

## On the Theory of Coherent Scattering Processes in Liquids\*

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The coherent scattering structure factor of liquids for x-rays and slow neutrons are shown to determine completely both the correlation function and the direct local interaction function of liquids, which quantities are the only operating elements of the general static liquid model of Ornstein and Zernike. Of these functions only the former has been derived so far from the data accumulated essentially on the coherent scattering of x-rays by liquids. It is shown that the directly available experimental structure factors completely determine the even moments of these molecular distribution functions. The zeroth moment of the correlation function augmented by unity is essentially the liquid concentration fluctuation which determines its isothermal compressibility. These quantities become thus directly derivable from the structure factor measurements without any arbitrary and uncertain manipulations. In terms of the model, a straightforward method leads, with the empirically obtainable total cross section, to the total incoherent slow neutron scattering cross sections in liquids. These should yield information on their energy spectrum not available through other types of scattering processes, such as x-rays, for instance.

### I. INTRODUCTION

THE knowledge of the distribution of the atoms or molecules, around one chosen arbitrarily, in a liquid in statistical equilibrium enables one to evaluate rigorously the intensity of coherently scattered waves of any type by this liquid. According to statistical mechanics, the knowledge of the intermolecular forces leads formally to the spatial distribution function of the liquid molecules which determines completely its coherent scattering properties. In practice such a procedure founded on first principles has not as yet led to definite results of a general character because of its analytical complexity.<sup>1</sup> In view of this complexity it was natural that a number of attempts should have been made in order to derive semi-empirical liquid models.<sup>2</sup> Among these the one suggested by Ornstein and Zernike<sup>3</sup> in connection with a possible solution of the critical opalescence problem of visible radiation appears to be quite general. As a matter of fact, one of the two operating elements of this liquid model, the two-atom or two-molecule spatial distribution function was shown to be directly accessible to experiment through the coherent scattering structure factor of x-rays and recently also of slow neutrons.<sup>4</sup> Since the derivation of this result, practically all work on the coherent scattering of x-rays by liquids culminated in the empirical determination of the local molecular or radial distribution function.<sup>5</sup> The Ornstein-Zernike

(O.Z.) liquid model is founded on the assumed existence of a direct intermolecular interaction function whose range would be expected to be of the same order of magnitude as that of the elementary intermolecular forces. This direct interaction function determines, in turn, an indirect interaction function which enters into the definition of the two-atom or two-molecule radial distribution function. The latter expresses the probability of finding a molecule in a volume element whose center is at some specified distance from a molecule chosen arbitrarily. As far as we are aware, the fundamental relation of the O.Z. liquid model which is actually the definition of the indirect interaction function in terms of the direct interaction function has been left partially out of account in x-ray work. It is one of the main points of this work to redirect attention to the possibility of a complete verification of the O.Z. liquid model through a fuller exploitation of the experimental data already accumulated on the coherent intensity structure factor of a number of monatomic or molecular liquids. The interest in the O.Z. static liquid model has been further widened recently through a study of the analogies existing between the molecular distributions of this model and that of ideal Bose-Einstein fluids undergoing condensation in momentum space, whose complete and rigorous formalism is based on first principles.<sup>6</sup> Also the possibility of using slow neutrons in the investigation of the coherent scattering by liquids in the critical region may lead to a further verification of the O.Z. theory in this region.<sup>6,7</sup> Furthermore, the basis of the model has been broadened somewhat through a new derivation of its central relation.<sup>8</sup>

The general coherent scattering properties of this model will of course be valid both for x-rays and slow

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<sup>1</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1941), where the theory of the equation of state of vapors illustrates the difficulties alluded to.

<sup>2</sup> J. Frenkel, *Theory of Liquids* (Oxford University Press, London, 1947).

<sup>3</sup> L. S. Ornstein and F. Zernike, *Amsterdam Proc.* **17**, 793 (1914); F. Zernike, *Amsterdam Proc.* **19**, 1520 (1916); L. S. Ornstein and F. Zernike, *Physik. Z.* **19**, 134 (1918) and **26**, 761 (1926).

<sup>4</sup> F. Zernike and J. A. Prins, *Z. Physik* **41**, 184 (1927).

<sup>5</sup> N. S. Gingrich, *Revs. Modern Phys.* **15**, 90 (1943); A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935); R. W.

James, *Diffraction of X-rays* (Bell and Sons, London, 1948). For the neutron experiments see O. Chamberlain, *Phys. Rev.* **77**, 305 (1950).

<sup>6</sup> L. Goldstein, *Phys. Rev.* **83**, 289 (1951).

<sup>7</sup> L. Goldstein, *Phys. Rev.* **81**, 326(A) (1951).

<sup>8</sup> M. J. Klein and L. Tisza, *Phys. Rev.* **76**, 1861 (1949).

neutrons and for visible radiation, in transparent liquids, in the limit appropriate to the latter case.

A second major point, although quite qualitative, of this work turns out to be the recognition that the experimental investigation of the slow neutron incoherent scattering processes might yield important information on the energy spectrum of liquids. While their coherent scattering phenomena is determined by the spatial distribution of the liquid molecules, whereby an averaging over all the possible states of liquid motion is automatically performed, the slow neutron incoherent processes associated with both energy and momentum exchange of the neutrons with the liquid as a whole appear to provide a unique set of information on the motions of the liquid as a whole in a relatively wide energy interval. This type of information is not available through x-rays.

It seems of interest to outline first the main features of the O.Z. static liquid model. We should like, in doing so, to go somewhat beyond the original presentation.<sup>3</sup> This will be attempted in the next section. The subsequent sections will then be devoted to the study of the general coherent scattering properties of this liquid model and to a qualitative discussion of the possible importance of the slow neutron incoherent scattering phenomena for obtaining information on the energy spectrum of a liquid as a whole.

## II. THE LIQUID MODEL<sup>3</sup>

Let the probability of finding a liquid molecule in a volume element  $dv(\mathbf{r})$  whose center is at a distance  $\mathbf{r}$  from the center of a molecule situated at the origin be given by

$$P(\mathbf{r})dv = [1 + Q(\mathbf{r})]dv/V, \quad (1)$$

where  $P(\mathbf{r})$  is the probability density and  $V$  stands for the total volume of the liquid. The mean number of molecules in  $dv(\mathbf{r})$  is

$$dn(\mathbf{r}) = (N/V)dv + (N/V)Q(\mathbf{r})dv. \quad (2)$$

where  $N$  is the total number of molecules in  $V$ . The accidental deviation of the concentration from its mean is thus,

$$dn(\mathbf{r})/dv - N/V = \delta(\mathbf{r}) = (N/V)Q(\mathbf{r}). \quad (3)$$

In order to derive the average deviation from the mean concentration at a point, chosen arbitrarily within the liquid to be the origin of the coordinate system, it will be assumed that this deviation is a linear superposition of the deviations in all neighboring volume elements. Adopting a continuum representation, one has thus

$$\delta(0) = \int_V \delta(\mathbf{r})f(\mathbf{r})dv(\mathbf{r}) = (N/V) \int_V Q(\mathbf{r})f(\mathbf{r})dv. \quad (4)$$

The direct influence function  $f(\mathbf{r})$ , depending only on the length of the radius vector  $\mathbf{r}$ , is determined by the intermolecular forces and its range should be about the

range of these forces. Hence, the integration in (4) may be extended over the volume  $V$  or even the whole space.

