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Interatomic Correlations in Liquid He^4

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The direct correlation functions, of generally short-range character over most of the liquid temperature interval, have been obtained with the liquid He^4 x-ray scattering data of Reekie, using the 701 IBM Electronic Calculator. The geometrical simplicity of these functions when compared with the indirect correlation functions, of more intuitive physical significance, is automatically demonstrated. They closely satisfy two types of integral test relations, and this fact proves their over-all correct character and the internal consistency of the numerical analysis.

The previously obtained indirect correlation functions will be used here in studying the interference properties of the liquid in slow-neutron scattering processes, in the limiting static approximation. At temperatures not too close to the critical region, the static interference integrals are always negative as a result of the preponderant destructive interference effects arising from the local density defects from the mean density, outweighing the local density excesses. At short and moderate neutron wavelengths, where the use of the static interference integrals is better justified, the total slow-neutron scattering cross sections in liquid He^4, and in liquids in general, always increase with increasing temperature. The static interference integrals will be shown to provide an additional integral test on the indirect correlation functions. The latter were found to satisfy this test relation with good accuracy.

Part of this paper is devoted to a numerical evaluation of mean kinetic energies per liquid He^4 atom as a function of the temperature. The existence of a large zero-point kinetic energy of the liquid as compared with the kinetic energy of thermal origin is demonstrated. Furthermore, the previously given qualitative proof of the kinetic energy origin of the lambda transition could be made semi-quantitative. Finally, root-mean-square forces acting on a liquid atom are evaluated, this physical quantity of elementary character having become, in principle at least, accessible through the experimental investigation of slow-neutron scattering properties of liquids.

1. INTRODUCTION

In a recent work, Reekie and the writer[1] have given an extensive analysis of the liquid helium indirect correlations described by the space- and temperature-dependent functions $g(r,T)$. The latter define the local positive or negative deviations of the atomic concentration from its mean value $n(T)$ in a liquid in thermodynamic equilibrium. The indirect correlations result from the ever present concentration fluctuations of the liquid under isothermal conditions. For physical processes of short duration in comparison with the finite time needed by the liquid to establish the local concentration deviations from the mean, the functions $g(r,T)$ may be considered to express a permanent or static feature of the atomic distribution in a liquid viewed from an origin atom, all surface effects being neglected. The functions $g(r,T)$ enter into the static two-atom or pair distribution functions $n(r,T)$, which define the probability per unit volume of finding an atom at some specified distance r from the origin atom. These functions are isotropic.

In addition to the indirect correlation functions $g(r,T)$, one also defines a direct correlation function $f(r,T)$ which is indicative, so to speak, of the first-neighbor correlations. The functions f and g are connected by an unique relation given by Ornstein and Zernike,[2] who were also the first to introduce the concepts of these two types of spatial correlation functions in statistical systems. We shall henceforth refer to f and g as interaction and correlation functions, and shall, occasionally, abbreviate them as i.f. and c.f., respectively. While the c.f.'s have a more intuitive physical interpretation, the i.f.'s are generally of shorter range, above all in the region of the critical temperature. The i.f.'s are expected to be analytically more regular than the c.f.'s at all temperatures. This property may thus make them preferable to handle in the critical region where the c.f.'s become of very long-range character.

Using the liquid helium x-ray scattering structure

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[1] L. Goldstein and J. Reekie, Phys. Rev. **98**, 857 (1955). This paper will be referred to in the text by S.D.

[2] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).

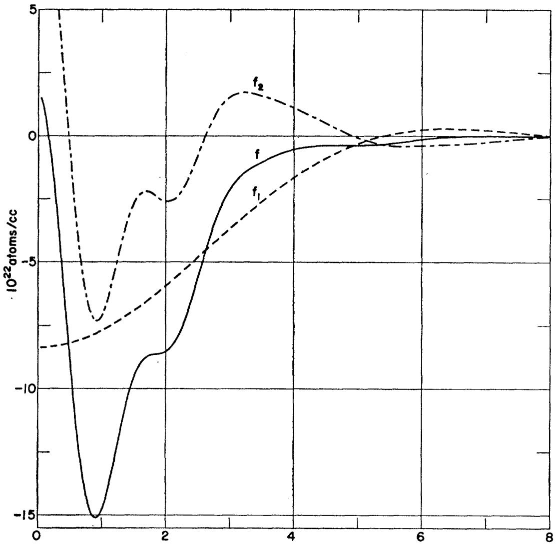

FIG. 1. Partial, $f_1(r,2.06°K)$, $f_2(r,2.06°K)$, and total interaction functions $f(r,2.06°K)$, (atoms/cc), *vs* the interatomic separation r, (A).

factors of Reekie,[3] we have here obtained, over a wide temperature interval and distance range, the functions $f(r,T)$. The expected moderate-ranged character of these functions, over most of the temperature interval, is hereby fully confirmed. Their geometrical simplicity, when compared with the $g(r,T)$ functions, is also demonstrated. To our knowledge, these $f(r,T)$ functions have not been derived for other liquids, in spite of the extensive x-ray scattering data available for some of them.

As in our work on the c.f.'s, the i.f.'s here obtained have been submitted to two types of integral checks. In one of these, their space integrals have been calculated. The latter are completely determined by some of the macroscopic properties of the liquid, and the calculations verify with good accuracy the predicted values. In the second type of integral check, they reproduced closely their generating functions, i.e., the x-ray scattering structure factors. These studies prove the over-all correctness of the numerical analysis. They also tend to support the likely possibility that the $f(r,T)$ functions here derived are fair approximations, over most of their range, to their presently unknown rigorous form.

