \quad (30)$$

$$d\sigma_{\text{inc}}/d\Omega=\{\langle a^2\rangle_{\text{Av}}-\langle a\rangle_{\text{Av}}{}^2\}N. \quad (31)$$

The incoherent cross section no longer depends on the structure of S. Equation (30), identical to the Zernike-

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[14] The relevant information on slow neutron scattering will be found, for example, in J. M. Cassels, Progr. Nuclear Phys. **1**, 185 (1950).

Prins formula for x-ray scattering, has often been used before in connection with slow neutrons.[15–19]

The physical interest of Eqs. (28) and (29) is entirely similar to that of the familiar Eq. (30). It mainly concerns systems for which a complete calculation of pair distributions in terms of elementary forces cannot be carried out. Indeed, whenever an explicit calculation is possible, it leads to the differential cross sections as directly as to the pair distributions. For more complicated systems, however, like liquids or dense gases, the pair distributions, dealing with two-particle configurations in space and time, are much easier to visualize than the cross sections, and a qualitative prediction of their behavior is almost always possible, thus providing great help in understanding the main features of the scattering. For such systems, on the other hand, the pair distribution is the proper quantity in terms of which to interpret the scattering data, and since it contains very important information on the local structure of the system, its experimental determination is desirable. Equations (28), (29) provide the basis for such a determination.

Complete measurements of $d^2\sigma/d\Omega d\epsilon$, i.e., of the angular and energy distribution of scattered neutrons, will provide a direct determination of G or G_s by inversion of a 4-dimensional Fourier integral (2-dimensional for isotropic systems). At present, for intensity reasons, energy distributions of scattered neutrons are still difficult to observe, even when they spread over wide ranges. Progress will, however, undoubtedly be made in this direction[20] and it is to be hoped that complete sets of experimental values for $d^2\sigma/d\Omega d\epsilon$ will eventually become available.

A simpler but much less direct and less satisfactory approach to the experimental study of G or G_s can be made by measuring transmissions (i.e., total cross sections) or angular distributions in their dependence on the incident wavelength λ_0. For angular distributions, the contribution to the scattering of values of G or G_s with $t\neq 0$ will manifest itself through the fact that the differential cross section

$$\int (d^2\sigma/d\Omega d\epsilon) f(\epsilon) d\epsilon, \tag{32}$$

where $f(\epsilon)$ is determined by the detector used, does no longer depend on λ_0 and on the scattering angle θ through the single combination $\lambda_0^{-1}\sin(\theta/2)$, as it does in the static approximation with $f(\epsilon)$ constant. Since a quantity like Eq. (32) has a complicated functional expression in G or G_s, the analysis of its experimental values is bound to be much more difficult than it would be for $d^2\sigma/d\Omega d\epsilon$, and the choice of a detailed procedure would require careful consideration.

The next sections deal with the properties of G and G_s for special systems. Their aim is to form a more accurate picture of the behavior to be expected for these functions and to illustrate the correspondence between some of their properties and simple features of the angular and energy distributions obtained in scattering.

IV. LIQUIDS AND DENSE GASES

The discussion of pair distributions in space and time for liquids and dense gases presents the same difficulties as the corresponding discussion for the instantaneous pair distribution $g(\mathbf{r})$. Although the general behavior of the distribution functions can easily and safely be guessed, no reliable method has yet been found to calculate them in terms of the intermolecular forces.[21] We will therefore limit ourselves to a description of their most immediate properties.

Except for the case of substances of light atomic mass taken at very low temperatures, like liquid helium for example, the particles in a liquid or a dense gas have a mean de Broglie wavelength $\lambda_B=\hbar(2Mk_BT)^{-\frac{1}{2}}$ small compared to the distance between particles or, what amounts to the same, to the range of interatomic forces. M is the mass of the particles in the system. Under these conditions, the distinction between $G_s(r,t)$ and $G_d(r,t)=G-G_s$ is possible and these functions, which are independent of the direction of $\mathbf{r}$, verify, as already mentioned,

$$G_s(r,0)=\delta(\mathbf{r}),\quad G_d(r,0)=g(r), \tag{33}$$

$$\lim_{r'\to\infty} G_s(r',t)=\lim_{|t'|\to\infty} G_s(r,t')=0, \tag{34}$$

$$\lim_{r'\to\infty} G_d(r',t)=\lim_{|t'|\to\infty} G_d(r,t')=\rho, \tag{35}$$

where ρ is the number density. Except in the neighborhood of the critical point, the convergence in Eqs. (34) and (35) takes place over a length R_0 of the order of intermolecular distances and a time T_0 of the order of the time needed by an average particle of the system to travel over a distance R_0. T_0 is essentially identical with the Debye relaxation time.

Under the same condition of a mean de Broglie wavelength small compared to interatomic distances ($\lambda_B\ll R_0$), no quantum effects will manifest themselves in G_d, which deals with pairs of particles separated by distances of order R_0, and $G_d(r,t)$ is thus a real-valued, positive function, even in t. The situation is slightly dif-

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

[16] Placzek, Nijboer, and Van Hove, Phys. Rev. **82**, 392 (1951).

[17] L. Goldstein, Phys. Rev. **84**, 466 (1951).

[18] P. C. Sharrah and G. P. Smith, J. Chem. Phys. **21**, 288 (1953).

[19] Henshaw, Hurst, and Pope, Phys. Rev. **92**, 1229 (1953).

[20] Crude information on energy distributions of neutrons scattered by solids has been obtained by P. Egelstaff, Nature **168**, 290 (1951); B. N. Brockhouse and D. G. Hurst, Phys. Rev. **88**, 542 (1952); R. D. Lowde, Proc. Roy. Soc. (London) **A221**, 206 (1954).