Assuming throughout central forces, the function  $Q(\mathbf{r})$  appearing in the two-particle probability density  $P(\mathbf{r})$ , Eq. (1), should depend only on the length  $|\mathbf{r}|$ . Furthermore, the presence of a molecule at the origin cannot very much affect the probability to find another one at a great distance from it. Hence, the function  $Q(\mathbf{r})$  should tend to vanish for large values of its argument or the mean concentration should prevail at large distances from a molecule chosen arbitrarily within the liquid. Surface effects will be omitted throughout this paper. On the other hand, the strongly repulsive character of the intermolecular forces at small separations will prevent two molecules from approaching each other, so that the probability (1) should tend to vanish at small distances.

Consider the problem of finding the mean deviation from the average concentration at some point  $\mathbf{r}$ , as caused by the indirect action of a given deviation at some other point, which may be chosen to be the origin of the coordinate system. This indirect action may be seen to come about through the local or short range interactions between the molecules situated in the space surrounding the one at the origin and the other at the point  $\mathbf{r}$ . Through these interactions any deviation from the average concentration  $\delta(0)$ , at the origin, will affect the deviation  $\delta(\mathbf{r})$  at the point  $\mathbf{r}$ , no matter how large  $\mathbf{r}$  is. This indirect action is already expressed by the function  $Q(\mathbf{r})$  defined by Eq. (3). It may be redefined more completely in the following way, as shown by Ornstein and Zernike.<sup>3</sup> Let

$$\delta(\mathbf{r}, 0) = g[\mathbf{r}, \delta(0)dv(0)]; \quad r > 0, \quad (5)$$

express the assumption that the deviation at  $\mathbf{r}$  is some function of  $\mathbf{r}$  and  $\delta(0)$ . This is equivalent to the following more general relation

$$\delta(\mathbf{r}, \mathbf{r}') = g[|\mathbf{r} - \mathbf{r}'|, \delta(\mathbf{r}')dv(\mathbf{r}')], \quad r \neq r', \quad (5a)$$

and, hence,

$$\delta(0, \mathbf{r}') = g[\mathbf{r}', \delta(\mathbf{r}')dv(\mathbf{r}')], \quad r' > 0. \quad (5b)$$

The preceding relation may now be used on the left-hand side of Eq. (4), while (5a) or  $\delta(\mathbf{r}, \mathbf{r}')$  may be used for  $\delta(\mathbf{r})$  in the integral on the right-hand side of Eq. (4). We thus obtain,

$$g[\mathbf{r}', \delta(\mathbf{r}')dv(\mathbf{r}')] = \int g[|\mathbf{r} - \mathbf{r}'|, \delta(\mathbf{r}')dv(\mathbf{r}')]f(\mathbf{r})dv(\mathbf{r}) + f(\mathbf{r}')\delta(\mathbf{r}')dv(\mathbf{r}'). \quad (6)$$

The second term on the right-hand side originates in that Eq. (5a) is not valid at  $r = r'$  and the right-hand side of Eq. (4) has to be completed by the direct action  $f(\mathbf{r})$ . Since the preceding equation cannot depend on any particular choice of  $\delta(\mathbf{r}')dv(\mathbf{r}')$ , one should have

$$g[\mathbf{s}, \delta(\mathbf{s})dv(\mathbf{s})] = g(\mathbf{s})\delta(\mathbf{s})dv(\mathbf{s}), \quad (7)$$

and, Eq. (6), becomes, switching primes,

$$g(\mathbf{r}) = \int g(|\mathbf{r}-\mathbf{r}'|)f(\mathbf{r}')d\mathbf{v}(\mathbf{r}') + f(\mathbf{r}). \quad (8)$$

This states that the indirect interaction or correlation between a molecule at the origin and one at a distance  $\mathbf{r}$  is equal to their short-range interaction  $f(\mathbf{r})$  augmented by the sum of the correlations of all those molecules which have a direct or short-range interaction with the one at the origin. This relation has been obtained recently in a more direct way by Klein and Tisza<sup>8</sup> in their discontinuous transcription of the O.Z. continuum liquid model.

We may write Eq. (5) in the following form

$$\delta(\mathbf{r}) = g(\mathbf{r})\delta(0)d\mathbf{v}(0), \quad (9)$$

which, when multiplied by  $\delta(0)$  and taking averages, over the liquid volume, leads to

$$\langle \delta(\mathbf{r})\delta(0) \rangle_{\text{av}} = g(\mathbf{r})\langle \delta(0)^2 \rangle_{\text{av}}d\mathbf{v}(0). \quad (10)$$

But this equation is evidently independent of the choice of the origin of the coordinate system, and one has to have also

$$\langle \delta(\mathbf{r})\delta(0) \rangle_{\text{av}} = g(\mathbf{r})\langle \delta(\mathbf{r})^2 \rangle_{\text{av}}d\mathbf{v}(\mathbf{r}). \quad (11)$$

Equations (10) and (11) impose that

$$\langle \delta(0)^2 \rangle_{\text{av}}d\mathbf{v}(0) = \langle \delta(\mathbf{r})^2 \rangle_{\text{av}}d\mathbf{v}(\mathbf{r}) = \dots = \text{constant}. \quad (12)$$

This constant may be obtained approximately in the following way. Since  $(N/V)$  is the mean concentration of the molecules in the liquid, in a volume element  $d\mathbf{v}$ , there are, on the average,  $(N/V)d\mathbf{v}$  molecules. If  $d\mathbf{v}$  is small enough, then there will be either one or no molecule in  $d\mathbf{v}$ . The deviations from the mean number of molecules, in the two eventualities, are, according to Eq. (3),

$$\delta_1 d\mathbf{v} = 1 - (N/V)d\mathbf{v}; \quad \delta_2 d\mathbf{v} = -(N/V)d\mathbf{v},$$

respectively. Hence,

$$\lim_{d\mathbf{v} \rightarrow 0} \delta_1(-\delta_2)d\mathbf{v} \cong \langle \delta^2 \rangle_{\text{av}}d\mathbf{v} = (N/V), \quad (13)$$

and Eq. (11) becomes, with Eqs. (3), (5), and (9),

$$\langle \delta(\mathbf{r})\delta(\mathbf{r}') \rangle_{\text{av}} = (N/V)g(\mathbf{r}-\mathbf{r}') = (N/V)^2Q(\mathbf{r}-\mathbf{r}'). \quad (14)$$

In a large volume, the accidental excess or defect in the total number of molecules may be written as

$$\Delta N = \int_V \delta(\mathbf{r})d\mathbf{v},$$

and,

$$\begin{aligned} \langle \Delta N^2 \rangle_{\text{av}} &= \int_V \int_V \langle \delta(\mathbf{r})\delta(\mathbf{r}') \rangle_{\text{av}}d\mathbf{v}(\mathbf{r})d\mathbf{v}(\mathbf{r}') \\ &\quad + \int_V \int_V \langle \delta(\mathbf{r})\delta(\mathbf{r}') \rangle_{\text{av}}d\mathbf{v}(\mathbf{r})d\mathbf{v}(\mathbf{r}') \\ &= N \left[ 1 + (N/V) \int_V Q(\mathbf{r})d\mathbf{v} \right], \end{aligned} \quad (15)$$

a relation which was proved rigorously in the statistical mechanics of ideal symmetric fluids where the correlation is strictly a quantum effect.<sup>6</sup>

