

Spatial Distribution of Atoms in Liquid He⁴

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The x-ray scattering diagrams of liquid helium, obtained by one of the authors, have been analyzed in this paper using the Los Alamos "701" IBM Electronic Calculator. The liquid He⁴ atomic correlation and pair distribution functions have thus been obtained over a wide range of interatomic separations and at a number of liquid temperatures between 1.25 and 4.20°K.

The limitations in the experimental scattering structure factors give rise, among others, to two types of limitations in the correlation functions. One of these concerns their behavior at small atomic separations; this limitation could be compensated for without difficulties. The second limitation, of more elusive character, appears to be connected with the lack in these functions of any manifest tendency toward their asymptotic behavior at large atomic separations. The here derived correlation or pair distribution functions should, nevertheless, be good approximations to their correct values at medium and intermediate separations extending to about fifteen angstroms, whereby the relevant range extends to 10–15 Å. This could be verified using two types of integral checks on the correlation functions. In one of these, their space integrals, out to relevant distances, turned out to be quite close to their expected values determined only by the macroscopic properties of the liquid. In the second series of

integral checks, they reproduced closely the original experimental structure factors. This verified the internal consistency of the calculations and indicated that the results should be correct at the relevant interatomic separations.

At all the liquid temperatures here investigated, in any sphere of given radius, around an origin atom, or in any spherical shell of given thickness, the computed number of atoms was always less than what one would compute neglecting the interatomic correlations.

An application, of major physical significance, of the correlation or pair distribution functions obtained in this work was made by deriving the approximate mean potential energies per liquid He⁴ atom at the various temperatures. The mean potential energy, as a function of the liquid temperature, has a cusp at the lambda point. Its temperature derivative, which is the configurational heat capacity, is thus discontinuous at the transition point with an inverted lambda type of discontinuity. The knowledge of this qualitative behavior of the configurational heat capacity was sufficient to prove, on quite general grounds, that the lambda transition of liquid He⁴ is of kinetic energy origin, i.e., it is connected with the momentum space behavior of the liquid atoms.

I. INTRODUCTION

AN analysis of the atomic distribution in liquid He⁴ has been first performed by one of us¹ using x-ray scattering data obtained recently.^{1,2} The x-ray scattering data communicated to Los Alamos have there been analyzed using the "701" IBM Electronic Calculator. Some of the results obtained in these machine calculations have already proved to be of great value in the interpretation³ of the Los Alamos slow-neutron total scattering cross-section measurements⁴ in liquid He⁴. While the machine calculations have fully confirmed the results derived by hand calculations,¹ they originated in that the necessarily slow hand calculations could not really fully exploit the available x-ray scattering data. These hand calculations succeeded in analyzing the spatial distribution of the helium atoms, around one chosen to be at the origin of the coordinate system, up to separations r of about 6 Å. This distance is only some 1.5 times the mean separation of the atoms resulting from the mean liquid concentration. Clearly, for purposes of deriving the neighborhood picture within the liquid, that is the number of first, second, and even third, neighbors of a given atom, the

previous analysis¹ was satisfactory. However, as recognized at Los Alamos, the restriction on the linear extension r of the region explored, resulting inevitably from the time-consuming hand calculations, could not lead to an entirely satisfactory picture of the interatomic correlations in liquid helium whose analytical description defines the liquid correlation function or correlation concentration. Indeed, the investigation of the space integral of the correlation function of restricted range showed its failure to satisfy the all-important statistical thermodynamic test requiring it to yield a quantity directly connected with the mean square fluctuation of the number of atoms, per atom, under isothermal conditions.⁵ It was then decided to reanalyze the x-ray scattering data with the Los Alamos "701" IBM Electronic Calculator. In so doing, however, it was fully realized that the results to be derived would be affected, inevitably, by limitations arising from various causes.

One of these was experimental and was associated with the restricted response of the measurements to temperature variations of the liquid. An attempt to compensate for this lack of sensitivity of the data, at small scattering angles, was made using a method of extrapolation of the scattering diagrams toward small angles, where the liquid temperature has a critical effect on the scattering. The method of extrapolation is based on the rigorous theory of small angle radiation scat-

¹ J. Reekie and T. S. Hutchison, *Phys. Rev.* **92**, 827 (1953); C. F. A. Beaumont and J. Reekie, *Proc. Roy. Soc. (London)* **A228**, 363 (1955).

² Reekie, Hutchison, and Beaumont, *Proc. Phys. Soc. London* **A66**, 409 (1953).

³ L. Goldstein and H. S. Sommers, Jr. (to be published).

⁴ Sommers, Dash, and Goldstein, *Phys. Rev.* **97**, 855 (1955).

⁵ L. S. Ornstein and F. Zernike, *Proc. Roy. Soc. (Amsterdam)* **17**, 793 (1914).

tering.⁶ The liquid correlation functions could thus be investigated here over a wide temperature interval, extending from 1.25 to 4.20°K. However, the correlation functions here derived are found to be better approximations at the low and the high temperatures, than at intermediate ones, such that

$$2.50 - 2.75 \leq T \leq 3.0 - 3.25^\circ\text{K}.$$

While a method of analysis exists for a fairly well approximated evaluation of the number of first-, second- and higher-order neighbors of the atom at the origin of the coordinate system within the liquid, this method is far from being simple in its applications at medium and larger separations. It has been used by one of us¹ to derive both the low- and high-temperature neighborhood picture in liquid helium. In the present work, we limited ourselves to a rigorous evaluation of the number of neighbors of the origin atom filling spheres of given radii, which in turn determine the number of atoms in spherical shells of any thickness. This method seems to be the only practical method of deriving a fair picture of the atomic distribution beyond the shells of neighbors of the first few orders.

The correlation functions will be seen to satisfy with good approximation their test relation based on their space integral, with the latter extended to the range of r at which they were evaluated, or r equal to 15–20 Å. Nevertheless, the experimental x-ray scattering data failed to yield the correct limit of these functions at vanishing separations⁶ $r \rightarrow 0$. While this appears to be a serious failure of local character, it could be obviated without too much difficulty. Another shortcoming of these functions appeared in that they did not exhibit any definite tendency to approximate their expected asymptotic large distance behavior.^{6,7}

A major application, along a line conjectured previously,³ was finally made of the correlation functions obtained in the present work, through the two-atom or pair distribution functions which they define. This consisted in a rigorous proof of the kinetic energy origin of the lambda transition in liquid helium. The proof could be based on quite general grounds and involved mainly the qualitative temperature behavior of the pair distribution function. This result, while justifying the current theoretical trends attempting to explain the lambda transition, should help to provide a solid guidepost for the establishment of an improved theory of liquid helium.

II. INTERATOMIC CORRELATION FUNCTION IN LIQUID He⁴

The coherent scattering cross section for radiation of wavelength λ , per liquid atom, and per unit solid angle whose axis is at an angle 2θ to the direction of incidence, can be shown to yield, with

$$\Delta k = |\Delta \mathbf{k}| = 2|\mathbf{k}| \sin\theta = 4\pi(\sin\theta)/\lambda, \quad (1)$$

⁶ L. Goldstein, Phys. Rev. 84, 466 (1951).

⁷ F. Zernike, Proc. Roy. Soc. (Amsterdam) 19, 1520 (1916).

the momentum change, in units of $\hbar/2\pi$, of the incident radiation on scattering in the direction 2θ , \mathbf{k} being its propagation vector, $F_L^2(\Delta k, T)$ standing for the experimentally derived scattering intensity structure factor per atom, and by the Fourier integral theorem, the correlation function⁸

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

In the limit of vanishing separations r , one obtains

$$\lim_{r \rightarrow 0} g(r, T) = (1/2\pi^2) \int_0^\infty [F_L^2(\Delta k, T) - 1] (\Delta k)^2 d(\Delta k) = -n(T), \quad (3)$$

because in this limit the two-atom distribution function $n(r, T)$ or $dN(r, T)/dv(r)$, the latter including the quantum-mechanical exchange effects,

$$dN(r, T) = n(r, T) dv(r) = [n(T) + g(r, T)] dv(r), \quad (4)$$

has to vanish; no two atoms being able to approach each other too closely, with finite probability, under equilibrium conditions of the liquid. Equation (3) constitutes a rigorous normalization or check relation for the experimental structure factors F_L^2 . It will, however, be seen below that this relation is not critical, in the sense that if it is not strictly satisfied, the empirically derived structure factors may still be fair approximations to the actual ones.

In the present work the portions of the structure factor functions $F_L^2(\Delta k, T)$ above $\Delta k \sim 0.9 \text{ \AA}^{-1}$ belonged to either the low- or high-temperature liquid. They have been obtained experimentally² from 0.9 to about 6 \AA^{-1} and they are given in Fig. 1. The regions $\Delta k < 0.9 \text{ \AA}^{-1}$ will be fully discussed below. The preceding Δk range is equivalent, for the Cu K_α radiation used in the scattering experiments,² to a scattering angular range $12^\circ \leq 2\theta \leq 100^\circ$. Limitations inherent in the very low scattering cross section of liquid helium and the experimental technique have prevented the effective exploration of a larger Δk or θ interval. It may, however, be expected that techniques with increased detection sensitivities should help to widen the explorable Δk range and to increase the over-all precision of the scattering structure factors. The estimated average relative error will be seen on Fig. 1 to be about 5 to 7 percent.

The first exploratory x-ray scattering experiments⁹ have already demonstrated the absence of any major change in the scattering diagram of liquid He⁴ over a

⁸ F. Zernike and J. A. Prins, Z. Physik 41, 148 (1927).