[21] The determination of pair distribution functions based on the superposition approximation of Kirkwood, J. Chem. Phys. **3**, 300 (1935), cannot be considered reliable for dense systems. It has been discussed for a gas of hard spheres by B. R. A. Nijboer and L. Van Hove, Phys. Rev. **85**, 777 (1952), and by B. R. A. Nijboer and R. Fieschi, Physica **19**, 545 (1953).

ferent for $G_s(r,t)$, which for very small times

$$|t|\sim\hbar/k_BT\sim(\lambda_B/R_0)T_0,$$

is entirely concentrated in the region $r\sim\lambda_B$ where quantum effects are appreciable. For small displacements of this order, however, the potential acting on a particle is practically constant, so that the ideal gas value can be adopted for G_s:

$$G_s(r,t)\simeq\{2\pi t(k_BTt-i\hbar)/M\}^{-3/2}\times\exp\{-Mr^2/[2t(k_BTt-i\hbar)]\}.$$

This holds for $|t|\ll T_0$. For larger times, the form of G_s is affected by the interatomic forces, but quantum effects become negligible, and G_s thus also becomes real-valued positive and even in t. Characteristic shapes of G_s and G_d are given in Fig. 1 for three ranges of t values: $|t|\ll T_0$ (the curve for G_s is to be understood as representing the real part of the function if $|t|\lesssim\hbar/k_BT$), $|t|\sim T_0$, and $|t|\gg T_0$.

For quantum liquids like liquid helium at low temperature the situation is, of course, entirely different. The distribution function G has complex values for all nonvanishing times. We will not try to make a guess at its theoretical shape but want to stress the interest of its experimental determination.

After these general considerations, let us return to the case of the so-called classical liquids ($\lambda_B\ll R_0$) which will now be studied in the neighborhood of the critical point. When critical conditions are approached, the qualitative behavior of G_s is not expected to be greatly modified. G_d, however, is known to exhibit long-range correlations resulting from the occurrence in the system of spontaneous density fluctuations of macroscopic size. In contrast with the short-range part of the pair distribution, these long-range phenomena can be explicitly studied, at least for temperatures T slightly above the critical temperature T_c, by the methods of macroscopic fluctuation theory. The applicability of such methods is actually not restricted to the neighborhood of the critical point. They make a general study possible for the scattering from macroscopic density fluctuations, by permitting the calculation of the value and the time dependence of the Fourier components of G_d:

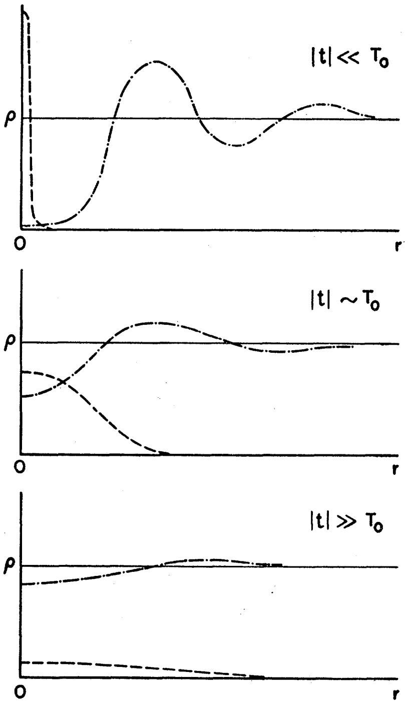

FIG. 1. The dependence of $G_s(r,t)$, (– – – –) and $G_d(r,t)$, (–·–·–) on r for three values of t. The solid line corresponds to the average density of the system.

$$\int\{G_d(r,t)-\rho\}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r},$$

for macroscopic κ^{-1}. This question, studied by Landau and Placzek for light scattering,[22] will not be treated in full generality in the present paper, where we limit ourselves to the more special case of critical fluctuations.

The behavior of $g(r)=G_d(r,0)$ near the critical point, for $T>T_c$ and for r large compared to the intermolecular distance, has been determined by Ornstein and Zernike.[23] It is given by

$$G_d(r,0)\simeq\rho+(4\pi r_0^2r)^{-1}e^{-\kappa_0r},\quad r\gg r_0, \tag{36}$$

where r_0 is a length slowly varying with temperature and density, of the order of the range of the forces, with value 1 at the critical point, and κ_0 is the reciprocal length

$$\kappa_0=r_0^{-1}(\rho k_BT\chi_T)^{-\frac{1}{2}}, \tag{37}$$

defined in terms of the isothermal compressibility $\chi_T=\rho^{-1}(\partial\rho/\partial p)_T$. Equation (36) holds for $r\gg r_0$, in the temperature and density region where $r_0\kappa_0\ll 1$. Its derivation assumes the system monophasic. Through its dependence on χ_T, the range κ_0^{-1} of the pair correlation becomes infinite at the critical point, where Eq. (36) reduces to

$$G_d(r,0)\simeq\rho+(4\pi r_0^2r)^{-1},\quad r\gg r_0. \tag{38}$$

We have now to determine the time variation of G_d for $r\gg r_0$. The long-range part of the pair distribution $G_d(r,t)$ can be identified with the average shape at time t of the spontaneous macroscopic density fluctuations in the system, as seen from a point through which a particle passed at time 0. Following Onsager,[24] it is

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[22] L. Landau and G. Placzek, Physik. Z. Sowjetunion **5**, 172 (1934). For a more detailed exposition, see J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), pp. 244 ff. The author is indebted to G. Placzek for illuminating discussions and communication of unpublished work on this subject.

[23] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914); Physik. Z. **19**, 134 (1918). The length r_0 in our Eq. (36) is related by $6r_0^2=\epsilon^2$ to the length ϵ defined in the latter paper.

[24] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

natural to assume that macroscopic variables which have taken nonequilibrium values as a consequence of spontaneous fluctuations have on the average in their return to equilibrium the same time variation as if their initial nonequilibrium values had been produced by suddenly released artificial constraints. This time variation is given by the well-known phenomenological laws of irreversible processes, in our case the Navier-Stokes equations for viscous flow supplemented by the continuity equation, and the equation for energy transport involving heat conduction.