While Eq. (8) cannot give the indirect interaction or correlation function  $g(\mathbf{r})$  unless  $f(\mathbf{r})$ , the possibly short-range direct interaction function, is known, it leads to a satisfactory determination of its asymptotic expression as shown by Zernike.<sup>3</sup>

Let

$$F = \int f(\mathbf{r})d\mathbf{v}; \quad r_{r^2} = \int f(\mathbf{r})r^2d\mathbf{v} = \epsilon^2, \quad (16)$$

$F$  is the space integral of the short-range direct interaction function and  $\epsilon^2$  is the mean square of its range. The quantity  $(\epsilon^2)^{1/2}$  is of the order of magnitude of the range of the intermolecular forces. At all distances  $r \gg \epsilon$  where  $f(\mathbf{r})$  is vanishingly small and provided that  $\rho > \epsilon$  one finds

$$\begin{aligned} g(\mathbf{r}) &= [3F/(2\pi\epsilon^2)]e^{-r/\rho}/r; \quad r \gg \epsilon, \quad (17) \\ \rho^2 &= \epsilon^2/6(1-F). \end{aligned}$$

With  $\epsilon$  being about the range of the intermolecular forces  $\epsilon^3$  is, approximately, the volume per molecule  $V/N$ , and

$$\begin{aligned} g(\mathbf{r})_{r \gg \epsilon} &= (3F/2\pi\epsilon^3)e^{-r/\rho}/(r/\epsilon) \\ &= (N/V)(3F/2\pi)e^{-r/\rho}/(r/\epsilon). \end{aligned} \quad (18)$$

The correlation function is thus, in this approximation,

$$Q(\mathbf{r})_{r \gg \epsilon} = (3F/2\pi)e^{-r/\rho}/(r/\epsilon), \quad (19)$$

and the two-particle probability density defined by Eq. (1) becomes, asymptotically,

$$\begin{aligned} P(\mathbf{r})_{r \gg \epsilon} &= (1+Q(\mathbf{r}))/V \\ &= [1 + (3F/2\pi)e^{-r/\rho}/(r/\epsilon)]V^{-1}. \end{aligned} \quad (20)$$

The latter, of course, has the required form, tending toward the constant limit  $V^{-1}$  at large separation  $r$ .

It is of interest to consider more closely the range  $\rho$ , Eq. (17), of the correlation function  $Q(\mathbf{r})$  or the indirect interaction function  $g(\mathbf{r})$  which is proportional to it. According to Eq. (15),

$$\langle \Delta N^2 \rangle_{\text{av}}/N = 1 + \int g(\mathbf{r})d\mathbf{v} = 1 + G. \quad (21)$$

But in a large volume and as long as the state of the fluid is different from the critical state,  $\langle \Delta N^2 \rangle_{\text{av}}/N$  is determined by statistical thermodynamics<sup>9</sup> to be

$$\langle \Delta N^2 \rangle_{\text{av}}/N = NkT\chi_T/V, \quad (22)$$

the fluid having temperature  $T$ ,  $k$  denoting Boltzmann's constant and  $\chi_T$  the isothermal compressibility in this state. Multiplying both sides of the integral equation (8) by  $d\mathbf{v}(\mathbf{r})$  and integrating over the whole volume  $V$  or the whole space, one obtains

$$G(1-F) = F, \quad 1+G = (1-F)^{-1} = NkT\chi_T/V. \quad (23)$$

<sup>9</sup> M. v. Smoluchowski, Ann. Physik **25**, 205 (1908).

Hence, the range  $\rho$  of the  $g$ -function, or the correlation function  $Q(r)$ , is, according to (17),

$$(\rho)^2 = (\epsilon^2/6)(1+G) = NkT\chi_T\epsilon^2/6V. \quad (24)$$

The space integrals  $F$ ,  $G$ , together with the functions  $f$  and  $g$  are, of course, temperature dependent.

In normal liquids at temperatures  $T$  small in comparison with the critical temperature  $T_c$ ,  $\langle\Delta N^2\rangle_{av}/N$  or  $(NkT\chi_T/V)$  may be small in comparison with unity. Hence, at these low temperatures,

$$-1 \leq G(T \ll T_c) < 0, \quad F(T \ll T_c) < 0, \quad |F(T \ll T_c)| > 1. \quad (25)$$

At such temperatures the range of the  $g$ -function is thus small compared with the range  $\epsilon$  of the  $f$ -function. Under these conditions with the molecular distribution function, Eq. (1), being

$$\begin{aligned} dn(r)/dv &= NP(r) = (N/V) + (N/V)Q(r) \\ &= (N/V) + g(r), \end{aligned} \quad (26)$$

$g(r)$  vanishing at small distances already, this function or  $Q(r)$  has to be negative essentially over the interval  $r \lesssim \rho \ll \epsilon$ . This is of course necessary for the probability density  $P(r)$  has to become small at small separations.

As the liquid temperature increases, the right-hand side of Eq. (23) increases, both  $G$  and  $F$  increase algebraically and vanish when the classical value of the fluctuation  $\langle\Delta N^2\rangle_{av}$  is reached from below. That is, when classical or ideal conditions prevail, at some temperature  $T_i$ ,

$$\begin{aligned} \langle\Delta N^2\rangle_{av}/N &= NkT_i\chi_T/V = 1; \quad T_i = (V/Nk\chi_T), \\ G(T_i) &= F(T_i) = 0, \end{aligned} \quad (27)$$

and

$$(\rho)^2_{T_i} = \epsilon^2/6, \quad (28)$$

the two functions have about the same range. The fact that the space integrals increase indicates that with the  $g$ -function becoming necessarily negative at close distances, there is a distance interval  $r$  over which  $g(r, T)$  becomes positive so as to compensate for the negative portion of the space integral. The oscillatory character of  $g(r, T)$ , and also of  $f(r, T)$  may thus be safely inferred from these general results.

At temperatures  $T > T_i$ , both  $G(T)$  and  $F(T)$  become positive, with  $F(T)$  tending toward unity and  $G(T)$  toward large positive values as the temperature approaches the critical temperature  $T_c$ . Simultaneously the range of  $g(r, T)$  becomes very large, of the order of magnitude of the linear dimensions of the vessel containing the liquid. One thus obtains

$$g(r, T) \underset{r \gg \epsilon, T \rightarrow T_c}{=} \frac{3}{2\pi\epsilon^2 r}, \quad (29)$$

i.e., the correlation density function becomes the long-range  $(1/r)$  function. Explicitly, one has thus

$$\lim_{T \rightarrow T_c} G(T) \gg 1, \quad \lim_{T \rightarrow T_c} F(T) = 1. \quad (30)$$

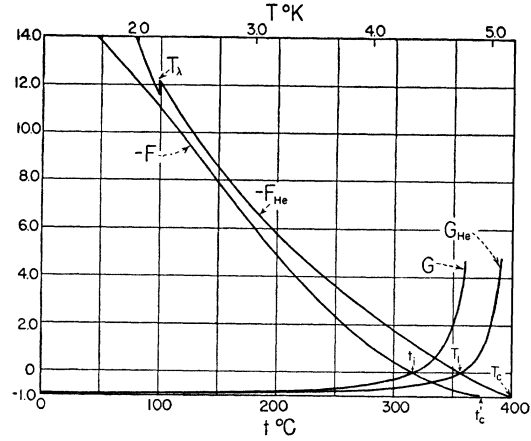


FIG. 1. The space integrals ( $F, G$ ) for liquid water, and ( $F_{He}, G_{He}$ ) for liquid helium as a function of the temperature. The lower abscissa scale in  $^{\circ}\text{C}$  (water) and the upper in  $^{\circ}\text{K}$  (helium).