⁹ W. H. Keesom and K. W. Taconis, Physica 5, 270 (1938); J. Reekie, Proc. Cambridge Phil. Soc. 36, 236 (1941); 43, 262 (1947).

temperature range extending from well below to somewhat above the lambda point. The more recent data^{1,2} fully confirm the above results and tend to indicate that in the explored Δk -range the scattering structure factor does not change, within experimental errors, up to temperatures approaching the normal boiling point. The total liquid density change in the temperature range 1.25–4.2°K, with the apparent density cusp at the lambda point, is relatively small. The interference factor in the integrand appearing in the scattering cross section⁶ will tend to minimize the expected changes in the correlation function $g(r, T)$ over this temperature interval. This then is probably the main cause of the absence of any easily detectable variation in the structure factor F_L^2 over a relatively wide temperature interval and for Δk -values larger than 0.9 or 1.0 Å⁻¹.

The structure factors should exhibit, however, considerable temperature variations at small momentum changes or small scattering angles⁶ or precisely in a Δk range which remained unexplored in the experiments.² At $\Delta k \leq 0.5$ Å⁻¹ or so, it should be possible to observe the relatively large variations of the structure factor as shown in the rather difficult experiments of Tweet¹⁰ on the very small angle x-ray scattering as well as in the small angle slow neutron scattering work of London and Egelstaff¹¹ in liquid He⁴. More recent x-ray scattering work, using counter detection techniques, by Gordon *et al.*¹² where the explored scattering angular range extended from 1.5 to 90°, again confirms at small angles the expected large variations of the structure factor with liquid temperature. The small angle scattering structure factors are determined essentially by the macroscopic concentration fluctuations of the liquid,

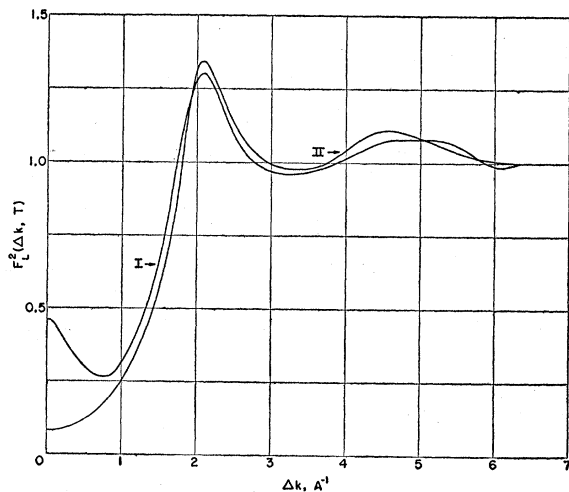


FIG. 1. The experimental structure factors $F_L^2(\Delta k, T)$ vs Δk , at two liquid temperatures I (4.20°K); II (2.06°K). For the extrapolated portions of these graphs at $\Delta k < 0.9$ Å⁻¹ see the text.

¹⁰ A. G. Tweet, Phys. Rev. **93**, 15 (1954).

¹¹ H. London and P. A. Egelstaff, Proceedings of the Third International Conference on Low Temperature Physics and Chemistry (Rice Institute, Houston, 1953).

¹² Gordon, Shaw, and Daunt, Phys. Rev. **96**, 1444 (1954).

under isothermal conditions.⁶ The simple physical basis of the following rigorous result has been discussed previously¹³ and need not be considered here,

$$\lim_{\Delta k \text{ small}} F_L^2(\Delta k, T) = n(T)kT\chi_T - r_G^{(2)} \frac{(\Delta k)^2}{6}, \quad (5)$$

where

$$r_G^{(2)} = 4\pi \int r^4 g(r, T) dr, \quad (6)$$

is the second moment of the correlation function.

In the present analysis of the atomic distribution in liquid He⁴, the low-temperature structure factor, the one at 2.06°K, where $\Delta k \gtrsim 0.9$ –1.0 Å⁻¹, was taken to be the same, approximately, at all temperatures $T < 3^\circ$ K. The observed structure factor at the normal boiling point was taken to be the same, approximately, in the above mentioned Δk -range, at the temperatures $3 \leq T \leq 4.2^\circ$ K. In spite of the rather large experimental errors, the structure factor curves of Fig. 1 suggest that there should be a rather smooth change-over from the low- to the high-temperature structure factors at $\Delta k \gtrsim 0.9$ –1.0 Å⁻¹. It is thus expected, as a consequence of the above-mentioned approximate groupings of the structure factors, that the results obtained in the present analysis, with the low- and high-temperature structure factors, will not join smoothly. They will thus be affected with greater errors in the transition region 2.50 – $2.75 \leq T \leq 3$ – 3.25° K than at the other temperatures.

The structure factors at the different temperatures and at $0 \leq \Delta k \leq 0.9$ Å⁻¹ have been obtained by interpolation between their rigorous value at vanishing Δk , where they reduce to $n(T)kT\chi_T$, Eq. (5), and the measured value of $F_L^2(\Delta k, T)$ at the smallest Δk -value of about 0.9 Å⁻¹. The interpolation was facilitated by the somewhat rough knowledge of the second moments $r_G^{(2)}(T)$ of the correlation function $g(r, T)$. These moments became available through the analysis of the small angle x-ray¹⁰ and slow neutron¹¹ scattering experiments, to a rather limited degree of approximation. The parabolic behavior at small Δk , as shown by (5), tended to simplify considerably the interpolation procedure at these small Δk -values. It should be noted that in considering $F_L^2(\Delta k, T)$ as a function of $(\Delta k)^2$ rather than Δk , a change in independent variable evidently justified by the even character of F_L^2 in Δk , the structure factor has a small linear region in $(\Delta k)^2$. It becomes parabolic through the term in $(\Delta k)^4$ which follows the quadratic term in the expansion of $F_L^2(k, T)$.⁶ The interpolation procedure out to $\Delta k \sim 0.9$ Å⁻¹ entailed, inevitably, a good many uncertainties. These, however, are minimized in the Fourier integral (2) in this same range of small Δk values. We give in Fig. 2 a series of the interpolated approximate small Δk structure factors at various temperatures. The behavior of the small Δk

¹³ L. Goldstein, Phys. Rev. **83**, 289 (1951).

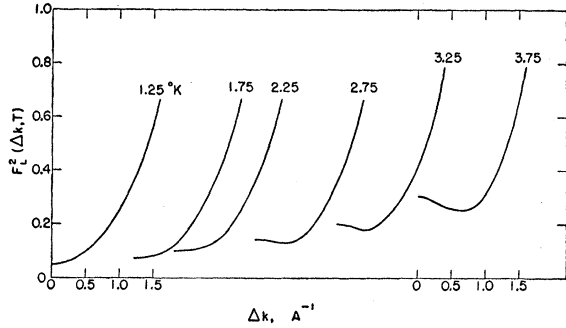


FIG. 2. The extrapolated small Δk structure factors at various liquid temperatures. The origin and the common abscissa scales are given only for the first and last curves. All structure factors start at vanishing Δk .

structure factors has been discussed previously in various connections.^{6,13,14}

It does not seem superfluous to restate here briefly some general properties of the correlation functions valid in all liquids. Physically the correlations cannot but vanish at large separations r , or, we have at both limits of r , with (3),

$$\lim_{r \rightarrow 0} g(r, T) = -n(T); \quad \lim_{r \rightarrow \infty} g(r, T) = 0. \quad (7)$$

At small separations, around the atom chosen to be at the origin of the coordinate system, there is a very large density defect as a result of the interatomic repulsion at such separations. Actually, at vanishing separations $g(r, T)$ reaches its minimum minimum. This largest density defect is then followed by a large density excess at increasing separations, with a damped oscillatory behavior at larger distances. It is easy to see that the zero order moment of the correlation function, which is the fluctuation integral $G(T)$,

$$\begin{aligned} r_G^{(0)}(T) &= \int g(r, T) dv(r) \\ &= G(T) \\ &= n(T)kT\chi_T - 1, \end{aligned} \quad (8)$$

is such that there is a single characteristic temperature¹⁵ T_0 , in any liquid, whereby, T_c being the critical temperature,

$$\begin{aligned} r_G^{(0)}(T \leq T_0) &= G(T \leq T_0) \leq 0; \\ r_G^{(0)}(T_0 \leq T \leq T_c) &= G(T_0 \leq T \leq T_c) \geq 0. \end{aligned} \quad (9)$$

Similarly, if T_n denotes that liquid temperature at which the n 'th moment, of the correlation function, $r_G^{(n)}$, n even, vanishes, one has

$$r_G^{(n)}(T \leq T_n) \leq 0; \quad r_G^{(n)}(T \geq T_n) \geq 0. \quad (10)$$

It can be shown that the characteristic temperatures

¹⁴ L. Goldstein, Phys. Rev. **85**, 35 (1952).

¹⁵ In reference 6 this was denoted by T_i .

T_n form the sequence

$$\cdots < T_{n+2} < T_n < T_{n-2} < \cdots < T_4 < T_2 < T_0 < T_c. \quad (11)$$

Indeed, a moment $r_G^{(n)}$ which is negative at some low temperature will increase faster with liquid temperature the higher is its order, because the negative contributions to the moment integrals decrease with decreasing density. The higher the order of the moment the faster the decrease,¹⁴ because the negative contributions are due predominantly to regions of $g(r, T)$ at small r or $r < z_1$, z_1 being the first zero of $g(r, T)$. It will be seen that the sequence (11) is finite, since, if n is large enough there is no liquid temperature at which the corresponding moment can become negative.