Since we deal with fluctuations of small amplitude, all equations can be linearized and treated by Fourier analysis. We then find three independent plane-wave fluctuations of wave vector $\mathbf{k}$: two corresponding to damped waves propagating with sound velocity in the directions of $\mathbf{k}$ and $-\mathbf{k}$, and one of nonpropagating nature, with a time dependence given by the factor

$$\exp(-\tfrac{1}{4}\Lambda_0 k^2 t), \tag{39}$$

with

$$\Lambda_0 = 4\varkappa(\rho c_p)^{-1} = 4\varkappa(\rho c_v)^{-1}(\chi_S/\chi_T). \tag{40}$$

$\varkappa$ is the coefficient of heat conduction, c_p and c_v are the specific heats per particle, at constant pressure and volume, respectively, and χ_S is the adiabatic compressibility

$$\chi_S = \rho^{-1}(\partial\rho/\partial p)_S$$

(S: entropy). As expected, the fluctuations of the two first modes are found to be adiabatic and the third mode is a fluctuation at constant pressure.[25]

When the critical point is approached, whereas fluctuations of the two first modes remain normal, the magnitude of the spontaneous fluctuations at constant pressure increases indefinitely. They alone thus contribute to the long-range part of the pair correlation, and the time dependence of G_d for $r \gg r_0$ and $t > 0$ can be obtained by multiplying each Fourier component of Eq. (36) by the corresponding factor (39), i.e., by calculating the convolution of Eq. (36) with the Fourier transform,

$$\frac{1}{(2\pi)^3}\int \exp(-\tfrac{1}{4}\Lambda_0 k^2 t)\exp(i\mathbf{k}\cdot\mathbf{r})d\mathbf{k} = (\pi\Lambda_0 t)^{-3/2}\exp\left(-\frac{|\mathbf{r}-\mathbf{r}'|^2}{\Lambda_0 t}\right),$$

of (39). One has thus, remembering that G_d is even in t,

$$G_d(r,t) \simeq \rho + (4\pi r_0^2)^{-1}(\pi\Lambda_0|t|)^{-3/2} \times \int \exp\left\{-\frac{|\mathbf{r}-\mathbf{r}'|^2}{\Lambda_0|t|} - \kappa_0 r'\right\}\frac{d\mathbf{r}'}{r'}. \tag{41}$$

Integration over the angles then gives

$$G_d(r,t) \simeq \rho + (4\pi r_0^2 r)^{-1}\Psi[\kappa_0(\Lambda_0|t|)^{\frac{1}{2}}, r(\Lambda_0|t|)^{-\frac{1}{2}}], \tag{42}$$

where the function Ψ of two dimensionless arguments is defined by

$$\Psi(v,w) = 2\pi^{-\frac{1}{2}}\exp(-w^2) \times \int_0^\infty \exp(-x^2 - vx)\sinh(2wx)dx. \tag{43}$$

It is easily expressed in terms of the error integral:

$$\Psi(v,w) = \exp(\tfrac{1}{4}v^2 - vw)\cdot\psi(\tfrac{1}{2}v - w) - \exp(\tfrac{1}{4}v^2 + vw)\cdot\psi(\tfrac{1}{2}v + w),$$

$$\psi(x) = \frac{1}{\pi^{\frac{1}{2}}}\int_x^\infty \exp(-y^2)dy.$$

The behavior of G_d for large r and for large and small $|t|$ is immediately obtained from

$$\Psi(v,w) \simeq \exp(-vw), \qquad \text{for } w \gg 1,\ w \gg v; \tag{44}$$

$$\Psi(v,w) \simeq 4\pi^{-1/2}v^{-2}w\exp(-w^2), \qquad \text{for } v \gg 1,\ v \gg w. \tag{45}$$

Equation (44) shows that the expression Eq. (42) reduces to Eq. (36) in the limit of $t \to 0$. Its strict validity is, however, restricted to values of $|t|$ large compared to the microscopic relaxation time T_0 considered before, since the phenomenological equations used in our derivation apply only to quantities averaged over a time interval large compared to the duration of microscopic fluctuations. This limitation accounts for the occurrence of a spurious discontinuity at $t=0$ in the derivative of the right-hand side of (42) with respect to t; this derivative, if calculated correctly for t of microscopic order of magnitude, would be found continuous and equal to zero at $t=0$. Apart from the condition $|t| \gg T_0$, the derivation of Eq. (42) requires of course $r_0\kappa_0 \ll 1$ and $r \gg r_0$ as for Eq. (36). It is, however, interesting that the latter condition can be abandoned for all times for which the expression (42) differs appreciably from its value (36) at $t=0$. Indeed, it follows from (41) that whenever $|t| \gg \Lambda_0^{-1}r_0^2$ the value of $G_d(r,t)$ for all r, even of order r_0, is overwhelmingly determined by the values of $G_d(r,0)$ for $r \gg r_0$. If now $|t|$ is not large enough to satisfy this condition

$$|t| \lesssim \Lambda_0^{-1}r_0^2,$$

we get

$$v \lesssim \kappa_0 r_0 \ll 1, \quad w \gtrsim r/r_0.$$

Hence, for $r \gg r_0$, the asymptotic form (44) of Ψ can be used, and $G_d(r,t) \simeq G_d(r,0)$ for $r \gg r_0$. To present this conclusion differently, we can say that as $|t|$ increases, the time dependence of the long-range part of G_d sets in only for times[26]

$$|t| \gg \Lambda_0^{-1}r_0^2 \sim (\chi_T/\chi_S)T_0 \sim (\kappa_0 r_0)^{-2}T_0 \gg T_0,$$

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[25] The foregoing analysis of spontaneous fluctuations has been carried out by L. Landau and G. Placzek (reference 22) to account for the occurrence of a triplet line in the fluctuation scattering of light by liquids, and to calculate the line widths.

[26] The following estimate is made by using values of $\varkappa$, c_v, and χ_S calculated for rarefied gases, with the help of kinetic theory for $\varkappa$.

at which the short-range part of the pair distribution has completely reduced to the instantaneous value of the local macroscopic density, the variation of which is correctly described by Eq. (42) for all r. It is finally to be remarked that Λ_0^{-1} increases indefinitely when the critical point is approached, corresponding to an increasingly slower time variation of the macroscopic part of the pair correlation.

The above discussion is valid for monophasic systems near the critical point, i.e., for gases at densities near the critical density ρ_c and temperatures slightly above the critical temperature T_c. The relevant condition for its applicability is that the dimensionless quantity,

$$\kappa_0 r_0 = (\rho k_B T \chi_T)^{-\frac{1}{2}},$$

be small compared to one, let's say of order 0.1 or smaller. A more concrete idea about the corresponding density and temperature ranges is obtained by using the approximate expression for χ_T given by the van der Waals equation of state. One finds that at the critical density or a density differing from it by less than some 5 percent, one must have $T - T_c \lesssim 0.005 T_c$.[23]

For temperatures approaching T_c from below, the system is no longer monophasic at densities near ρ_c and the previous treatment is then not strictly applicable. It seems, however, likely that the long-range part of the pair distribution and its time variation will not be radically different from what we have found them to be for T above T_c.