We have represented, in Fig. 1,  $F(T)$  and  $G(T)$  for water and liquid helium. The over-all similarity in the behavior of these so different liquids with respect to the space integrals of their direct and indirect interaction functions is evident. The radical change in the behavior of  $g(r, T)$  at temperatures  $T > T_i$  is clearly exhibited by these curves. The  $\lambda$ -anomaly in liquid He appears through the slight discontinuity in  $F(T)$  at the  $\lambda$ -point. This indicates already that any experimental data which may yield  $F(T)$  or some quantities closely connected with it cannot show but a small temperature effect in crossing the  $\lambda$ -point. This is so because the spatial arrangement of the atoms in liquid helium, associated with a complete averaging over the states of motion of the liquid as a whole will likely change only slightly in crossing the  $\lambda$ -point. It is to be noted that the water curves refer to the saturated liquid, while the helium curves correspond to slightly compressed helium.

### III. THE COHERENT SCATTERING STRUCTURE FACTOR OF LIQUIDS

It is easy to prove that the liquid coherent scattering cross section per atom or molecule, per unit solid angle, is

$$\sigma_L(\lambda, \theta) = \sigma(\lambda, \theta)F_L^2(\lambda, \theta), \quad (31)$$

where  $\sigma(\lambda, \theta)$  is the individual bound atom coherent scattering cross section and  $F_L^2(\lambda, \theta)$  is the coherent intensity structure factor of the liquid. The structure factor  $F_L^2$  is the same for all types of waves. The specificity of the liquid cross sections for the different types of waves is included into  $\sigma(\lambda, \theta)$ . For unpolarized incident electromagnetic waves,  $\sigma(\lambda, \theta)$  is supposed to include the polarization factor  $\frac{1}{2}[1 + \cos^2(2\theta)]$ , beside the elementary atomic cross section. In the case of molecules it is assumed to include also the elementary intramolecular structure factor. For an unpolarized beam of slow neutrons incident on a monatomic liquid

of a single isotope with vanishing nuclear spin,

$$\sigma(\lambda, \theta) = \sigma_\infty = \sigma_s(1 + A^{-1})^2, \quad (32)$$

$A$  being the mass number of the liquid atom and  $\sigma_s$  the free solitary atom slow neutron scattering cross section per unit solid angle. This is  $(\sigma_t/4\pi)$ ,  $\sigma_t$  being the total free atom slow neutron scattering cross section, which is an energy-independent quantity. In these monatomic liquids, one has

$$\sigma_L(\lambda, \theta)/\sigma(\lambda, \theta) = 1 + N^{-1} \sum_{\substack{i, j \\ i \neq j}}^N \cos[\Delta \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]; \quad (33)$$

$$|\Delta \mathbf{k}| = 2|\mathbf{k}| \sin\theta = (4\pi \sin\theta)/\lambda,$$

$\mathbf{k}$  is the propagation vector and  $2\theta$  the scattering angle. In monatomic liquids, with a single isotope with spin or several isotopes, one finds, for slow neutrons, with  $\sigma_\infty$  denoting the bound atom elastic cross section per unit solid angle, averaged over the different isotopes and spin configurations and  $\sigma_c$  the bound atom coherent scattering cross section averaged again over the different isotopes and spin configurations of the neutron and scattering nuclei,

$$\frac{\sigma_L(\lambda, \theta)}{\sigma_\infty} = 1 + \tau N^{-1} \sum_{\substack{i, j \\ i \neq j}}^N \cos[\Delta \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)], \quad (34)$$

$$\tau = \sigma_c/\sigma_\infty < 1,$$

showing that the right-hand side contains the ratio of the cross sections  $\tau$  and ceases to be a purely kinematical quantity.

In terms of the continuous two-atom distribution function, Eq. (1),

$$P(r_{nm}, T) = V^{-2} [1 + Q(r_{nm}, T)]; \quad r_{nm} = |\mathbf{r}_n - \mathbf{r}_m|,$$

the liquid structure factor per atom may be written as

$$F_L^2(\Delta \mathbf{k}, T) = 1 + N^{-1} \sum_{\substack{n, m \\ n \neq m}}^N \int \cos[\Delta \mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)] \times P(r_{nm}, T) dv_n dv_m. \quad (35)$$

Explicitly,

$$F_L^2(\Delta \mathbf{k}, T) = 1 + \frac{N}{V^2} \int \cos[\Delta \mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)] dv_n dv_m + \frac{N}{V} \int \cos(\mathbf{r} \cdot \Delta \mathbf{k}) Q(r, T) dv. \quad (36)$$

The second term on the right-hand side yields the uncorrelated or ideal fluid structure factor, which is extremely small for all scattering angles and  $\Delta k$  values, with the exception of the immediate vicinity of the forward direction or almost completely vanishing  $\Delta k$  values, it shall be omitted henceforth. Hence, the liquid

structure factor (36) becomes

$$F_L^2(\Delta \mathbf{k}, T) = 1 + \int g(r, T) \cos(\mathbf{r} \cdot \Delta \mathbf{k}) dv, \quad (37)$$

according to the definition of the indirect interaction function  $g(r, T)$  in terms of the correlation function  $Q(r, T)$ , Eq. (14). Integrating over the angles, one finds

$$F_L^2(\Delta k, T) = 1 + 4\pi \int_0^\infty \frac{\sin(r\Delta k)}{(r\Delta k)} g(r, T) r^2 dr. \quad (38)$$

In the limit of small  $\Delta k$ , one obtains, at once,

$$\lim_{\Delta k \rightarrow 0} F_L^2(\Delta k, T) = 1 + \int_0^\infty g(r, T) dv = 1 + G(T). \quad (39)$$

But the right-hand side is, according to the properties of the liquid model,  $\langle \Delta N^2 \rangle_w / N$ , Eq. (21). Hence, away from the critical state of the fluid,

$$\lim_{\Delta k \rightarrow 0} F_L^2(\Delta k, T)_{T \neq T_c} = \langle \Delta N^2 \rangle_w / N = NkT\chi_T/V. \quad (40)$$