The small angle scattering structure factors of liquids can be at once understood on the basis of the preceding results which are rigorous. These structure factors are defined by their limiting $\Delta k \rightarrow 0$ value, that is $[1 + G(T)]$ or $n(T)kT\chi_T$ and by their slope at Δk small, or, by (5),

$$\lim_{\Delta k \text{ small}} \frac{dF_L^2(\Delta k, T)}{d(\Delta k)} = - (r_G^{(2)}/3)(\Delta k). \quad (12)$$

The mean square fluctuation in the number of atoms, per atom, $n(T)kT\chi_T$, is a monotonically increasing function of the temperature. Even in liquid helium where the compressibility might have a very slight discontinuity and where $n(T)$ has a cusp at the lambda point, the over-all behavior of $n(T)kT\chi_T$ in the liquid in equilibrium with its vapor is a monotonic increase. Hence the family of structure factor curves represented as a function of Δk , the temperature being a parameter, reaches the ordinate at vanishing Δk , with values such that

$$\begin{aligned} n(T_M)kT_M\chi_T(T_M) &\leq \lim_{\Delta k \rightarrow 0} F_L^2(\Delta k, T) \\ &\leq n(T_c')kT_c'\chi_T(T_c'), \end{aligned} \quad (13)$$

T_M being the ordinary melting point and T_c' a temperature close to the critical point. The temperature T_M is to be replaced by the absolute zero in liquid He⁴ and He³, according to all evidence available at the present time. In the latter limit, the structure factor vanishes identically with $\Delta k \rightarrow 0$.

According to the behavior of the first positive moments of the correlation function, Eqs. (9) and (10), at all temperatures $T \leq T_2$, $r_G^{(2)}$ is negative. Hence, at these temperatures the initial small Δk slope of the structure factors, Eq. (12), is positive. They are concave upward. At all temperatures $T_2 \leq T \leq T_c$, the small Δk slopes are negative, the structure factors start to decrease from their limiting values, the vertices of the oscillating parabolas (5). At small Δk -values, at these higher temperatures, the structure factors are convex upward.¹⁶ These results have the strength of a rigorous

¹⁶ The discussion of the small Δk structure factors in reference 14 was led with the characteristic temperature T_0 allowing only the use of the inequalities $T < T_0$ and $T > T_0$.

theorem and are valid in all liquids.¹⁴ The proof given above is based on monatomic liquids. It should, however, remain valid in molecular liquids also, provided one considers only that part of their structure factor which is determined by the intermolecular interference effects. The wide generality of the preceding results stems from the following facts: their derivation assumes only the existence of a correlation function which is used in a rigorous theory of radiation scattering phenomena by a collection of scattering atoms with the assumed spatial correlations.

The structure factor F_L^2 is an even function of Δk , while $g(r, T)$ is an even function of r . Since an extremely general argument based on the repulsion of two atoms at close distances yields the rigorous result (3), the latter may be used to obtain semi-quantitatively the very large Δk -behavior of the structure factor. Equation (3) requires that

$$\lim_{\Delta k \text{ large}} [F_L^2(\Delta k, T) - 1] \leq \varphi(T) / (\Delta k)^n; \quad n > 3. \quad (14)$$

Here $\varphi(T)$ is some function of the temperature only. The structure factor of liquids has to tend toward unity, at very large Δk , faster than $(\Delta k)^{-3}$.

We are now prepared to discuss the various details of the results obtained in the present analysis of the liquid He⁴ structure factors. As previously intimated,

the Fourier integrals (2) have been obtained as sums of two integrals, namely,

$$g(r, T) = g_1(r, T) + g_2(r, T) \\ = (1/2\pi^2 r) \left\{ \int_0^{\Delta k} [F_L^2(\Delta k, T) - 1] [\sin r(\Delta k)] \right. \\ \times (\Delta k) d(\Delta k) + \int_{\Delta k}^{\infty} [F_L^2(\Delta k, T) - 1] \\ \left. \times [\sin r(\Delta k)] (\Delta k) d(\Delta k) \right\}, \quad (15)$$

where Δk was 1.0 \AA^{-1} . The upper limit in the second integral $g_2(r, T)$ is only symbolic, inasmuch as the integrand vanishes at a finite Δk -value. The approximate experimental structure factors reach unity at a finite Δk ; the data used here suggested that, within experimental errors, F_L^2 was unity beyond about 6 \AA^{-1} .

We have to consider now the limiting $r \rightarrow 0$ value of $g(r, T)$ or $[-n(T)]$, by Eq. (3). The latter rigorous relation was not found to be satisfied by the experimental structure factors. This indicates, of course, the complete deficiency of the data as far as the important and rigorous relation (3) is concerned. The $g(r, T)$ functions had thus to be cut-off at small separations r . The following cut-off procedure has been used here:

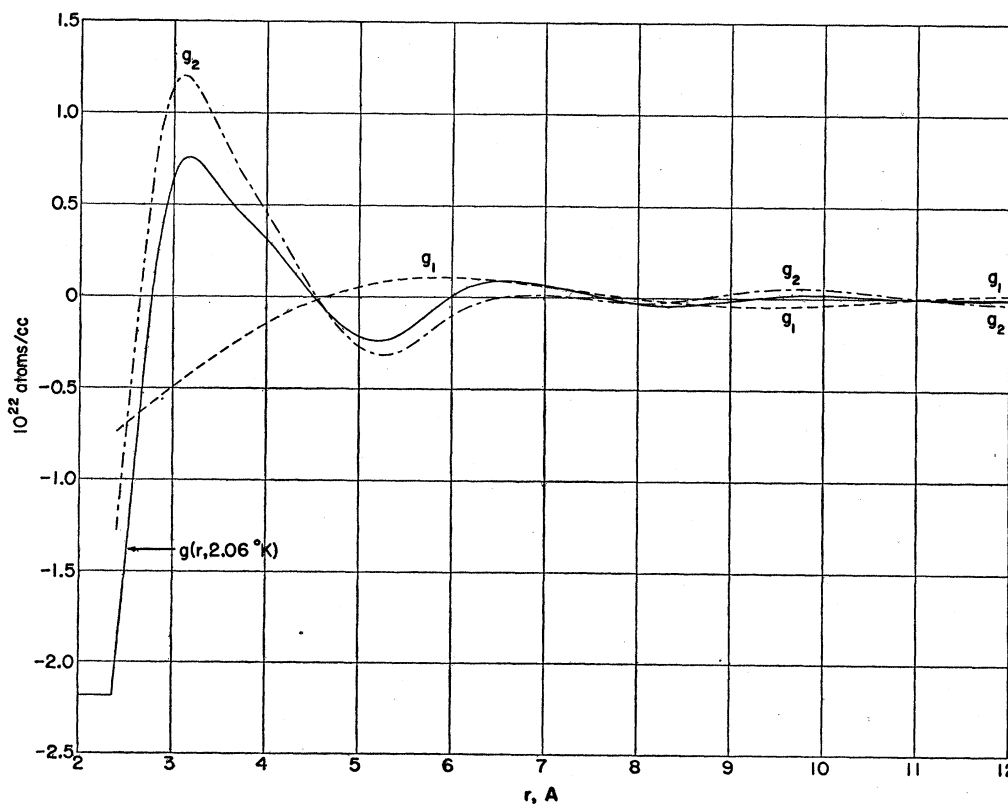


FIG. 3. Partial, $g_1(r)$, $g_2(r)$, and total correlation functions $g(r, T)$ as a function of the interatomic separation at 2.06°K .

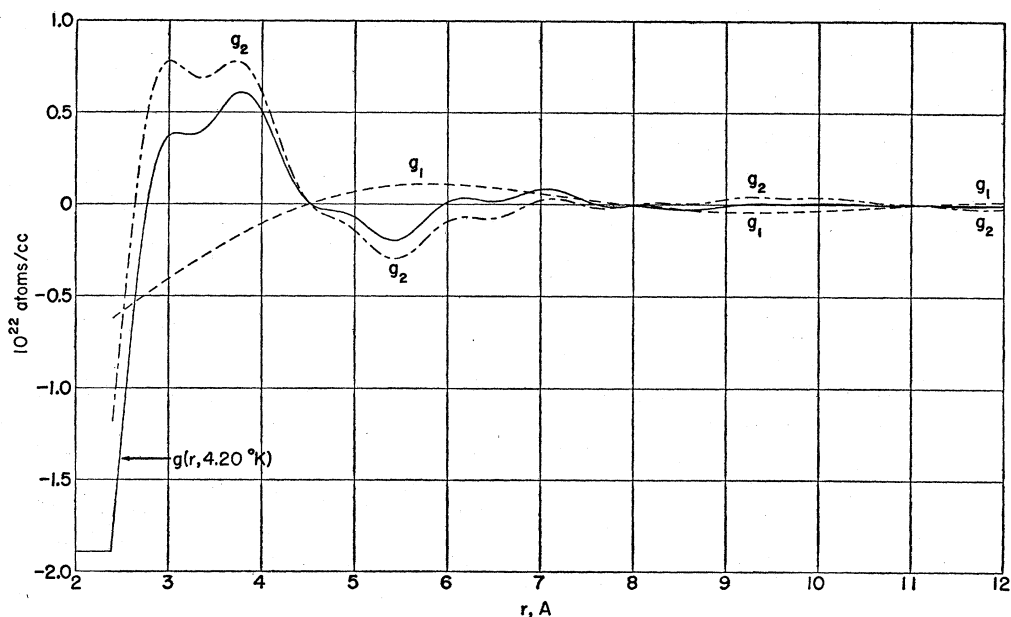


FIG. 4. Partial, $g_1(r)$, $g_2(r)$, and total correlation functions $g(r, T)$ as a function of the interatomic separation at 4.20°K.

the correlation functions had their first zero at about 2.8 Å. At $r < 2.8$ Å, they fell toward increasingly large negative values, as they should. When they reached the value of $[-n(T)]$ at some value a of r , they were taken to be equal to $[-n(T)]$ at all $r \leq a$. At $r \geq a$ they were of course determined by the Fourier integrals (15). This procedure appears to be reasonable in spite of the angular point introduced into $g(r, T)$ at a . Physically this cut-off procedure is equivalent to postulating that the minimum closest distance of approach of two atoms is $a(T)$; this is a function of T .