Let us now indicate a few consequences of the above discussion for the scattering of neutrons by liquids and dense gases, for neutron wavelengths of the order of the separation between particles or larger. Away from critical conditions and apart from the forward elastic peak, which is entirely coherent, the differential cross section $d^2\sigma/d\Omega d\epsilon$ is a smooth function of outgoing energy and angle of scattering, corresponding to average momentum and energy transfers or order $\hbar R_0^{-1}$ and $\hbar T_0^{-1}$, respectively. This applies to coherent and incoherent scattering alike, although the collective properties of the liquid will evidently affect the scattering to a greater extent in the coherent case. Qualitative shapes to be expected for the angular and energy distribution could easily be obtained from Fig. 1 by Fourier transformation.

When critical conditions are approached, whereas no rapid change is expected to occur for incoherent scattering, the occurrence of a tail of increasing range in the pair distribution G_d reflects itself in an increasing amount of coherent scattering characterized by small momentum and energy transfers. Using for the latter our customary notations $\hbar\boldsymbol{\kappa}$, $\hbar\omega$, we obtain by Fourier transformation of Eq. (41) over space and time [the Fourier transform over space gives the product of Eq. (39) by the Fourier transform of Eq. (36); one has then to make a Fourier transformation over time] the following expression,

$$\left(\frac{d^2\sigma_{\mathrm{coh}}}{d\Omega d\epsilon}\right)_{\mathrm{crit}} = \frac{4\langle a\rangle_{\mathrm{Av}}{}^2 N}{\pi\hbar}\cdot\frac{k}{k_0}\cdot\frac{1}{r_0{}^2(\kappa^2+\kappa_0{}^2)}\cdot\frac{\Lambda_0\kappa^2}{\Lambda_0{}^2\kappa^4+16\omega^2}, \tag{46}$$

for the part of the differential cross section originating from long-range correlations. Near the critical point ($\kappa_0 r_0 \lesssim 0.1$), it is the main part of the cross section in the region $\kappa \ll r_0^{-1}$. From Eq. (46) this critical scattering is seen to have momentum and energy transfers of order $\kappa \sim \kappa_0$, $\omega \sim \Lambda_0\kappa_0{}^2/4$, respectively. Their relative magnitude compared to average momentum and energy transfers in noncritical scattering is easily estimated to be, very crudely,[26]

$$R_0\kappa_0 \sim (\rho k_B T \chi_T)^{-\frac{1}{2}},$$
$$\tfrac{1}{4} T_0 \Lambda_0 \kappa_0{}^2 \sim (R_0\kappa_0)^4 \sim (\rho k_B T \chi_T)^{-2}.$$

The most important feature revealed by this estimate is that in critical scattering, the energy transfers decrease very much faster than the momentum transfers when the critical point is approached, thus restoring the validity of the static approximation and causing the scattering to be not only more abundant than under normal conditions but also completely different in all its properties. The total cross section, for example, which under normal conditions is proportional to the incident neutron wavelength $2\pi/k_0$ as soon as the incident energy is small compared to $\hbar/T_0$,[27] has a completely different wavelength dependence in the immediate neighborhood of the critical point. Its main contribution comes then from the critical scattering represented by Eq. (46), which has to be integrated over outgoing energies and angles, with the result:

$$\sigma_{\mathrm{coh}} \simeq \frac{\pi\langle a\rangle_{\mathrm{Av}}{}^2 N}{(r_0 k_0)^2}\log\left(\frac{4k_0{}^2}{\kappa_0{}^2}+1\right). \tag{47}$$

Application of Eq. (46) at the critical point itself, where κ_0 and Λ_0 vanish, would lead to an infinite value for the total cross section (47). As was shown by Placzek for the case of light scattering,[28] the occurrence of this spurious conclusion is due to the fact that our entire treatment of scattering assumes the range of the pair correlations to be small compared to the dimensions of the vessel containing the system. We indeed have always assumed the system large enough to make surface effects negligible. Application of Eqs. (46) and (47) therefore requires κ_0^{-1} to be small compared to the dimensions of the vessel. Practically this condition is violated only in a temperature interval of $\sim 10^{-12}$ degree around T_c, in which the scattering would depend on the size and shape of the vessel.

We will not in the present paper consider the case of rarefied gases. The natural way of treating it is by an

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[27] This dependence on incident wavelength follows directly from the presence of the denominator k_0 in Eq. (28).

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

expansion of G_s and G_d in powers of the density, entirely similar to the familiar expansion of the $g(r)$ function. The ideal Bose-Einstein and Fermi-Dirac gases will be considered in Sec. VI.

V. CRYSTALS

For crystals, the harmonic nature of the forces permits explicit calculations of the scattering cross sections and pair distributions. Such calculations have often been made for scattering.[29] We will here briefly derive the expressions for the $G(\mathbf{r},t)$ function, describing the correlations in position between any two particles of the crystal, and the $G_s(\mathbf{r},t)$ function, describing the correlation of a particle with itself. The calculation is most easily done by starting from Eq. (8), a fact generally valid for systems which have plane waves as independent modes of motion.

We restrict ourselves to a single crystal of infinite extension, with Bravais lattice (one atom per cell). The lattice vectors are denoted by $\mathbf{R}$, and the position vector of the particle with equilibrium position at $\mathbf{R}$ is written $\mathbf{R}+\mathbf{u}_R$.[30] Defining for each $\mathbf{R}$, including the origin $\mathbf{R}=0$ of the lattice, the pair distribution G_R for particles of equilibrium positions 0 and $\mathbf{R}$, we have

$$G=\sum\nolimits_R G_R,\quad G_s=G_0. \tag{48}$$

From Eq. (8),

$$G_R(\mathbf{r},t)=(2\pi)^{-3}\int d\boldsymbol{\kappa}\cdot\exp\{-i\boldsymbol{\kappa}\cdot(\mathbf{r}-\mathbf{R})\}$$
$$\cdot\langle\exp\{-i\boldsymbol{\kappa}\cdot u_0(0)\}\cdot\exp\{i\boldsymbol{\kappa}\cdot\mathbf{u}_R(t)\}\rangle_T. \tag{49}$$

The Heisenberg operators are defined as usual. The subscript T indicates that the thermal distribution must be used in the definition (9) of the average.