The very small angle coherent scattering structure factor is independent of the details of the scattering process, that is  $\Delta k$  or  $\sin\theta/\lambda$ ,  $\lambda$  being the wavelength of the incident waves in the medium surrounding the scattering liquid. The structure factor in this limit depends only on the over-all statistical properties of the liquid, the molecular concentration ( $N/V$ ), the temperature and the isothermal compressibility in the state of equilibrium under consideration. The general result (40) has been first obtained by Brillouin<sup>10</sup> in his investigation of x-ray scattering in fluids using the method of Einstein<sup>11</sup> elaborated in his theory of scattering of visible radiation arising from density fluctuations in a fluid in statistical equilibrium as suggested by Smoluchowski.<sup>9</sup> Again for x-rays, using a different approach, the result (40) has been given by Zernike and Prins.<sup>4</sup> The same result obtains in the coherent scattering of slow neutrons with vanishing momentum change and for atoms with zero spin nuclei.<sup>6,7</sup> One obtains at once for bound scatterers, whose elastic scattering cross section is different from their coherent scattering cross section, using Eq. (34) together with (36),

$$\lim_{\Delta k \rightarrow 0} F_L^2(\Delta k, T)_{T \neq T_c} = 1 + \tau G(T) = (1 - \tau) + \tau \langle \Delta N^2 \rangle_w / N = (1 - \tau) + (NkT\chi_T/V). \quad (41)$$

Here  $\tau$  is the cross-section ratio  $\sigma_c/\sigma_\infty$  defined in connection with Eq. (34).

We should like to investigate further the complete structure factor formula (37). If the indirect interaction or correlation interaction  $g(r, T)$  or  $Q(r, T)$  were known,

<sup>10</sup> L. Brillouin, Ann. Phys. 17, 88 (1922).

<sup>11</sup> A. Einstein, Ann. Phys. 33, 1275 (1910).

the structure factor would be completely determined. This is, however, not the case. We may now express the structure factor (38) in terms of the direct interaction function  $f(r, T)$  of the liquid model. To do this we have to use the integral equation (8) connecting  $f(r, T)$  and  $g(r, T)$ . Multiplying both sides of this equation by  $\cos(\mathbf{r} \cdot \Delta \mathbf{k})$  and integrating over the liquid volume or the whole space, we obtain

$$G(\Delta k, T) = F(\Delta k, T)[1 - F(\Delta k, T)]^{-1}, \quad (42)$$

where<sup>12</sup>

$$G(\Delta k, T) = \int \cos(\mathbf{r} \cdot \Delta \mathbf{k}) g(r, T) dv(r), \quad (43)$$

$$F(\Delta k, T) = \int \cos(\mathbf{r} \cdot \Delta \mathbf{k}) f(r, T) dv(r).$$

Clearly, in the limit  $\Delta k \rightarrow 0$ ,

$$\lim_{\Delta k \rightarrow 0} G(\Delta k, T) = G(T), \quad \lim_{\Delta k \rightarrow 0} F(\Delta k, T) = F(T), \quad (44)$$

and, in this limit, Eq. (42) reduces to Eq. (23). The structure factor (37) becomes thus

$$F_L^2(\Delta k, T) = 1 + G(\Delta k, T) = [1 - F(\Delta k, T)]^{-1}, \quad (45)$$

and for the cross-section ratio (34) different from unity, in the coherent scattering of slow neutrons,

$$F_{L^2}(\Delta k, T) = 1 + \tau G(\Delta k, T) = \frac{1 - (1 - \tau)F(\Delta k, T)}{1 - F(\Delta k, T)}. \quad (46)$$

Integrating over the angles in  $F(\Delta k, T)$ , one obtains

$$F(\Delta k, T) = 4\pi \int \frac{\sin(\Delta k r)}{(\Delta k r)} f(r) r^2 dr. \quad (47)$$

If we denote by  $r_F^{2n}$ , the  $2n$ -th moment of the direct interaction function  $f(r, T)$ , we find, expanding  $\sin(\Delta k r)/\Delta k r$  and integrating term by term,

$$F(\Delta k, T) = \sum_0^\infty (-)^n \frac{(\Delta k)^{2n} r_F^{2n}}{(2n+1)!}, \quad (48)$$

$$r_F^{2n} = \int r^{2n} f(r, T) 4\pi r^2 dr; \quad r_F^0 = F(T).$$

Writing  $F(\Delta k, T)$  in the form,

$$F(\Delta k, T) = F(T) + \sum_1^\infty (-)^n \frac{(\Delta k)^{2n} r_F^{2n}}{(2n+1)!},$$

<sup>12</sup> The  $F(\Delta k, T)$  integral should not be confused with the liquid structure factor  $F_L^2(\Delta k, T)$  which we always write as a square with the subscript  $L$ .

the structure factor (45) becomes, with (22) and (23),

$$F_L^2(\Delta k, T) = \left[ 1 - F(T) + \sum_{n=1}^\infty (-)^{n+1} \frac{(\Delta k)^{2n} r_F^{2n}}{(2n+1)!} \right]^{-1}$$

$$= [\langle \Delta N^2 \rangle_w / N] \left[ 1 + \langle \Delta N^2 \rangle_w / N \right. \\ \left. \times \sum_1^\infty (-)^{n+1} \frac{(\Delta k)^{2n} r_F^{2n}}{(2n+1)!} \right]^{-1}. \quad (49)$$

Again, denoting by  $r_G^{2n}$  the  $2n$ -th moment of the  $g(r, T)$  function, one obtains, with (43) and (45), another expression for the structure factor,

$$F_L^2(\Delta k, T) = 1 + 4\pi \int \frac{\sin(\Delta k r)}{\Delta k r} g(r, T) r^2 dr$$

$$= 1 + G(T) + \sum_1^\infty (-)^n (\Delta k)^{2n} r_G^{2n} / (2n+1)!$$

$$= [\langle \Delta N^2 \rangle_w / N] + \sum_1^\infty (-)^n (\Delta k)^{2n} r_G^{2n} / (2n+1)! \quad (50)$$

where use has been made of Eq. (23) and where

$$r_G^0 = G(T); \quad r_G^{2n} = \int r^{2n} g(r, T) dv. \quad n \geq 1. \quad (50a)$$

The structure factor formulas (49) and (50) are, of course, rigorous within the formalism of the liquid model. However, the model does not determine  $f$  and  $g$ , but operates only with these quantities. It is, however, of interest to discuss these structure factors in terms of what is known of the  $f$ - and  $g$ -functions. Assume first that  $\Delta k$  is quite small or that the series in the denominator of (49) or (50) may be neglected in comparison with  $\langle \Delta N^2 \rangle_w / N$ . Then one sees that the very small angle coherent scattering structure factor will vary with the liquid temperature so as to increase with it. This point was discussed in detail in an earlier paper.<sup>6</sup>

Consider the liquid at some low temperature  $T < T_i$ ,  $T_i$  being the characteristic temperature defined above, Eq. (27). And assume further that the first term in the infinite series appearing in (49) is large enough to be included in the structure factor, for small  $\Delta k$  values. At low temperatures, we have seen that the space integral of the  $f$ -function is large and negative; see Fig. 1 for the case of water and liquid He, for instance. This makes it likely that  $r_F^2$  is also negative, so that for small but finite  $\Delta k$  values the structure factor will tend to increase from its minimum value at the limit  $\Delta k \rightarrow 0$ . Or, using (50), inasmuch as at low temperatures  $G(T)$  is again negative of the order of  $(-1)$ , one might

expect  $r_G^2$  to be also negative on account of its very short range at these temperatures. This again would tend to indicate, as in Eq. (49), an increase of the structure factor with increasing  $\Delta k$ -values, for small  $\Delta k$ .