We should like to give now some numerical results on the correlation functions resulting from the integrals (15). These results are presented in graphical form through Figs. 3 and 4. These refer to the two liquid temperatures of 2.06 and 4.20°K and are thus representative of the low- and high-temperature correlation functions. At both temperatures, we give the functions $g_1(r, T)$, $g_2(r, T)$, and their algebraic sum or the correlation function itself, $g(r, T)$. These results show that the contributions to $g(r, T)$ of the function $g_1(r, T)$ are of considerable importance not only at larger separations, as one might have expected, but throughout the whole r -range investigated here. Figures 3 and 4 exhibit clearly the application of the cut-off procedure just discussed.

A superficial examination of the $g(r, T)$ functions might lead one to underestimate the importance of these functions beyond the third extremum. It will, however, be shown below that this procedure is quite unjustified, unless, of course, one is prepared to analyze only the very close neighborhood picture.

It is believed that the results based on the evaluations

of the component functions $g_1(r, T)$ and $g_2(r, T)$ are of interest for the whole field of the determination of atomic distributions in liquids. It is thus realized that the procedure of the extrapolation of the structure factors toward their vanishing Δk -value previously discussed acquires added importance in the light of the relative values of the functions $g_1(r, T)$ and $g_2(r, T)$. It is entirely outside the scope of the present work to review, even in the most cursory fashion, the rather considerable amount of experimental work accumulated on the analysis of atomic distributions in liquids, and this even from the sole point of view of the small momentum change structure factors. We cannot but emphasize here, on the basis of the results obtained by us over the whole temperature interval investigated, the considerable care which is necessary in dealing with the structure factors in the Δk -range $0 \leq \Delta k \leq 1.0 \text{ \AA}^{-1}$, or at values of $(\sin\theta)/\lambda$ in the range $0 \leq \Delta k/4\pi \leq 0.08 \text{ \AA}^{-1}$. Failure to include the structure factors over all or part of the preceding Δk -intervals in attempts to derive the correlation function cannot but yield results which, though, may have some resemblance to the correct function, might not have very much quantitative connection with it at medium and larger separations.

A glance at the representative correlation function graphs, Figs. 3 and 4, shows that there are characteristic differences between the low- and high-temperature functions. These differences originate with the g_2 functions. The oscillatory character of the correlation function is of course evident, with a slow damping of the amplitudes of the oscillations at large separations.

It is to be noted here that the evaluations of the Fourier integrals (15) were made with the help of the

experimental structure factors, Figs. 1 and 2, at every 0.025 Å⁻¹ interval in Δk . The $g(r, T)$ functions have been obtained at every 0.05 Å in r , out to r equal to 20 Å. The necessity of obtaining $g(r, T)$ at such close intervals was imposed by their future use which involved their integration. Since the Δk -intervals of integration were kept constant, it was of course realized that at increasing r -values, the integrand was approximated with a polygon of decreasing number of sides. Hence, at increasing r , the functions $g(r, T)$ tended to become less accurate. However, even at the largest separation of 20 Å, the number of integration intervals per half cycle of the sine function in the integrands of (15) was never less than six. Indeed, with the Δk -interval of 0.025 Å⁻¹, $r\Delta k$ is 0.5 radian at r equal to 20 Å, and, hence, per half-cycle of the sine function, there were 2π integration intervals.

It is entirely outside the scope of the present work to investigate methods of evaluating numerically Fourier integrals. Nevertheless, an independent evaluation of $g(r, T)$ was made at 2.06°K liquid He temperature using a method¹⁷ which did not have the limitations arising from the decreasing accuracy of integrations at large separations. In this method no approximations have been made at all in the integration of the sine function of the integrand of $g(r, T)$.

Let us, indeed, define the function $f(\Delta k, T)$ by

$$f(\Delta k, T) = [F_L^2(\Delta k, T) - 1]/(\Delta k), \quad (16)$$

and rewrite (15) as

$$g(r, T) = (1/2\pi^2 r) \int_0^\infty f(\Delta k, T) \sin(r\Delta k) d(\Delta k), \quad (17)$$

the interval of integration is finite and extends from zero to ΔK . Assume that this finite interval has been divided into equal segments ϵ . Then,

$$g(r, T) = (1/2\pi^2 r) \left[\int_0^\epsilon f(\Delta k, T) \sin(r\Delta k) d(\Delta k) + \int_\epsilon^{2\epsilon} f(\Delta k, T) \sin(r\Delta k) d(\Delta k) + \dots \right]. \quad (18)$$

The function $f(\Delta k, T)$, varying slowly in any small interval, may be replaced by $\bar{f}(\Delta k, T)$ its value in the middle of the small interval ϵ and we may thus write, with good approximation, integrating the sine function,

$$\begin{aligned} g(r, T) &\cong (1/2\pi^2 r^2) [-\bar{f}(0, \epsilon) \cos r\Delta k]_0^\epsilon \\ &\quad - \bar{f}(\epsilon, 2\epsilon) \cos r\Delta k |_{\epsilon^2} - \dots] \\ &= (1/2\pi^2 r^2) [\bar{f}(0, \epsilon) + [\bar{f}(\epsilon, 2\epsilon) - \bar{f}(0, \epsilon)] \cos r\epsilon \\ &\quad + [\bar{f}(2\epsilon, 3\epsilon) - \bar{f}(\epsilon, 2\epsilon)] \cos 2r\epsilon + \dots] \\ &= (1/2\pi^2 r^2) \left[f_1 + \sum_{n=1}^N (f_{n+1} - f_n) \cos(nr\epsilon) \right]. \quad (19) \end{aligned}$$

¹⁷ This was suggested by Mr. Bengt Carlsson who is in charge of the Numerical Analysis Group.

Here, the range of integration has been divided into N equal intervals, and

$$f_n = \bar{f}((n-1)\epsilon, n\epsilon),$$

denotes the value of the function $f(\Delta k, T)$ in the center of the n th interval.

Using the preceding method at 2.06°K, the results of the direct method of integration have been fully checked. An advantage of this last method lies in the possibility of extending the evaluation of $g(r, T)$ over much wider separations r without loss of accuracy, in contrast with the more primitive method of direct integration, whose accuracy decreases at $r > 15$ Å.

The correlation function at 2.06°K has been studied with the help of Eq. (19) to rather large r -values. The function was found to be oscillatory and relatively slowly damped. But apart from the very large r -behavior of $g(r, T)$, one might have expected to find some tendency of these functions toward an asymptotic type of behavior below 20 Å. This was not observed. It is true that the characteristic asymptotic expression of $g(r, T)$,⁶

$$\lim_{r \gg \rho} g(r, T) \cong (G(T)/4\pi\rho^2) \exp(-r/\rho)/r, \quad (20)$$

is derived⁶ from considerations which do not involve scattering theory. But the scattering structure factors $F_L^2(\Delta k, T)$ determine uniquely the correlation functions $g(r, T)$ over their whole range and, in particular, at very large r , where the asymptotic expression (20) should result from the straightforward analysis of the structure factors. The range $\rho(T)$ of $g(r, T)$ or its square is given⁶ by

$$[\rho(T)]^2 = r_G^{(2)}(T)/[6n(T)kT\chi_T], \quad (21)$$

where, on the right-hand side the absolute value is to be taken if $r_G^{(2)}(T)$ is negative at $T < T_2$. Numerically, $\rho(T)$ could have been expected to be moderate at all the liquid temperatures investigated here. Hence, the appearance of the asymptotic form (20) at the larger separations r studied by us seems to be possible. No attempt will be made here to supply an explanation for the absence, at large r , of any tendency of the $g(r, T)$ functions toward their asymptotic form (20). It is, however, clear that, as a result, the correlation functions here derived cannot be used safely in integrals over monotonically increasing functions of r . It should be noted that (20) and (21) lose their precise meaning at the temperature T_2 .