We have first, since the commutator is a c number,

$$\begin{aligned}\langle\exp\{-i\boldsymbol{\kappa}\cdot\mathbf{u}_0(0)\}\cdot\exp\{i\boldsymbol{\kappa}\cdot\mathbf{u}_R(t)\}\rangle_T&\\ =\langle\exp\{i\boldsymbol{\kappa}\cdot[\mathbf{u}_R(t)-\mathbf{u}_0(0)]\}\rangle_T&\\ \cdot\exp\{\tfrac{1}{2}[\boldsymbol{\kappa}\cdot\mathbf{u}_0(0),\ \boldsymbol{\kappa}\cdot\mathbf{u}_R(t)]\}&.\end{aligned} \tag{50}$$

Next, in view of the fact that

$$\boldsymbol{\kappa}\cdot\{\mathbf{u}_R(t)-\mathbf{u}_0(0)\}$$

is a linear combination of coordinates of independent harmonic oscillators and has thus a Gaussian probability distribution,[31] the first factor in the right-hand side of Eq. (50) has the value

$$\exp\{-\tfrac{1}{2}\langle[\boldsymbol{\kappa}\cdot(\mathbf{u}_R(t)-\mathbf{u}_0(0))]^2\rangle_T\}.$$

Replacing the commutator in the second factor by its average, we get

$$\begin{aligned}\langle\exp\{-i\boldsymbol{\kappa}\cdot\mathbf{u}_0(0)\}\cdot\exp\{i\boldsymbol{\kappa}\cdot\mathbf{u}_R(t)\}\rangle_T&\\ =\exp\{-\sum_{\beta,\gamma}[M_{\beta\gamma}(0,0)-M_{\beta\gamma}(\mathbf{R},t)]\kappa_\beta\kappa_\gamma\}&,\end{aligned} \tag{51}$$

where $\beta,\gamma=x,\ y,\ z$ and

$$M_{\beta\gamma}(\mathbf{R},t)=M_{\gamma\beta}(\mathbf{R},t)=\langle u_0{}^\beta(0)u_R{}^\gamma(t)\rangle_T. \tag{52}$$

Inserting into (49), we get

$$\begin{aligned}G_R(\mathbf{r},t)=\{N(\mathbf{R},t)/8\pi^3\}^{\frac{1}{2}}&\\ \times\exp\{-\tfrac{1}{2}\sum_{\beta,\gamma}N_{\beta\gamma}(\mathbf{R},t)(r_\beta-R_\beta)(r_\gamma-R_\gamma)\}&,\end{aligned} \tag{53}$$

with the 3×3 matrix $N_{\beta\gamma}(\mathbf{R},t)$ defined as the inverse of

$$2\{M_{\beta\gamma}(0,0)-M_{\beta\gamma}(\mathbf{R},t)\},$$

and with

$$N(\mathbf{R},t)=\det\{N_{\beta\gamma}(\mathbf{R},t)\}.$$

Equation (53) is a Gaussian distribution around the equilibrium position $\mathbf{R}$. For $t\neq 0$ it has complex coefficients, the imaginary parts of which are of quantum origin.[32]

The correlation equation (52) between displacements is easily calculated using the functions $\omega_j(\mathbf{q})$, $\mathbf{e}_j(\mathbf{q})$ which express the frequency and unit vector of polarization of a plane-wave vibration (phonon) in terms of the wave vector $\mathbf{q}$ and the polarization index $j=1,\ 2,\ 3$. One finds

$$\begin{aligned}M_{\beta\gamma}(\mathbf{R},t)=\{\hbar v_0/(16\pi^3M)\}&\\ \times\sum_j\int d\mathbf{q}\{e_j{}^\beta(\mathbf{q})e_j{}^\gamma(\mathbf{q})/\omega_j(\mathbf{q})\}\cdot\{1-\exp(-\hbar\beta\omega_j(\mathbf{q})\}^{-1}&\\ \cdot\{\exp[-i(\mathbf{R}\cdot\mathbf{q}-t\omega_j(\mathbf{q}))]+\exp[-\hbar\beta\omega_j(\mathbf{q})]&\\ \times\exp[i(\mathbf{R}\cdot\mathbf{q}-t\omega_j(\mathbf{q}))]\}&,\end{aligned} \tag{54}$$

where M is the atomic mass of the crystal, v_0 the volume of the cell, β^{-1} the quantity k_BT and where the integration is extended over a cell of the reciprocal lattice.[33] As functions of $\mathbf{q}$, ω_j, and $\mathbf{e}_j$ have the periodicity of the reciprocal lattice.

Equation (54) shows that $M_{\beta\gamma}(\mathbf{R},t)$ approaches zero when R or $|t|$ increase indefinitely. $N_{\beta\gamma}(\mathbf{R},t)$ approaches then the inverse $N_{\beta\gamma}{}^{(\infty)}$ of the real matrix $2M_{\beta\gamma}(0,0)$. Hence, asymptotically, for large $|t|$ or for large R but finite $|\mathbf{r}-\mathbf{R}|$,

$$\begin{aligned}G_R(\mathbf{r},t)\simeq G_R{}^{(\infty)}(\mathbf{r})=\{N^{(\infty)}/8\pi^3\}^{\frac{1}{2}}&\\ \times\exp\{-\tfrac{1}{2}\sum_{\beta,\gamma}N_{\beta\gamma}{}^{(\infty)}(r_\beta-R_\beta)(r_\gamma-R_\gamma)\}&.\end{aligned}$$

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[29] A. fairly complete list of references is given in G. Placzek and L. Van Hove, Phys. Rev. **93**, 1207 (1954). The unpublished work of R. J. Glauber (reference 10), which makes use of the correlations (52) below, must also be mentioned.

[30] When in subscript, R stands for the vector $\mathbf{R}$.

[31] This theorem is due to F. Bloch, Z. Physik **74**, 295 (1932), especially footnote on p. 309.

[32] The above method for the calculation of scattering cross sections or pair distributions is applicable quite generally to systems with harmonic forces. Its main advantage is the very brief derivation of Eq. (51) based on Bloch's theorem. Alternative methods found in the literature are less general or more laborious: they have to rederive Bloch's theorem in disguised form.

[33] We define here the reciprocal lattice vectors as the vectors whose inner products with the vectors $\mathbf{R}$ of the crystal lattice are integral multiples of 2π.