At high temperatures,  $T > T_i$ , approaching the critical region, both  $F$  and  $G$  are positive. One then finds at once that for small  $\Delta k$  values the structure factor decreases from its limiting value for vanishing  $\Delta k$ , that is from  $\langle \Delta N^2 \rangle_w / N$  or  $(NkT\chi_T/V)$ . At  $T > T_i$  and for  $\Delta k$  values where only the first term in the series appearing in (49) or (50) may be considered to be significant, these results are seen to be rigorous. For small  $\Delta k$  values the theory gives a good qualitative account of the observed structure factors in liquids,<sup>13</sup> particularly at higher temperatures.

It is of course visible in (37) or (43) that in the limit of  $\Delta k$  becoming large,

$$\lim_{\Delta k \rightarrow \text{large}} F_L^2(\Delta k, T) = 1.$$

The difficulty associated with this limit has been pointed out previously<sup>6</sup> and will not be discussed here.

In the critical region, which has been discussed in some detail,<sup>6</sup> in particular for small angle scattering, we see at once from (49), remembering that the space integral  $F(T)$  tends toward unity as  $T \rightarrow T_c$ , that

$$\lim_{T \rightarrow T_c} F_L^2(\Delta k, T)$$

$$= \left[ \sum_{n=1}^{\infty} (-)^{n+1} (\Delta k)^{2n} r^{2n} / (2n+1)! \right]^{-1} \quad (51)$$

For small  $\Delta k$  values the preceding structure reduces to the one given previously.<sup>6</sup> The singular character of this formula in the limit of  $\Delta k \rightarrow 0$  does not seem to create any particularly great difficulties, on account of the necessarily finite solid angles at which the observations are made. However, this structure factor may become quite large for small  $\Delta k$  values, a result which agrees qualitatively with the experimental data available in a very few cases, such as argon, nitrogen,<sup>13</sup> and ether.<sup>14</sup>

We may add here that the oscillatory character of  $F(\Delta k, T)$  or  $G(\Delta k, T)$  make it evident that the liquid structure factors should exhibit the same type of behavior. Since the  $f$ - and  $g$ -functions are unknown, we close this discussion of the structure factors based on the rather meagre information available on these functions and turn rather to the problem of their determination through the experimental investigation of the coherent scattering properties of liquids for x-rays and slow neutrons.

<sup>13</sup> See the review article, quoted in reference 5 and the exhaustive work on argon, both liquid and vapor, by A. Eisenstein and N. S. Gingrich, Phys. Rev. **58**, 307 (1940), and **62**, 261 (1942). See also the recent work on nitrogen by R. L. Wild, J. Chem. Phys. **18**, 1627 (1950).

<sup>14</sup> F. H. W. Noll, Phys. Rev. **42**, 337 (1932).

#### IV. THE DETERMINATION OF THE DIRECT ( $f$ ) AND INDIRECT ( $g$ ) INTERACTION FUNCTIONS

The experimental data on the coherent scattering structure factor allow one to obtain the indirect interaction function  $f(r, T)$  in addition to the correlation density  $g(r, T)$  which alone was, so far, the ultimate goal of most experimental work on the coherent scattering of x-rays by liquids. The molecular distribution function

$$\begin{aligned} dn(r)/dv &= (N/V)(1+Q(r, T)) = (N/V)P(r, T) \\ &= (N/V) + g(r, T), \quad (3) \end{aligned}$$

is of course one of the important quantities characterizing a liquid, and the preceding definition may be looked upon as being quite general and independent to a large extent of any liquid model. It is thus justified to attempt to derive, from the experimentally determined coherent structure factor, the distribution function (3). One finds at once, using Eq. (38),

$$\int_0^{\infty} \sin(\Delta k, r) g(r, T) r dr = [F_L^2(\Delta k, T) - 1] (\Delta k / 4\pi), \quad (52)$$

and, by Fourier's theorem,

$$\begin{aligned} g(r, T) &= (1/2\pi^2 r) \int_0^{\infty} [F_L^2(\Delta k, T) - 1] \\ &\quad \times (\Delta k) \sin(\Delta k r) d(\Delta k), \quad (53) \end{aligned}$$

a relation first obtained by Zernike and Prins.<sup>4</sup> By Eq. (46) and for slow neutrons in liquids with the cross-section ratio  $\tau$  or  $(\sigma_c/\sigma_{\infty})$ , assumed to be known, one has to divide the right-hand side by  $\tau$ . A normalization relation<sup>15</sup> resulting from the definition of the distribution function may be of interest here. Since the probability density, Eq. (1)

$$P(r, T) = [1 + (V/N)g(r, T)]V^{-1},$$

has to vanish at very small separations,  $g(r, T)$  has to tend toward  $(-N/V)$  and (53) yields

$$\begin{aligned} \lim_{r \rightarrow 0} g(r, T) &= -\frac{N}{V} \\ &= \frac{1}{2\pi^2} \int_0^{\infty} (\Delta k)^2 [F_L^2(\Delta k, T) - 1] d(\Delta k). \quad (54) \end{aligned}$$

Again, for slow neutrons, the right-hand side is to be divided by  $\tau$  if the latter is different from unity.

The knowledge of the correlation density  $g(r, T)$  enables one to determine the  $f$ -function according to the central theorem of the liquid model expressed by the integral equation (8). While an analytical discussion of this equation would be difficult because of the fact that the  $g$ -function resulting from the measured structure factors, according to Eq. (53), becomes available

<sup>15</sup> See the last work quoted in reference 5.

only in tabular form, nevertheless numerical methods applied to Eq. (8) should lead to the determination of the function  $f(r, T)$ . This procedure may, however, be avoided. Indeed, Eq. (45) yields

$$1 - F(\Delta k, T) = 1 - 4\pi \int_0^\infty \frac{\sin(\Delta kr)}{(\Delta kr)} f(r, T) r^2 dr$$

$$= F_L^{-2}(\Delta k, T), \quad (55)$$

or

$$\int_0^\infty \sin(\Delta kr) f(r, T) r dr = [1 - F_L^{-2}(\Delta k, T)] (\Delta k / 4\pi),$$

and, using again Fourier's theorem,

$$f(r, T) = (1/2\pi^2 r) \int_0^\infty [1 - F_L^{-2}(\Delta k, T)] \times (\Delta k) \sin(\Delta kr) d(\Delta k). \quad (56)$$

In the case of slow neutrons and with  $\tau \neq 1$ , one finds

$$f(r, T) = \frac{1}{2\pi^2 r} \int_0^\infty \frac{F_L^{-2} - 1}{F_L^{-2} - 1 + \tau} (\Delta k) \sin(\Delta kr) d(\Delta k). \quad (57)$$

Hence the numerical analysis which has to be applied to the experimental data in order to derive from them  $g(r, T)$ , leads equally well to the determination of  $f(r, T)$ . One has thus the following result: the coherent scattering structure factor of a liquid completely determines the molecular type of interaction functions  $g(r, T)$  and  $f(r, T)$  which are the basic elements of the liquid model. The theory can now be directly checked by a substitution of these functions into the integral equation (8).