The problem of the convergence of the correlation functions may be considered also from the point of view of rather simple physical arguments. These functions give, by definition, the local excess or defect of the atomic concentrations from their mean value. Since the mean values $n(T)$ are not known to better than about a fraction of a percent, it would be somewhat illusory to use the correlation functions in regions of r where their extrema, positive or negative, reached values of, say, $\pm[n(T)/500]$, approximately. We give

TABLE I. Extrema of $g(r, T)$ and of the ratios $g(r, T)/n(T)$ at two liquid temperatures ($r > 10$ Å).

r Å	$g(r, 2.06^\circ\text{K})$ 10^{22} atoms/cc	$\frac{g(r, 2.06^\circ\text{K})}{n(2.06^\circ\text{K})}$ %	r Å	$g(r, 4.20^\circ\text{K})$ 10^{22} atoms/cc	$\frac{g(r, 4.2^\circ\text{K})}{n(4.2^\circ\text{K})}$ %
11.65	-0.00921	-0.420	10.10	0.00983	0.520
13.05	0.00841	0.383	10.70	-0.00210	-0.111
14.70	-0.00423	-0.193	11.10	0.00181	0.0959
15.75	0.00231	0.105	11.65	-0.00522	-0.276
17.05	-0.00156	-0.0711	12.25	0.00488	0.258
17.65	-0.00479	-0.0218	12.80	0.00105	0.0553
18.15	-0.00102	-0.0466	13.05	0.00169	0.0896
19.45	0.00213	0.0970	13.65	-0.00305	-0.161
			14.20	0.00108	0.0571

in Table I, the positions and values of the positive and negative extrema of $g(r, T)$, $r > 10$ Å, as well as the ratios g/n , at the two liquid temperatures of 2.06 and 4.20°K, with $n(2.06^\circ\text{K})$ and $n(4.20^\circ\text{K})$ equal, respectively, to 2.194 and 1.892×10^{22} atoms/cc. This Table I indicates that with the just-mentioned limitation of the physical significance of the values of $g(r, T)$, the latter would be well determined to separations $r \lesssim 10 - 15$ Å. One would thus expect that all those physical properties of the liquid which are evaluated as integrals with the correlation functions should be, in turn, determined by integrations extending to 10–15 Å. Any extension of these integrals beyond these separations should not modify sensibly their values obtained at the limits of 10–15 Å. It will be seen below that this is generally the case. It is to be remembered, however, that the preceding situation will be realized actually only if the integrands in question are sufficiently convergent. With fast monotonically increasing functions, as mentioned already, the preceding integration procedure with the $g(r, T)$ functions here derived cannot lead to the desired result.

In order to achieve a more rapid convergence of the $g(r, T)$ functions, a rather customary method could have been used, in principle. Namely, the direct method of evaluation of the integrals (15) could have been followed up to say 10–15 Å. Beyond these separations, one might start integrating by parts the sine function in the Fourier integrals. This yields integrals which fall as r^{-2} , r^{-3} , \dots , etc. However, this necessitates the numerical evaluation of the successive derivatives, with respect to Δk , of the structure factors $F_L^2(\Delta k, T)$, an operation fraught with considerable difficulties and uncertainties. This method did not appear to be usable here.

In concluding the study of the liquid helium correlation functions, we cannot but state that neither the expected very small r nor the possible very large r behavior of these functions have been verified. It is to be expected, however, that at the intermediate separations, $a \lesssim r \lesssim 15$ Å, the directly evaluated $g(r, T)$ functions should be good approximations to the presently unknown correct correlation functions of this liquid. That this is the case, essentially, will be shown

below by investigating some integral properties of these functions.

An interesting method has been worked out¹⁸ for the determination of the numbers of these first, second, \dots , neighbors with the help of the surface concentrations $4\pi r n(r, T)$, and it has been used by one of us¹ to separations $r \sim 6$ Å. This method, though somewhat laborious at even relatively small separations, becomes quite difficult to use at larger separations where the peaks of the distributions $n(r, T)$ or $4\pi r n(r, T)$ become more and more smeared and less pronounced.

We have here obtained the function

$$N(r, T) = \int_0^r 4\pi r'^2 n(r', T) dr', \quad (22)$$

which gives the number of atoms surrounding the origin atom in any sphere of radius r , complete isotropy being assumed throughout in the spatial distribution of the atoms. Clearly, the number of atoms in the spherical shell of thickness $(r' - r)$, is

$$N(r' - r, T) = N(r', T) - N(r, T). \quad (23)$$

If the function $N(r, T)$ is known for all relevant r -values, it becomes a relatively easy matter to locate the approximate positions of the successive spherical shells with their number of atoms in conjunction with the peaks in $g(r, T)$, $n(r, T)$, $4\pi r n(r, T)$, and $4\pi r^2 n(r, T)$. Such an analysis of the spatial distribution of atoms and molecules in liquids has been made use of by Hildebrand.¹⁹

As an illustration of the spatial distribution of atoms in liquid helium we give in Fig. 5, the functions $N(r, 2.06^\circ\text{K})$ and $N(r, 4.20^\circ\text{K})$. To distances $r \approx 6$ Å, these distribution numbers will be seen to be the same as those given before by one of us.¹ A comparison of these numbers with the limiting numbers

$$\bar{N}(r, T) = (4\pi r^3/3)n(T), \quad (24)$$

shows that the correct distribution (22) is always smaller than the limiting distribution (24). This is, of course, always the case at the temperatures $T < T_0$, T_0 being the intermediate temperature defined above, Eq. (9), at which $G(T)$ vanishes or at which the mean square isothermal fluctuation of the number of liquid atoms per atom is unity as in an ideal classical gas.⁶ At temperatures $T_0 < T < T_c$, the opposite situation prevails, insofar as the correct distributions $N(r, T)$ are in excess of the limiting distributions (24). In liquid He⁴, the intermediate temperature T_0 was found to be⁶ about 4.6°K.

Since, in the liquid He II region, the liquid contracts with increasing temperature at $1.25 \leq T \leq 2.18^\circ\text{K}$, the

¹⁸ G. S. Rushbrooke and C. A. Coulson, Phys. Rev. **56**, 1216 (1939).

¹⁹ See the book of J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes* (Reinhold Publishing Corporation, New York, 1950), third edition, pp. 62–105. See also, Henshaw, Hurst, and Pope, Phys. Rev. **92**, 1229 (1953).

pair distribution functions $n(r, T)$ automatically exhibit a parallel behavior insofar as their space integrals are increasing functions of the temperature. The liquid contraction also manifests itself somewhat through the slight decrease of the values of the cut-off separations $a(T)$, at and below which $n(r, T)$ vanishes. In the He II region, one finds that $da(T)/dT < 0$, while $da(T)/dT > 0$ in the He I region.

For the sake of completeness, we give in Table II a series of values, at $r \geq 6$ Å, of the pair distribution functions $n(r, T)$ at the two temperatures of 2.06 and 4.20°K, respectively.²⁰ While these functions have been calculated at many temperatures and close r -intervals, we give only these two distributions, representatives of the low- and high-temperature groups, at intervals of 0.2 Å.

The limitations in the pair distribution functions are, of course, similar to those of the correlation functions. These concern their precise meaning at large separation, $r > 15-20$ Å, as well as their relative poorness at intermediate temperatures $2.50 \leq T \leq 3.00-3.25^\circ\text{K}$, as discussed above and in Sec. III.

III. THE FLUCTUATION INTEGRAL. THE DEGREE OF APPROXIMATION ACHIEVED IN THE DERIVATION OF THE CORRELATION FUNCTIONS

We have seen in the preceding section that at one and only one of its points the value of the structure factor $F_L^2(\Delta k, T)$ is determined by purely macroscopic properties of the liquid. This is the value of F_L^2 at

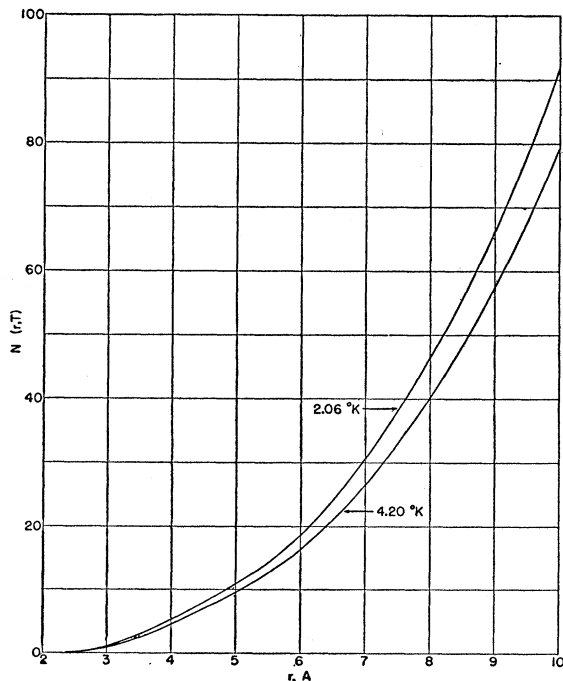


FIG. 5. The total number of liquid atoms $N(r, T)$ in spheres of radius r , around the central atom, at 2.06 and 4.20°K.

²⁰ For $r \leq 6$ Å, see reference 1.

TABLE II. The pair distribution functions $n(r, T)$ at two temperatures, in units of 10^{22} atoms/cc.

r Å	$n(r, 2.06^\circ\text{K})$ [$a = 2.360$ Å]	$n(r, 4.20^\circ\text{K})$ [$a = 2.384$ Å]
6.0	2.20	1.90
6.2	2.25	1.92
6.4	2.277	1.910
6.6	2.283	1.913
6.8	2.277	1.95
7.0	2.26	1.974
7.2	2.24	1.966
7.4	2.22	1.93
7.6	2.20	1.89
7.8	2.18	1.879
8.0	2.16	1.883
8.2	2.15	1.882
8.4	2.15	1.87
8.6	2.16	1.864
8.8	2.17	1.87
9.0	2.18	1.88
9.2	2.19	1.894
9.4	2.20	1.894
9.6	2.209	1.893
9.8	2.214	1.896
10.0	2.214	1.90

$\lim_{r \text{ large}} n(r, T) \rightarrow 2.194$ $\lim_{r \text{ large}} n(r, T) \rightarrow 1.892$

vanishing Δk , where Eq. (5) reduces strictly to

$$\lim_{\Delta k \rightarrow 0} F_L^2(\Delta k, T) = 1 + G(T) = n(T)kT\chi_T. \quad (25)$$

The space integral of the correlation function, the fluctuation integral, is $[n(T)kT\chi_T - 1]$. This quantity is actually independent of the scattering data. It appears thus reasonable to state that the evaluation of the fluctuation integral $G(T)$ constitutes, at the present time, a method of checking the correlation functions $g(r, T)$ derived from the scattering data. It is to be remembered here that by the use of the rigorous limiting relation (3), which was adapted to our evaluation of the $g(r, T)$ functions through a cut-off method described in Sec. II, we have, strictly speaking, modified the experimental structure factor functions $F_L^2(\Delta k, T)$. It is, of course, expected that this modification should affect predominantly the F_L^2 functions at larger Δk values. One should also expect, nevertheless, that the F_L^2 functions derived from the correlation functions, modified in the sense of Eq. (3), should not be too different from the experimental structure factor functions.