This equation expresses the asymptotic vanishing of correlations between particles with widely separated equilibrium positions, and between neighboring particles considered at widely separated times.

For $t=\pm\infty$, the limiting values of the pair distributions Eq. (48) are thus

$$G(\mathbf{r},\infty)=\sum_R G_R{}^{(\infty)}(\mathbf{r}), \tag{55}$$

$$G_s(\mathbf{r},\infty)=G_0{}^{(\infty)}(\mathbf{r}). \tag{56}$$

The elastic part of coherent and incoherent neutron scattering follows immediately by insertion into Eqs. (28) and (29):

$$\left(\frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon}\right)_{\text{el}}=\left[\langle a\rangle_{\text{Av}}{}^2\frac{(2\pi)^3N}{\hbar v_0}\right] \times\exp\{-\sum_{\beta,\gamma} M_{\beta\gamma}(0,0)\kappa_\beta\kappa_\gamma\}\delta(\omega)\sum_{\boldsymbol{\alpha}}\delta(\boldsymbol{\kappa}-\boldsymbol{\alpha}),$$

$$\left(\frac{d^2\sigma_{\text{incoh}}}{d\Omega d\epsilon}\right)_{\text{el}}=\left[(\langle a^2\rangle_{\text{Av}}-\langle a\rangle_{\text{Av}}{}^2)\frac{N}{\hbar}\right] \times\exp\{-\sum_{\beta,\gamma} M_{\beta\gamma}(0,0)\kappa_\beta\kappa_\gamma\}\delta(\omega).$$

It contains the familiar Debye-Waller factor and, in the coherent case, the interference condition $\boldsymbol{\kappa}=\boldsymbol{\alpha}$, where $\boldsymbol{\alpha}$ denotes the vectors of the reciprocal lattice.[33] The cross sections for inelastic scattering can be derived from the difference between G, G_s and their asymptotic values (55), (56); one obtains then immediately expressions previously derived by Glauber.[10]

It is of some interest to study the nature of the convergence of G and G_s toward their asymptotic limits. G is found to approach (55) both for $|t|\rightarrow\infty$, r fixed and for $r\rightarrow\infty$, t fixed, the convergence being in $|t|^{-3/2}$ in the former case, in r^{-1} in the latter. G_s approaches (56) for $|t|\rightarrow\infty$, with a convergence in $|t|^{-3/2}$. The convergence is very slow in all cases. As seen from Eqs. (28) and (29), this fact is closely related to the occurrence of singularities in the angular and energy distribution of neutrons scattered inelastically by a single crystal; these singularities have been studied in detail elsewhere.[34] The convergence of the pair distributions for large $|t|$ has also another important physical significance: it implies that the crystal, despite its over-all lack of ergodicity, exhibits locally a type of ergodic behavior, the return toward local equilibrium being in $|t|^{-3/2}$.[35]

We will here restrict ourselves to establishing the law of asymptotic convergence of pair distributions for $|t|\rightarrow\infty$. This law is entirely determined by certain special crystal vibrations, already met before in connection with the frequency distribution function of the crystal.[36] Applying the result thus obtained to G_s, we will then establish in an indirect way the existence, asserted before without proof,[34] of singularities in the energy distribution of incoherently scattered neutrons.

The convergence of G_R to $G_R{}^{(\infty)}$ is determined by the convergence of $M_{\beta\gamma}(\mathbf{R},t)$ to 0 for $|t|\rightarrow\infty$, which according to Eq. (54) is to be discussed by the method of stationary phases. For large $|t|$, the main contribution to the integral in (54) comes from the neighborhood of the points $\mathbf{q}_c$ where for some $j=j_c$,

$$\text{grad}\omega_j(\mathbf{q})=0. \tag{57}$$

It has been shown that such points always exist for general values of the force constants of the crystal.[36] Their existence is implied by the periodicity of $\omega_j(\mathbf{q})$ in $\mathbf{q}$. In suitable local coordinates preserving the volume element $d\mathbf{q}$, the expansion of $\omega_{j_c}(\mathbf{q})$ near $\mathbf{q}_c$ can be written

$$\omega_{j_c}(\mathbf{q})=\omega_c+a_c\sum_{\beta=1,2,3}\epsilon_\beta{}^c\xi_\beta{}^2+\cdots,\quad \boldsymbol{\xi}=\mathbf{q}-\mathbf{q}_c,$$

with $\omega_c=\omega_{j_c}(\mathbf{q}_c)$, $\epsilon_\beta{}^c=\pm1$, $a_c>0$. Inserting in (54) and carrying out the integration over $\boldsymbol{\xi}$, one gets for $M_{\beta\gamma}(\mathbf{R},t)$ the asymptotic form:

$$M_{\beta\gamma}(\mathbf{R},t)\simeq\{\hbar v_0/(16\pi^{\frac{3}{2}}M|t|^{\frac{3}{2}})\}\sum_c\{e_{j_c}{}^\beta(\mathbf{q}_c)e_{j_c}{}^\gamma(\mathbf{q}_c)/(a_c{}^{\frac{3}{2}}\omega_c)\}\{1-\exp(-\hbar\beta\omega_c)\}^{-1}\{\exp(-i\mathbf{R}\cdot\mathbf{q}_c)\mathcal{E}_c(t)+\exp(-\hbar\beta\omega_c+i\mathbf{R}\cdot\mathbf{q}_c)\mathcal{E}_c{}^*(t)\}, \tag{58}$$

with

$$\mathcal{E}_c(t)=\exp[it\omega_c+i(\pi/4)(t/|t|)\sum_\beta\epsilon_\beta{}^c].$$

$\mathcal{E}_c{}^*$ is the complex conjugate of $\mathcal{E}_c$. The sum $\sum_c$ extends over all solutions of Eq. (57). The decrease of $M_{\beta\gamma}$ for large $|t|$ is seen to be in $|t|^{-3/2}$. From (58) it is now an elementary matter to find the following asymptotic formula for G_R:

$$G_R(\mathbf{r},t)-G_R{}^{(\infty)}(\mathbf{r})\simeq G_R{}^{(\infty)}(\mathbf{r})|t|^{-3/2} \times\sum_c\{P_c(\mathbf{r})\mathcal{E}_c(t)+P_c{}'(\mathbf{r})\mathcal{E}_c{}^*(t)\}. \tag{59}$$

P_c and $P_c{}'$ denote polynomials of second degree in the components of $\mathbf{r}$. Their explicit expression is not needed for our purpose. The asymptotic convergence of G_R, and thus of G and G_s, is again in $|t|^{-3/2}$.