Another method can, however, be followed here leading directly to the value  $\langle \Delta N^2 \rangle_{av} / N$  at the temperature or temperatures at which  $g(r, T)$  and  $f(r, T)$  have been determined. The mean square fluctuation  $\langle \Delta N^2 \rangle_{av} / N$  or  $(nkT\chi_T)$  may or may not be known, depending on the knowledge of the compressibility  $\chi_T$ . In general the latter quantity is unknown. A rather good check on the  $f$ - and  $g$ -function may be obtained by evaluating their space integrals,  $F(T)$  and  $G(T)$ , respectively. Then,

$$1 + G(T) = [1 - F(T)]^{-1} = (nkT\chi_T) \quad (23)$$

the first equation is fully equivalent to the integral equation. While the knowledge of  $G(T)$  and  $F(T)$  leads to  $\langle \Delta N^2 \rangle_{av} / N$  or the compressibility  $\chi_T$ . It seems that the preceding method of obtaining the compressibility is of interest insofar as it should yield values whose precision is closely connected with the one reached in obtaining  $G(T)$  or  $F(T)$ . This method does not involve any particular uncertainties such as the one associated with obtaining the extrapolated structure factor in the forward direction from the small angle coherent scattering structure factor.<sup>16</sup> Also, the first equality in (23),

<sup>16</sup> See J. Yvon, J. phys. et radium 7, 201 (1946), and the recent work of Wild quoted in reference 14.

if verified with the  $g$ - and  $f$ -functions may indicate that the mean square fluctuation so obtained could yield a fair value of the compressibility.

The experimental data on the coherent structure factor of liquids may be further exploited since they give rise to a more complete determination of the direct and indirect interaction functions of the model. Equation (49) gives, indeed

$$-F(T) + \sum_1^\infty (-)^{n+1} \frac{(\Delta k)^{2n} r_F^{2n}}{(2n+1)!} = F_L^{-2}(\Delta k, T) - 1. \quad (58)$$

Since  $F(T)$  is the zeroth moment of the  $f$ -function, Eq. (48), the left-hand side contains all the even moments of this function. Now, in the limit of very small  $\Delta k$  values the moments  $r_F^{2n}$  ( $n \geq 1$ ) do not contribute at all. As the value of  $\Delta k$  increases the higher order moments become operative. Suppose now, that one chooses a series of  $\Delta k$  values, which are rather moderate so that all terms beyond the  $i$ 'th in the infinite series may be neglected. Then with  $(i+1)$  different  $\Delta k$  values and the associated structure factor values, one may set up a system of  $(i+1)$  linear equations in the unknowns  $F(T), r_F^2, r_F^4, \dots, r_F^{2i}$ . Hence, these moments of the  $f$ -function may be obtained with an accuracy depending on the choice of the  $\Delta k$  values beside that of the  $F_L^{-2}$ -values. But the larger  $i$  is, the better is the accuracy of the moments. Hence both  $\langle \Delta N^2 \rangle_{av} / N$  or  $(nkT\chi_T)$  and the moments of the  $f$ -function are obtained directly from the structure factor, without taking its Fourier transform which is a cumbersome procedure. Clearly if the  $f$ -function itself has been obtained with Eq. (57), its moments may be evaluated and compared with the ones derived with Eq. (58). This affords a further check on the degree of validity of keeping only a finite number of terms in the moment series in Eq. (58). Similarly, Eq. (50) yields, with a similar treatment, the even moments of the  $g$ -function.

It is now necessary to compare the moments of the  $f$ - and  $g$ -functions. We have multiplying both sides of Eq. (8) by  $r^2$  and integrating over the whole space,

$$r_G^2 = r_F^2 \frac{1 + r_G^0}{1 - r_F^0} = r_F^2 \frac{1 + G}{1 - F} = r_F^2 (nkT\chi_T)^2, \quad (59)$$

where use has been made of the definitions (48) and (23). One then finds in a similar way the following general relation between the even moments of these functions,

$$r_G^{2n} - r_F^{2n} = \sum_{2\lambda=0}^n \sum_{\mu=0}^{n-2\lambda} \frac{2^{2\lambda}}{2\lambda+1} \binom{n}{2\lambda} \binom{n-2\lambda}{\mu} \times r_G^{2n-2\lambda-2\mu} r_F^{2\lambda+2\mu}, \quad (60)$$

$$r_G^0 = G; \quad r_F^0 = F; \quad \binom{\alpha}{\beta} = \frac{\alpha!}{(\alpha-\beta)! \beta!}$$



With the preceding relation one obtains for the fourth and sixth moments, denoting by  $\nu(T)$  the quantity  $(nkT\chi_T)$ ,

$$\begin{aligned} r_G^4 &= \nu^2[r_F^4 + (10/3)(r_F^2)^2\nu]; \\ r_F^4 &= \nu^{-2}[r_G^4 - (10/3\nu)(r_G^2)^2]; \\ r_G^6 &= \nu^2[r_F^6 + 14\nu r_F^4 r_F^2 + (70/3)(r_F^2)^3\nu^2]; \\ r_F^6 &= \nu^{-2}[r_G^6 - (14/\nu)r_G^4 r_G^2 + (70/3\nu^2)(r_G^2)^3]. \end{aligned}$$

The relations between the higher order moments increase in complexity, but can be obtained without any difficulty. The moments  $r_F^{2n}$  and  $r_G^{2n}$  ( $2n=0, 2, 4, \dots$ ) obtained directly from the structure factors have to satisfy the preceding relations. A direct check on the liquid model is thus obtained again.

#### V. REMARKS ON THE SCATTERING OF SLOW NEUTRONS BY LIQUIDS

A rather important and difficult problem arises now in connection with slow neutron coherent scattering, namely the problem of their incoherent scattering. The incoherently scattered neutrons are, of course, observed simultaneously with those scattered coherently. While in the x-ray case the incoherently scattered radiation intensity can be evaluated and the observed scattered radiation corrected for it,<sup>5</sup> in the case of slow neutron scattering the incoherent process associated with the exchange of both energy and momentum between the neutrons and the liquid as a whole appears to be considerably more complicated than in x-ray scattering. In solids the slow neutron incoherent scattering may be described as a process of energy and momentum exchange described with the help of a model of  $3N$  harmonic oscillators, for a solid formed of  $N$  atoms for instance. The corresponding problem in liquids has not even been set up because of a complete lack of a satisfactory molecular liquid model.