The present attempt at assessing the degree of approximation achieved in the $g(r, T)$ functions, derived in the preceding section, is thus two-fold. On the one hand, the space or fluctuation integrals $G(T)$ have been obtained over the whole liquid He⁴ temperature interval explored. On the other hand, the $F_L^2(\Delta k, T)$ functions have been evaluated with the here-derived $g(r, T)$ functions at two representative temperatures, 2.06 and 4.20°K. These two types of checking of the correlation functions will now be discussed.

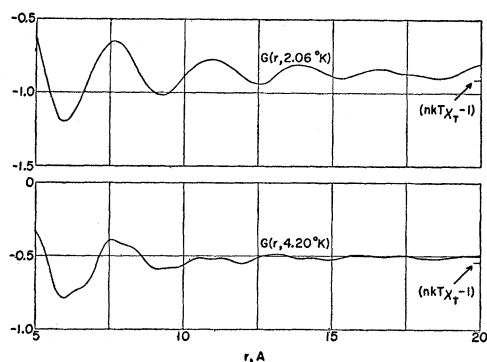


FIG. 6. The fluctuation integrals $G(r, T)$ as a function of r , at 2.06 and 4.20°K.

As far as the fluctuation integral $G(T)$ is concerned, it is being calculated with a function $g(r, T)$ which is known only to a finite though relatively large value of r , $r \approx 20$ Å. Hence we can obtain only

$$G(r, T) = \int_0^r 4\pi r^2 g(r, T) dr, \quad (26)$$

and we have to study this integral $G(r, T)$ as a function of its upper limit r . This was done at all the liquid temperatures investigated here. We give in Fig. 6 the $G(r, 2.06^\circ\text{K})$ and $G(r, 4.20^\circ\text{K})$ functions. The values of $\lim_{r \rightarrow \infty} G(r, T)$ or $[n(T)kT\chi_T - 1]$ are also indicated in these graphs. It will be observed that beyond about $r \approx 10-12$ Å, the $G(r, T)$ functions closely approximate their limiting values $G(T)$ or $[n(T)kT\chi_T - 1]$. Clearly, the $g(r, T)$ functions being oscillatory over their whole range at which they are available, the $G(r, T)$ functions, being negative at all the temperature $T \leq 4.20^\circ\text{K}$, exhibit a series of extrema.

We give in Table III the last minima of the $G(r, T)$ functions. These are all negative, but their sign has been changed in the table. The third column gives the limiting $r \rightarrow \infty$ value of $[-G(r, T)]$ or $[1 - n(T)kT\chi_T]$. An examination of the $G(r, T)$'s shows that beyond about 10–12 Å they closely approximate their experimental values of $[n(T)kT\chi_T - 1]$. One may thus feel justified in stating that as far as their fluctuation integral test is concerned, the $g(r, T)$ functions obtained in the present work are satisfactory. Clearly, there being no direct elementary test on the point behavior of the $g(r, T)$ functions themselves, the fact that they satisfy the integral test appears to be a justification for their use as representing at the present time the best available correlation functions of liquid He⁴ in the temperature interval investigated.

The use of the minima of the $G(r, T)$ functions as the best representative of the $G(T)$ integrals originates in the following property of the correlation functions. The asymptotic behavior of the $g(r, T)$'s at the temperatures $T \leq 4.20^\circ\text{K}$ requires that they tend toward the r -axis from below. This is apparent from the perma-

nently negative values of $G(T)$ or $[n(T)kT\chi_T - 1]$ at $T \leq 4.20^\circ\text{K}$. This is interpreted by saying that the oscillatory functions $G(r, T)$ are better approximated at some finite r , if this r -value coincides with such a zero of this function which was reached from the negative side. The minima of the $G(r, T)$ integrals correspond precisely to these zeros r_0 of the $g(r, T)$'s at which $g(r_0 - \epsilon, T) < 0$, $\epsilon/r_0 \ll 1$.

That the $G(r, T)$ values do not join smoothly in going from $T \leq 2.75$ to $T \geq 3.01^\circ\text{K}$ was expected on the basis of the approximated structure factors, which are poorer in the transition region $2.50 \leq T \leq 3.25^\circ\text{K}$ than outside of it. This was briefly discussed in Sec. II.

In the evaluation of those properties of liquid helium which involve an integration of some function of the atomic separation r , with the correlation functions $g(r, T)$ as weight functions, one may expect that the so calculated quantity would be as well approximated as the approximation achieved by the $G(r, T)$ functions on their limit $G(T)$. The latter may be said, according to the present work, to amount to a few percent, at worst, in the relevant range of r , that is $r \approx 15$ Å. This will hold, provided that the quantity calculated is associated with a rigorous analytical expression of r . If, however, the analytical expression in question is only an approximation itself, then the accuracy with which this physical quantity has been obtained, after integration with $g(r, T)$, will be determined essentially by the over-all precision with which the analytical expression used in the calculations approximates the actual and correct expression of the physical property under consideration.

As discussed briefly in the preceding section, in those calculations of quantities which involve integration of the correlation function out to separations $r > 15-20$ Å, where the representation here obtained is either deficient or not available, as would be the case in the direct calculation of the positive even moments of the $g(r, T)$'s, one could not expect satisfactory results. This is, of course, an important limitation of the correlation functions here derived.

A method to obtain indirectly the lower order even

TABLE III. The last computed extrema of $[-G(r, T)]$ at various temperatures.

$T^\circ\text{K}$	$-G(r, T)$	
	$18.55 \leq r \leq 18.65$ Å	$1 - n(T)kT\chi_T$
1.25	0.922	0.953
1.50	0.913	0.942
1.75	0.900	0.931
2.06	0.901	0.915
2.25	0.886	0.902
2.50	0.860	0.884
2.75	0.827	0.860
3.01	0.887	0.830
3.25	0.845	0.802
3.50	0.784	0.757
3.75	0.689	0.697
3.97	0.624	0.628
4.20	0.520	0.542

positive moments of the correlation functions $g(r, T)$ has been discussed previously⁶ and there is no need to consider it here again. A second indirect method exists also and we shall briefly describe it here. This consists in the fitting, by the method of least squares, for instance, the experimental structure factors or the difference,

$$\begin{aligned} F_L^2(\Delta k, T) - F_L^2(0, T) \\ = F_L^2(\Delta k, T) - n(T)kT\chi_T \\ = \sum_1^{\infty} (-)^n (\Delta k)^{2n} [r_G^{(2n)} / (2n+1)!], \quad (27) \end{aligned}$$

where use was made of the definition of the moments (6), (8), and (10). A relatively low-order polynomial in $(\Delta k)^2$ should yield, in principle, with a fair degree of approximation the moments $r_G^{(2n)}$.

We should like to turn now to the second type of control of the correlation functions mentioned above. This concerns the numerical evaluation of the generalized structure factors, or

$$F_L^2(\Delta k, T, r) = 1 + \int_0^r \frac{\sin(r\Delta k)}{r\Delta k} 4\pi r^2 g(r, T) dr, \quad (28)$$

with the correlation function obtained here and modified at small separations r as discussed in Sec. II. These generalized structure factors depend on the upper limit r of the integral through which they are defined. The actual structure factors at liquid temperatures T not too close to the critical temperature, are the limits $r \rightarrow \infty$ of the $F_L^2(\Delta k, T, r)$ functions. The latter have been calculated at two liquid temperatures, 2.06 and 4.20°K, at intervals of Δk of 0.25 Å⁻¹, and at intervals of 0.05 Å in r , from the origin to 20.0 Å. These integrals do not change practically beyond about 12 Å and evidently belong to that class which should be fairly well approximated by the correlation functions derived here. We give in Table IV the values of $F_L^2(\Delta k, T, 20 \text{ Å})$ and compare these calculated structure factors with the original experimental ones $(F_L^2)_{\text{exp}}$ given in Fig. 1. It will be seen that the agreement, in spite of the modification of the $g(r, T)$ functions, is satisfactory and these calculations provide us with a control of the internal consistency of the method of derivation of the $g(r, T)$ functions as well as of the numerical methods used in obtaining the generalized structure factors $F_L^2(\Delta k, T, r)$. The values at vanishing Δk are the arithmetic means at the three largest r -values of $G(r, T)$ at 2.06 and 4.20°K. A glance at Table IV shows that the modified $g(r, T)$ functions give rise, at $\Delta k > 3 \text{ Å}^{-1}$, to structure factors which are smaller than the experimental ones. Still these calculated structure factors lie well within the estimated $\pm(5-7)$ percent mean errors given on the experimental values. At the smaller Δk -values the calculated structure factors $F_L^2(\Delta k, T, r)$ are larger than the experimental ones. It is to be remem-

TABLE IV. The experimental $(F_L^2)_{\text{exp}}(\Delta k)$ and the calculated $F_L^2(\Delta k, T, 20 \text{ Å})$ structure factors at 2.06 and 4.2°K.