Through the Fourier transform over t in Eq. (29), each term of the expression (59), taken for $\mathbf{R}=0$, contributes a singularity to the energy distribution of incoherently scattered neutrons. The analytic nature of the singularity is best obtained by Fourier transformation of simple functions of t with asymptotic behavior $|t|^{-3/2}\mathcal{E}_c(t)$ or $|t|^{-3/2}\mathcal{E}_c{}^*(t)$ for large $|t|$. We take for example the function,

$$f_c(t)=|t|^{-3/2}\mathcal{E}_c(t)(1\pm i\alpha/t)^{-3/2},$$

where $\alpha>0$ and the upper (lower) sign is taken when $\epsilon_c=\sum_\beta\epsilon_\beta{}^c=3$ or -1 (-3 or 1). It has the following

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[34] See G. Placzek and L. Van Hove, reference 29.

[35] Properties of local ergodicity have been studied for a one-dimensional system of particles with harmonic interaction between nearest neighbors by G. Klein and I. Prigogine, Physica **19**, 1053 (1953).

[36] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

Fourier transform:[37]

$$\bar{f}_c(\omega)=\int_{-\infty}^{\infty}e^{-i\omega t}f_c(t)dt=\begin{cases}\bar{f}(\omega-\omega_c) \text{ for } \epsilon_c=3\\ -\bar{f}(\omega_c-\omega) \text{ for } \epsilon_c=1\\ -\bar{f}(\omega-\omega_c) \text{ for } \epsilon_c=-1\\ \bar{f}(\omega_c-\omega) \text{ for } \epsilon_c=-3\end{cases},$$

with

$$\bar{f}(\omega)=\begin{cases}0 \text{ for } \omega<0\\ 4(\pi\omega)^{\frac{1}{2}}\exp(-\alpha\omega) \text{ for } \omega>0.\end{cases}$$

Hence, in the energy distribution of neutrons scattered in an arbitrary direction, the term in $\mathcal{E}_c(t)$ of (59) produces a singularity at $\omega=\omega_c$: near $\omega=\omega_c$, the energy distribution has the form $A\bar{f}_c(\omega)+F(\omega)$, where A is a constant and $F(\omega)$ a continuous function, the first derivative of which has at most a finite discontinuity at $\omega=\omega_c$. Both A and F depend on the scattering direction. One can easily show that the scattering processes responsible for this singularity involve excitation by the neutron of one phonon of wave vector $\mathbf{q}_c$ and polarization j_c.[38] Similarly, the term in $\mathcal{E}_c^*(t)$ produces a singularity at $\omega=-\omega_c$, with an energy distribution of form $A'\bar{f}_c(-\omega)+F'(\omega)$, where A' and F' have meanings similar to A and F. This singularity is due to annihilation by the neutron of one phonon again characterized by $\mathbf{q}_c$ and j_c.

VI. IDEAL QUANTUM GASES

To illustrate the effect of Bose-Einstein and Fermi-Dirac statistics on pair correlations we treat very briefly the case of ideal quantum gases. It is instructive to consider particles with nonvanishing spin and to study simultaneously the correlations imposed by the statistics on particle positions and on spin orientations. This is done by calculating the spin-dependent pair distribution function Γ defined in Eq. (24); a_j is an arbitrary function of the jth particle spin, the same function for each particle.

The expressions of Γ for the Fermi gas and for the Bose gas without condensed phase are very similar and their derivation, to be based on the analog of Eq. (8) for Γ, is quite straightforward. Only the final result will be given here:

$$\Gamma(r,t)=\rho\langle a^2\rangle_{\text{Av}}\{f(r,t)\pm(2s_0+1)^{-1}n_{\mp}(r,t)\}\cdot\{n_{\mp}(r,t)\}^*+\rho\langle a\rangle_{\text{Av}}^2. \quad (60)$$

The upper and lower signs refer to Bose and Fermi particles, respectively. The averages $\langle a^2\rangle_{\text{Av}}$ and $\langle a\rangle_{\text{Av}}^2$ have the same meaning as in Eq. (25). s_0 is the spin of the particles in units of $\hbar$. The functions f and $n_{\pm}$ are defined by

$$f(r,t)=(2\pi)^{-3}\rho^{-1}\int\exp\{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)\}d\mathbf{k}$$

$$=-\frac{2}{\rho}\left(1-i\frac{|t|}{t}\right)\left(\frac{M}{4\pi\hbar|t|}\right)^{\frac{3}{2}}\exp\left(-\frac{iMr^2}{2\hbar t}\right),$$

$$n_{\mp}(r,t)=(2\pi)^{-3}\rho^{-1}\int\exp\{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)\}\cdot\{B\exp(\hbar\beta\omega_k)\mp1\}^{-1}d\mathbf{k}. \quad (61)$$

M is the mass of the particles, β is $(k_BT)^{-1}$, and ω_k stands for $\hbar k^2/2M$. The constant $B\geqslant\frac{1}{2}(1\pm1)$ is determined by $n_{\mp}(0,0)=1$.

According to Eq. (60), the range of the pair correlations in space and time is determined by the convergence of $n_{\mp}$ to zero for r or $t\rightarrow\infty$. This convergence can be discussed in all cases from Eq. (61). We consider here only the case $B>1$, for which expansion in powers of B^{-1} gives

$$n_{\mp}(r,t)\simeq\rho^{-1}\left(\frac{M}{2\pi\hbar}\right)^{\frac{3}{2}}\sum_{l=1}^{\infty}\frac{(\pm1)^{l-1}}{B^l(lt_T-it)^{\frac{3}{2}}}\times\exp\left\{-\frac{Mr^2}{2\hbar(lt_T-it)}\right\}, \quad (62)$$

where $t_T=\hbar\beta=\hbar/(k_BT)$ is a measure of the relevant relaxation time. For B not too close to one, an estimate of the spatial range of the pair correlations is obtained from the first term of the series. It gives

$$r\sim(\hbar/M)^{\frac{1}{2}}(t_T{}^2+t^2)^{\frac{1}{4}},$$

and for $t\lesssim t_T$, reduces essentially to the mean de Broglie wavelength $(\hbar^2\beta/2M)^{\frac{1}{2}}=\lambda_B$. The expansion Eq. (62) becomes impractical when B is close to one, in particular for the Bose gas. For the latter and for $0<B-1\ll1$ a more convenient expression has been obtained by Placzek[39] for $n_-(r,0)$; it can be used for $n_-(r,t)$ by introducing it into the identity,

$$n_{\mp}(r,t)=\rho\int n_{\mp}(r',0)f(|\mathbf{r}-\mathbf{r}'|,t)d\mathbf{r}',$$

and shows that the correlation range becomes of order $(B-1)^{-1/2}\lambda_B$, thus increasing indefinitely as condensation is approached.