There appears to be a possibility of obtaining some information on the incoherent scattering of slow neutrons by liquids. One may indeed evaluate the total coherent scattering cross section, within the framework of the present liquid model, by the use of Eq. (45). The coherent scattering cross section per atom, in a monatomic liquid, and per unit solid angle is

$$\sigma_{Lc}(\Delta k, T) = \sigma_{\infty} F_L^2(\Delta k, T) = \sigma_{\infty} [1 + G(\Delta k, T)], \quad (61)$$

with the cross-section ratio  $\tau$  supposed to be unity. The total coherent cross section becomes

$$\begin{aligned} \sigma_{Lc}(k, T) &= 2\pi \int_0^{\pi/2} \sigma_L(\Delta k, T) \sin 2\theta d(2\theta) \\ &= 4\pi \sigma_{\infty} \left\{ [(\Delta N^2)_{Av}/N] \right. \\ &\quad \left. + \sum_1^{\infty} (-)^n \frac{(2k)^{2n} r_G^{2n}}{(n+1)(2n+1)!} \right\}, \quad (62) \end{aligned}$$

$\sigma_{\infty}$  being independent of the scattering angle. In a molecular liquid the situation is more complicated since the angular integration involves also the coherent cross sections of the molecule per unit solid angle depending on  $\Delta k$  because of intramolecular and elementary intermolecular interference effects.<sup>17</sup>

The preceding total coherent cross-section formula is of interest insofar as it may yield the moments  $r_G^{2n}$ . Indeed, at small neutron energies where the total incoherent scattering cross section should be small in comparison with the total coherent one, or with x-rays, a series of transmission measurements as a function of the wavelength of the incident waves leads to a system of linear equations in the moments  $r_G^{2n}$ .

The moments  $r_G^{2n}$ , and also  $(\Delta N^2)_{Av}/N$ , may be evaluated from the structure factor according to the procedure described above. In order to minimize the intervention of the incoherent scattering, which is unknown, it would be necessary to derive them from those structure factor values which correspond to peak values or from regions in the vicinity of peaks. It is indeed reasonable to assume that the intensity of the incoherently scattered neutrons near the coherent peaks, and particularly near the main peak, would be relatively smaller than in other regions. Then, with the moments so derived, Eq. (62) enables one to obtain a fair value of the total coherent cross section. Slow neutron transmission measurements at the same temperature yield  $(\sigma_{Lc} + \sigma_{Li})$ , the sum of the total coherent,  $\sigma_{Lc}$ , and total incoherent,  $\sigma_{Li}$ , cross sections per liquid atom.<sup>18</sup> It is hereby assumed that the pure absorption of the slow neutrons is completely absent or that the absorption cross section is quite small in comparison with the smaller of the two scattering cross sections  $\sigma_{Lc}$  and  $\sigma_{Li}$ . The difference between the scattering cross section resulting from the transmission measurements and the one computed by (62) is the total incoherent cross section per liquid atom. It should be noted that (62) cannot be used in the critical region, although it should be valid close to it.

One would expect that the incoherent cross section be smaller for heavier than for lighter liquids, in a way similar to the case of solids. Here, at neutron energies small in comparison with the Debye energy  $k\Theta$ ,  $\Theta$  being the characteristic temperature of the solid, a practically rigorous evaluation of the incoherent cross section per solid atom is possible.<sup>19</sup> In general, however, the evaluation of the solid incoherent cross sections appears to be extremely laborious. But since the total coherent cross section may be obtained rigorously, it is seen that this result combined with transmission

<sup>17</sup> That the elementary molecular cross sections multiplying the diffuse coherent structure factor term, unity in Eq. (61), and the normal interference term,  $G(\Delta k, T)$ , were different for x-rays already has been shown by P. Debye, J. Math. Phys. 4, 153 (1925).

<sup>18</sup> In a detailed investigation of  $\sigma_{Li}$  the spin and isotope incoherence should be separated from the direct momentum-energy exchange effect.

<sup>19</sup> See A. Akhiezer and I. Pomeranchuk, J. Exp. Theoret. Phys. 17, 770 (1947).

measurements might again yield the unknown solid incoherent cross section. The latter of course should become identical at higher neutron energies with the free atom scattering cross section, both in solids and liquids. Here the following rather interesting problem automatically suggests itself. This is a comparative study of the solid and liquid incoherent cross sections per atom, for the same element. Because of the temperature and structure difference existing between the two phases, one would expect that the incoherent cross sections be different. The incoherent cross section of the solid or liquid is indeed a measure of the probability for the slow neutron to exchange energy and momentum with the solid and liquid as a whole. There is therefore no reason, *a priori*, that these cross sections, or their detailed behavior with the neutron energy be similar. On the contrary, one might expect to obtain from the variations of the incoherent cross section in monatomic liquids, as a function of the neutron energy and liquid temperature, some pertinent elementary information which may prove useful for the understanding of the possible states of motion of liquids.

The total slow neutron coherent scattering cross section may also be obtained directly from the experimental data. If the data are uncorrected for incoherent scattering, one may obtain by a numerical or graphical integration the total scattering cross section. Slow neutron transmission measurements should then check these results.

In the only systematic experiments on the coherent scattering of slow neutrons on liquid sulfur, lead, and bismuth by Chamberlain,<sup>5</sup> the incoherent cross sections of these elements have been determined by identifying the observed differential cross section at the smallest value of the parameter  $\sin\theta/\lambda$  with the differential cross section per unit solid angle of the incoherent process. This appears to be justified in these cases because the limiting forward coherent scattering structure factor ( $nkT\chi_T$ ), which we have evaluated only approximately because of lack of data, leads for these liquids to a very small forward differential coherent cross section. Even though in liquid lead and bismuth the smallest ( $\sin\theta/\lambda$ ) values at which observations have been made are not so small, one finds that by taking into account approximately the first term in the infinite series in the denominator of the right-hand side of Eq. (49), using for  $|r_{p^2}|$  the value  $n^{-1}$ ,  $n$  being the approximate concentration, the omission of the coherent

scattering at small angles appears to be justified. The observed small angle scattering cross section may thus be ascribed to the incoherent process. Assuming further approximate angular independence of the incoherent scattering cross section per unit solid angle, a correction for this process may thus be performed. Difficulties may arise in liquids and under conditions where ( $nkT\chi_T$ ) is large, as it certainly is above the temperature  $T_i$ , defined by Eq. (27), and also at temperatures  $T$  not too small compared with  $T_i$ . It should be noted that if the incoherent scattering has been taken into account correctly, the new coherent structure factor should lead to correct moments  $r_{p^{2n}}$  and  $r_{\sigma^{2n}}$  independently of the choice of the parameter ( $\sin\theta/\lambda$ ), that is, structure factor values near the coherent minima should then yield the same moments as those near peaks.

A final remark may be of interest here. We have assumed throughout this work that the coherent and elastic free or bound atom cross sections were known. It is seen that in those liquids where x-ray structure factors are available, a measurement of the slow neutron coherent cross section per liquid atom, under the same temperature and pressure conditions as the x-ray measurements, could yield the free or bound atom cross sections averaged over the different isotopes. The same remark applies to molecular liquids, although here conditions become considerably more complicated and a careful evaluation of the molecular coherent scattering structure factor is indispensable.

In conclusion we may then say that the coherent scattering data in liquids determine both the correlation density function  $g(r, T)$  and the direct interaction function  $f(r, T)$  of the Ornstein-Zernike static liquid model. A direct use of the experimental coherent structure factors allows one to determine with a fair degree of accuracy the mean square fluctuation of the concentration and with it the liquid compressibility in the thermodynamic state under investigation. The difficult problem of disentangling the coherent from the incoherent scattering process in the case of slow neutrons has been shown to be soluble in terms of the total cross sections associated with these processes. Simultaneously, it is shown that the experimental investigations of the slow neutron incoherent scattering in liquids may yield information on the energy spectrum of liquids, whose knowledge might be helpful for the establishment of a dynamic liquid model.