Δk Å ⁻¹	$(F_L^2)_{\text{exp}}(\Delta k,$ 2.06°K)	$F_L^2(\Delta k,$ 2.06°K, 20 Å)	$(F_L^2)_{\text{exp}}(\Delta k,$ 4.2°K)	$F_L^2(\Delta k,$ 4.2°K, 20 Å)
0.0	0.0820	0.089	0.458	0.478
0.25	0.0875	0.128	0.381	0.429
0.50	0.116	0.157	0.300	0.337
0.75	0.172	0.208	0.265	0.284
1.00	0.255	0.277	0.313	0.317
1.25	0.383	0.392	0.448	0.431
1.50	0.575	0.565	0.665	0.639
1.75	0.909	0.891	1.02	0.990
2.00	1.32	1.28	1.28	1.25
2.25	1.27	1.26	1.23	1.21
2.50	1.13	1.12	1.09	1.07
2.75	1.04	1.02	1.01	1.00
3.00	1.00	0.974	0.970	0.972
3.25	0.978	0.946	0.959	0.961
3.50	0.979	0.938	0.970	0.964
3.75	0.999	0.947	0.990	0.974
4.00	1.04	0.984	1.01	0.984
4.25	1.09	1.02	1.05	1.00
4.50	1.11	1.04	1.07	1.01
4.75	1.10	1.03	1.08	1.02
5.00	1.08	1.02	1.08	1.02
5.25	1.06	1.00	1.07	1.02
5.50	1.04	0.990	1.06	1.01
5.75	1.02	0.985	1.02	0.987
6.00	1.00	0.986	0.990	0.970

bered here that the uncertainties on the experimental structure factors are the largest at small and large Δk -values.

In closing this section on the verification of the correlation functions derived in Sec. II, it appears reasonable to say that, on the whole, the analysis performed in this work on the basis of the data of one of us^{1,2} has led to a picture of the indirect atomic correlations, expressed by the $g(r, T)$'s, which should be rather good approximations to the actual correlations, at least out to separations $r \approx 15 \text{ Å}$. It is, indeed, felt that the checking of the limiting large r -values of the $G(r, T)$'s at all the liquid temperatures here investigated, as well as the structure factors, Tables III and IV, constitute reasonable grounds for this belief. Clearly, the preceding method of checking does not provide us with a proof for the completely correct character of the correlation functions derived above. We are unaware of any existing methods of supplying for these functions a closer check than the one used by us.

IV. THE MEAN POTENTIAL ENERGY PER LIQUID He⁴ ATOM, CONFIGURATIONAL HEAT CAPACITIES. A PROOF OF THE KINETIC ENERGY ORIGIN OF THE LAMBDA TRANSITION

In any applications of the atomic distributions derived from x-ray scattering data in liquids, one has to keep in mind the inevitable limitations of the correlation functions $g(r, T)$ or the pair distribution functions $n(r, T)$. In addition, the physical property of the liquid under consideration, which is to be evaluated, has its own limitations. Such evaluations of elementary physical properties involve functions depending on interatomic or intermolecular separations r , their spatial

isotropy being actually realized or assumed. Here one has to face, in general, the contingency that the elementary physical property in question has only a more or less well justified analytical form, the latter being an approximation of its unknown correct analytical expression. In spite of these limitations which cannot but decrease the degree of quantitative or numerical approximations achieved on any elementary or atomic property in liquids, it is felt that unless the distribution functions derived are made use of in furthering the knowledge of elementary physical quantities in liquids, the derivation of the distribution functions *per se*, or for the sole purpose of comparison with distributions in the solid phase, tends to lead to some kind of a scientific impasse.

The first important application of the distribution function data has been made by Hildebrand and his collaborators.²¹ They first used the distribution functions determined by them in liquid mercury for an investigation of the classical potential energy of this liquid. Subsequently, Hildebrand studied the potential energy in different liquids.

In these studies it is assumed that the total potential energy of the liquid formed by N atoms, or molecules, is the sum of the spatially isotropic potential energies of all its $N(N-1)/2$ pairs. In the present work on liquid He^4 this assumption will be retained. We have defined by Eq. (4), $dN(r, T)$ as the differential probability to find an atom in the volume element $dv(r)$, whose center is at a distance r from the origin atom. The differential potential energy, per atom, of the pair of atoms at the origin and at r , is

$$\begin{aligned} d\Phi(r, T) &= \frac{1}{2} \varphi(r) dN(r, T) \\ &= 2\pi \varphi(r) n(r, T) r^2 dr, \end{aligned} \quad (29)$$

where $\varphi(r)$ is the isotropic mutual potential energy of two stationary atoms in the system, separated by the distance r . The total potential energy, per atom, in the whose system is thus, exchange energy included,

$$\Phi(T) = 2\pi \int_V \varphi(r) n(r, T) r^2 dr, \quad (30)$$

where the integral extends over the volume V of the system. At liquid temperatures $T < T_c$, T_c being its critical temperature, the integration may be extended over the whole space. The remarkable and simple formula due to Hildebrand²¹ is rigorous within the limitations of the above mentioned assumption on the representation of the total potential energy of the liquid. At any rate, it seems reasonable to say that (30) is expected to be at least a first approximation to the classical potential energy, per atom, of the system in the case where the linear superposition of the pair potential energies turned out to be only the first term

²¹ J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.* **1**, 817 (1933). For the literature of the work of the Berkeley group see the book quoted in reference 19.

of a possible series expansion representation of the total potential energy of the liquid.

One of the major obstacles in the path of the extensive use of Eq. (30) is the general unavailability of the mutual potential energy function $\varphi(r)$ of two stationary atoms or molecules of the liquid under study.

In our case of liquid He^4 , two approximate analytical expressions are available^{22,23} for the total mutual potential energy of two stationary He^4 atoms. These two differ only in their attractive parts, the one including the mutual induced dipole-quadrupole interaction,²³ beside the dipole-dipole one, leads to a distinctly lower total potential energy. These two potential energy expressions are, respectively,

$$\begin{aligned} \varphi_I(r) &= A e^{-\alpha r} - B_I r^{-6}, \\ \varphi_{II}(r) &= A e^{-\alpha r} - B_{II} r^{-6} - C_{II} r^{-8}. \end{aligned} \quad (31)$$

The approximate range is $(1/\alpha)$, with α equal to 4.60 \AA^{-1} , r is in angstrom units, and the various constants are the following, in units of 10^{-11} ergs:

A	B_I	B_{II}	C_{II}
77	0.149	0.139	0.370

Using the forms (31), we have calculated $\Phi_I(T)$ and $\Phi_{II}(T)$ at the various liquid temperatures at which the pair distribution functions $n(r, T)$ have been obtained. The mean potential energies per atom $\Phi(T)$ had, of course, to be studied as a function of the upper limit r of the integral in their definition of Eq. (30). In view of the rapid convergence of the potential energy inte-

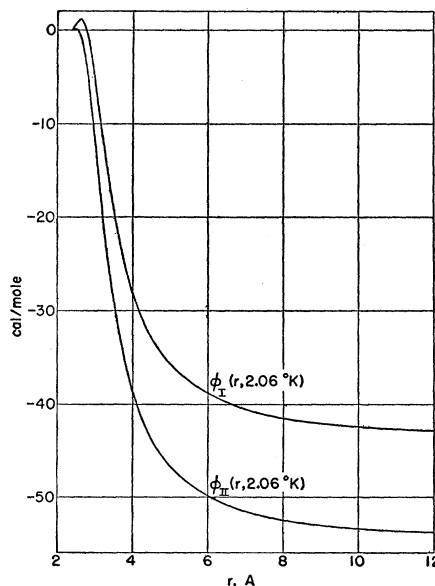


FIG. 7. The mean potential energies per liquid He^4 atom $\Phi_I(r, T)$ and $\Phi_{II}(r, T)$, at 2.06°K , as a function of r , for the two analytical approximations of the mutual potential energy of two stationary isolated He^4 atoms.

²² J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

²³ H. Margenau, *Phys. Rev.* **56**, 1000 (1939).

grals (30), the limiting large r values of the potential energies are reached already at the relevant separations $r \approx 10-12$ Å. This is seen in Fig. 7 which gives $\Phi_I(r, 2.06^\circ\text{K})$ and $\Phi_{II}(r, 2.06^\circ\text{K})$. We give in Table V the values of $\Phi_I(T)$ and $\Phi_{II}(T)$ at the various liquid temperatures at the extreme separation of 20 Å. It will be seen that $\Phi_{II}(T)$ is about $(5/4)\Phi_I(T)$. In part of the present investigation, however, the actual numerical values of the mean potential energies are of no importance. What is, however, of major qualitative significance is their decreasing trend with increasing liquid temperature in the He II region, and their increasing trend with increasing temperature in the He I region. The potential energy functions $\Phi_I(T)$ and $\Phi_{II}(T)$ have a cusp at the lambda point. This result is in agreement with what one might have expected on the basis of the observed peculiar contraction of liquid He II, at $T \geq 1.25^\circ\text{K}$, with increasing temperature and the normal expansion of liquid He I with increasing temperatures.