From Eq. (60) the difference between Γ and its asymptotic value $\rho\langle a\rangle_{\text{Av}}^2$ is seen to depend on the spin through $\langle a^2\rangle_{\text{Av}}$ only. This fact is obviously due to the absence of spatial correlation between particles in different spin states. Applied to neutron scattering by

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[37] The various cases correspond to the possible signatures of the stationary point of $\omega_{jc}(\mathbf{q})$ at $\mathbf{q}_c$: minimum, saddle point of one of two types, maximum, respectively.

[38] This is shown for cubic crystals in reference 34.

[39] G. Placzek, Proceedings of the Second Berkeley Symposium on Mathematical Statistics and Probability (University of California Press, Berkeley, 1951), pp. 581–588, especially Eq. (36).

nuclei with spin-dependent scattering length a, it illustrates how little sense is made by the conventional terminology of calling coherent (or incoherent) the part of the scattering containing $\langle a\rangle_{\mathrm{Av}}^2$ (or $\langle a^2\rangle_{\mathrm{Av}}-\langle a\rangle_{\mathrm{Av}}^2$), as soon as some correlation exists between spins, resulting either from symmetry requirements of the wave function or from spin interactions. It is only for systems of Boltzmann particles with free nuclear spins that this terminology is physically reasonable.[40]

For a Bose gas in the condensation region, the pair distribution Γ has the following expression:

$$\begin{aligned}\Gamma(r,t)=\rho\langle a^2\rangle_{\mathrm{Av}}[\{f(r,t)+(2s_0+1)^{-1}(n(r,t)+n_0)\}\\ \cdot(n(r,t)+n_0)^*-(2s_0+1)^{-1}n_0^2]+\rho(\langle a^2\rangle_{\mathrm{Av}}-\langle a\rangle_{\mathrm{Av}}^2)\\ \times(2s_0+2)^{-1}n_0^2+\rho\langle a\rangle_{\mathrm{Av}}^2.\end{aligned} \quad (63)$$

The function f is the same as above; n and n_0 are defined by

$$n(r,t)=(2\pi)^{-3}\rho^{-1}\int\exp\{-i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)\}\cdot\{\exp(\hbar\beta\omega_k)-1\}^{-1}d\mathbf{k},$$

$$n_0=1-n(0,0)=1-(\rho_c/\rho),$$

where ρ_c is the condensation density at temperature T. The quantity $\rho-\rho_c=n_0\rho$, supposed to be positive, is the density of the condensed phase. The asymptotic behavior of n is easily shown to be in λ_T/r for $r\rightarrow\infty$ and in $(t_T/|t|)^{\frac{3}{2}}$ for $t\rightarrow\infty$.

In the derivation of Eq. (63), the only point which is not quite elementary is the calculation of the thermal average $\langle N_\alpha N_\beta\rangle$, where N_α, N_β denote the number of particles of momentum zero in spin states α, β ($\alpha,\beta=1,\cdots 2s_0+1$). With the help of generating functions for the distribution of values of the N_α's, one easily shows that

$$\langle N_\alpha N_\beta\rangle=\frac{2s_0+1}{2s_0+2}\langle N_\alpha\rangle^2-\frac{1}{2s_0+1}\langle N_\alpha\rangle,\quad(\alpha\neq\beta)$$

$$\langle N_\alpha^2\rangle=2\frac{2s_0+1}{2s_0+2}\langle N_\alpha\rangle^2+\frac{2s_0}{2s_0+2}\langle N_\alpha\rangle.$$

In the right-hand sides, the second terms can be neglected in comparison with the first ones in the limit of an infinite number of particles.

In the special case $t=0$, $a_j=1$, Eqs. (60) and (63) reduce to the instantaneous pair distributions derived for ideal quantum gases by London.[41]

VII. CONCLUDING REMARKS

Our aims have been to introduce the time-dependent generalization of the familiar pair distribution function, to indicate its interest from the standpoint of statistical mechanics, and to establish its role in scattering theory, showing at the same time how slow neutron scattering makes it experimentally accessible.

The use of scattering experiments for the study of the pair distribution in space and time seems to us to be of real interest for systems of nontrivial and poorly known dynamical properties, mainly liquids and dense gases. It is our hope that increasingly complete and accurate data on such systems will become available. The case of liquid helium, with its marked quantum properties and its complex-valued pair distribution, undoubtedly deserves special attention.[42]

From the theoretical standpoint, the determination of the $g(\mathbf{r})$ function in terms of the intermolecular forces is well known to be a difficult and challenging problem for liquids and dense gases. Both the difficulty and the theoretical interest of a determination of the time-dependent pair distribution are likely to be greater, in view of the fact that the relaxation properties of the system are involved. On a more modest scale, approximate discussions of the time dependence of G, based on suitable models, would probably be instructive and might provide considerable help in the analysis of scattering experiments, since for some time to come, complete angular and energy distributions will not be readily measurable.

The author wishes to express his gratitude to Dr. G. Placzek for many stimulating discussions and suggestions on the various aspects of the present work.

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[40] This remark holds of course also for isotope disorder. Other terminologies, introduced by G. C. Wick, Physik. Z. **38**, 689 (1937), and J. M. Cassels, Progr. Nuclear Phys. **1**, 185 (1950), have the same limitation.

[41] F. London, J. Chem. Phys. **11**, 203 (1943).

[42] Theoretical discussions of neutron scattering for various models of liquid helium have been given by A. Akhiezer and I. Pomeranchuk, J. Phys. (U.S.S.R.) **9**, 461 (1945); Goldstein, Sweeney, and Goldstein, Phys. Rev. **77**, 319 (1950); L. Goldstein and D. W. Sweeney, Phys. Rev. **80**, 141 (1950).