In order to fully exploit the numerical results in Table V, it is necessary to write down formally the expression of the total energy of the liquid. In so doing, we shall still be on very general grounds. Indeed a rigorous quantum mechanical solution of the liquid He⁴ problem is expected to yield, after ensemble averaging, an expression of the type

$$E_{\text{tot}}(T) = E_{\text{kin}}(T) + \Phi(T). \quad (32)$$

The total energy of the liquid at temperature T , $E_{\text{tot}}(T)$ is the sum of the classical kinetic, E_{kin} , and potential plus quantum-mechanical exchange, $\Phi(T)$, energies. In forming the ensemble average of the energies in (32), the term E_{kin} will depend critically on the momentum space distribution of the system. Let us now define the configurational heat capacity of our system by

$$\Gamma(T) = d\Phi(T)/dT. \quad (33)$$

All heat capacities to be considered will be associated with the saturated liquid. With (32) and (33), we obtain

$$C_{\text{tot}}(T) = [dE_{\text{kin}}/dT] + \Gamma(T), \quad (34)$$

for the total calorimetrically measurable heat capacity of the liquid. Experimentally, $C_{\text{tot}}(T)$ is a rapidly increasing function of the temperature below the lambda point and a decreasing function above the lambda point, over some small temperature interval.²⁴ The characteristic lambda anomaly is expressed by

$$\Delta C_{\text{tot}} = C_{\text{tot}+} - C_{\text{tot}-} < 0, \quad (T = T_\lambda), \quad (35)$$

the + and - subscripts referring to the high- and low-temperature sides of the transition temperature T_λ . In contrast with the lambda anomaly of the total heat capacity, the configurational heat capacity has an inverted lambda anomaly. Since $\Phi(T)$ has a cusp at the lambda point, one finds Γ_- or $\Gamma(T < T_\lambda) < 0$, and Γ_+ or $\Gamma(T > T_\lambda) > 0$, as shown by the potential energies

²⁴ See the monograph of W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942), pp. 211-226.

TABLE V. Mean potential energies $\Phi_I(T)$ and $\Phi_{II}(T)$ per atom in liquid helium at various temperatures.

$T^\circ\text{K}$	$\Phi_I(T)$ cal/mole	$\Phi_{II}(T)$ cal/mole
1.25	-43.04	-53.95
1.50	-43.08	-54.00
1.75	-43.10	-54.03
2.06	-43.25	-54.29
2.25	-43.30	-54.34
2.50	-43.08	-54.02
2.75	-42.77	-53.58
3.01	-40.15	-50.69
3.25	-39.71	-50.07
3.50	-39.18	-49.33
3.75	-38.55	-48.48
3.97	-37.91	-47.58
4.20	-37.12	-46.47

$\Phi(T)$ of Table V. This was the behavior of major qualitative significance pointed out in the aforementioned. The discontinuity of the configurational heat capacity is

$$\Delta\Gamma(T_\lambda) = \Gamma_+(T_\lambda) - \Gamma_-(T_\lambda) > 0. \quad (36)$$

Its sign is opposite to that of the total heat capacity (35). Hence, independently of the actual numerical values of the configurational heat capacity $\Gamma(T)$, one has to conclude that the observed lambda anomaly of the total liquid helium heat capacity is strictly of kinetic energy origin. It is thus connected with the temperature variation of the distribution of the liquid He⁴ atoms in momentum space.

With the aforementioned behavior of $\Gamma(T)$, it will be seen that at $1.25^\circ\text{K} < T < T_\lambda$, the kinetic heat capacity is larger than the total heat capacity. Also, in a limited temperature range beyond T_λ , the decreasing kinetic heat capacity is still larger than the increasing positive configurational heat capacity.

The proof given here of the kinetic energy origin of the lambda anomaly in liquid helium appears to be quite general though involving the derived pair distribution functions and the use of the approximate mutual potential energies of a pair of stationary He⁴ atoms. The proof obtained seems to provide a solid foundation for the development of the theory of liquid helium concerning its momentum space behavior.

It is also of interest to consider the approximate numerical values of the configurational heat capacity $\Gamma(T)$ resulting from the approximate potential energies $\Phi_I(T)$ and $\Phi_{II}(T)$. In order to obtain $\Gamma_I(T)$ and $\Gamma_{II}(T)$ associated with the potential energies Φ_I and Φ_{II} , we have fitted these with parabolae of the form

$$\Phi_\sigma(T) = a_\sigma + b_\sigma T + c_\sigma T^2. \quad \sigma = \text{I, II}. \quad (37)$$

These yielded at once the heat capacities:

$$\begin{aligned} \Gamma_\sigma(T) &= d\Phi_\sigma/dT \\ &= b_\sigma + 2c_\sigma T, \end{aligned} \quad (38)$$

linear in T over the restricted temperature ranges where the parabolic fits have been obtained. The various constants of the parabolae (37) are given in Table VI

TABLE VI. Coefficients of the parabolic fits of the mean potential energies per atom in liquid helium.

Temperature range	a_I cal/mole	a_{II} cal/mole	b_I cal/mole \times deg	b_{II} cal/mole \times deg	c_I cal/mole \times (deg) ²	c_{II} cal/mole \times (deg) ²
$1.25 \leq T \leq 2.10^\circ\text{K}$	-43.17	-54.39	0.3192	0.8234	-0.1710	-0.3765
$3.05 \leq T \leq 4.20^\circ\text{K}$	-36.77	-46.33	-3.711	-4.957	0.8635	1.1705

in the two temperature intervals $1.25 \leq T \leq 2.10^\circ\text{K}$ and $3.05 \leq T \leq 4.20^\circ\text{K}$. The parabolas in the liquid He II range actually extend up to 2.25°K , which is the "apparent" lambda temperature in these calculations. Actually, if we had performed the calculation of the correlation function at the empirical lambda point of about 2.18°K , the pair distribution functions in Eq. (35) would have led to the inverted cusp of the $\Phi(T)$ functions at this correct lambda temperature. We give in Table VII the configurational heat capacities $\Gamma_c(T)/R$, in molar units. The heat capacities at $T < 2.25^\circ\text{K}$, refer to the decreasing negative branches of the discontinuous functions $\Gamma_I(T)$ and $\Gamma_{II}(T)$. It is expected that the potential energy function $\Phi_{II}(T)$, which is likely to overestimate the actual mean potential energy, in absolute value, should give rise to configurational heat capacities $\Gamma_{II}(T)$ in excess of their actual values. A glance at Table VII shows that, in the liquid He II range, $1.25^\circ\text{K} < T < T_\lambda$, the $\Gamma(T)$ values are quite small in comparison to the total heat capacities.²⁵ In the vicinity of the lambda point, on its low temperature side, Γ_I and Γ_{II} amount, respectively, to about 3 and 6 percent of the total heat capacity. While in the He II region, the Γ 's are small fractions of the total heat capacity, they tend to become dominant at high temperatures, in the He I region. At $T > 3^\circ\text{K}$, $\Gamma_I(T)$ seems to have plausible values, while Γ_{II} is quite large, and at $T > 3.5^\circ\text{K}$ it turns out to be larger than the total heat capacity, whose experimental accuracy may be low here. This indicates that $\Phi_{II}(T)$ is likely to be in excess, in absolute value, of the actual mean potential energy per atom at these temperatures. At any rate, there is a qualitative change in the roles played by the configurational heat capacity in the He II and He I regions, respectively, when compared to the total heat capacity.

The anomalous behavior of $\Gamma(T)$ in the He II region appears to be the manifestation of some elementary property of this liquid, wherein this potential part of the heat capacity tends to oppose the extreme anomaly exhibited by the kinetic heat capacity. In terms of a more elementary picture, not involving directly temperature derivatives, the peculiar behavior of the liquid density in the He II region seems to correspond to some kind of defense mechanism tending to counteract the dominating anomaly which originates in the momentum space properties of the liquid. It is noteworthy that the late F. London²⁵ has emphasized, through qualitative considerations, that the peculiar behavior

²⁵ F. London, *J. Chem. Phys.* **11**, 203 (1943).

of the density of liquid He II is a manifestation of the opposition by the liquid to its assumed Bose-Einstein condensation process. This opposition was presumed to originate in the classical mutual atomic interactions.

The quantitative results obtained in the present work which led to the picture just discussed by us, are based on quite general grounds. In particular the details of the mechanism of the dominant lambda phenomenon were not needed at all, while a proof could be given of its momentum space origin.

Finally, a few remarks may be of interest here concerning the expected behavior of $\Gamma(T)$ below 1.25°K . It is seen on Table VII that $\Gamma(T)$ increases with decreasing temperatures. It may be expected that $\Gamma(T)$ will vanish at some temperature below 1.25°K to reach a positive maximum and to remain positive at low temperatures, tending to vanish there, from positive

TABLE VII. Configurational heat capacities $\Gamma_I(T)$ and $\Gamma_{II}(T)$ in units of R at various temperatures.

T	$\Gamma_I(T)/R$	$\Gamma_{II}(T)/R$
1.25	-0.055	-0.059
1.50	-0.098	-0.154
1.75	-0.141	-0.249
2.10	-0.201	-0.381
2.25	-0.227	-0.428
3.05	0.784	1.10
3.25	0.958	1.33
3.50	1.17	1.63
3.75	1.39	1.92
4.00	1.61	2.22
4.20	1.78	2.45

values, at the approach of the absolute zero. This behavior would be similar to that of the expansion coefficient of liquid He II which, as predicted,²⁶ became positive at low enough temperatures.²⁷ This expansion coefficient should also have a positive maximum before tending to vanish, from the positive side, at the approach of the absolute zero.

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²⁶ L. Goldstein, *Phys. Rev.* **89**, 597 (1953).

²⁷ K. R. Atkins and M. H. Edwards, *Phys. Rev.* **93**, 1416 (1954).