A major part of the present work is devoted to the investigation of the static indirect interference integrals appearing in the total slow-neutron scattering cross sections in liquids. While these involve the c.f.'s or $g(r,T)$ functions of liquid helium, the results derived should have general significance and be valid, qualitatively, in all monatomic liquids. In these numerical calculations, only the so-called generalized indirect interference integrals can be obtained. These integrals depend not only on the liquid temperature and the de Broglie wavelength of the neutrons, but also on the upper limit of the radial integration through which they are defined. These limits determine the radii of spheres centered at the origin atom, the atoms of which contributed to the static interference term of the scattered intensity of the waves. The temperature effect on the interference integral will be shown to correspond to the competition of the constructive interference effects of the local positive density deviations from the mean, and the destructive interference effects arising from the local negative deviations from the mean density. The characteristic temperature T_i or T_0 defined previously[1,4] will be shown to divide approximately the liquid temperature interval, for not too short wavelengths, in such a way that for $T<T_0$ the interference term is completely destructive, while for $T_0 \leqslant T \leqslant T_c$, T_c being the critical temperature, it becomes positive. This forecasts, in the static approximation, the large increase in the total slow-neutron scattering cross section at medium or longer wavelengths, at the approach of the critical temperature, i.e., the occurrence of the slow-neutron critical opalescence effect.[5]

The static interference integral tends to lose its validity with increasing neutron wavelength, because of the increasingly important liquid relaxation type of time effects.[6] Stated in other terms, the static interference integral, which depends only on the momentum change on scattering by the assumed rigid atomic distribution, becomes, for slower neutrons, an increasingly worse approximation to the actual interference term which is associated with a nonrigid distribution and which depends also on the relatively large energy change of the slower neutrons on scattering. Should one consider the long-wavelength static interference integrals as only crude approximations, even of quite limited physical significance, their study and comparison with the direct interference integrals, defined by the x-ray scattering structure factors, may be looked upon as providing a new integral test for the $g(r,T)$ functions. In view of the latter fact that they are involved in the evaluation of various elementary physical properties of liquids, such an additional test of these functions is of evident importance.

As a further application of the mean potential energies per liquid He^4 atom obtained in S.D., we have evaluated, using the empirically determined latent heat values, the mean kinetic energies at various liquid temperatures. The results of these calculations may be said to be of twofold interest. On the one hand, they provide a proof for the large zero-point kinetic energy of the liquid He^4 atoms over the whole temperature range investigated. On the other hand, a semiquantitative sharpening of the

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

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

[5] L. Goldstein, Bull. Am. Phys. Soc. **25**, 38 (1950); Phys. Rev. **83**, 289 (1951).

[6] L. Van Hove, Phys. Rev. **95**, 249 (1954).

proof given in S.D. of the kinetic energy origin of the lambda transition has been achieved.

The paper ends with an evaluation of the root mean square forces per liquid He^4 atom, using the pair distribution functions derived in S.D. This elementary physical quantity is, in principle at least, experimentally accessible in liquids through their slow-neutron scattering properties, as shown recently by Placzek.[7]

2. THE DIRECT CORRELATION OR INTERACTION FUNCTION IN LIQUID He^4

The interaction function $f(r,T)$ may be defined either in terms of the indirect correlation function $g(r,T)$, or with the help of the scattering intensity structure factor for radiation. With the latter, one finds[4]

$$f(r,T)=(1/2\pi^2r)\int_0^\infty[1-F_L{}^{-2}(\Delta k,T)]\times(\sin r\Delta k)(\Delta k)d(\Delta k). \quad (2.1)$$

Here, Δk or $2|\mathbf{k}|\sin\theta$, or $(4\pi\sin\theta/\lambda)$, is the momentum change on scattering into the direction forming the angle 2θ with the direction of incidence of the radiation, and $F_L{}^2(\Delta k,T)$ is the scattering intensity structure factor, per atom, of the monatomic system. It is seen that

$$\lim_{r\to0}f(r,T)=(1/2\pi^2)\times\int_0^\infty[1-F_L{}^{-2}(\Delta k,T)](\Delta k)^2d(\Delta k), \quad (2.2)$$

showing that the finite limit $f(0,T)$ at the origin is fully determined by structure factor. In contrast, however, with the c.f.'s, there is no elementary physical significance attached to $f(0,T)$. The behavior of $f(r,T)$ at small separations results at once from (2.1). Expanding there $(\sin r\Delta k)/(r\Delta k)$, and keeping the first two terms, one finds

$$\lim_{r\text{ small}}f(r,T)=f(0,T)-(r^2/12\pi^2)\times\int_0^\infty[1-F_L{}^{-2}(\Delta k,T)](\Delta k)^4d(\Delta k), \quad (2.3)$$

showing the parabolic character of $f(r,T)$ at small r.

The structure factors are available in such a form[1] as to suggest the decomposition of the Fourier integral (2.1) into two integrals, namely,

$$f(r,T)=f_1(r,T)+f_2(r,T)=(1/2\pi^2r)\left[\int_0^1[1-F_L{}^{-2}(\Delta k,T)]\times(\sin r\Delta k)(\Delta k)d(\Delta k)+\int_1^{\Delta K}\cdots\right], \quad (2.4)$$

where the integrand of the second integral is identical with the integrand of the first, and where ΔK is the limiting value of Δk beyond which the experimental structure factor reduces approximately to unity, i.e., the integrand vanishes. As in the analysis of the c.f.'s given in S.D., the functions f_1 and f_2 have been obtained by numerical integration in intervals of 0.025 A^{-1} in Δk. These functions have been obtained at every 0.05 A in r, from vanishing r out to 20 A. The numerical integrations have been performed on the "701" IBM Electronic Calculator.

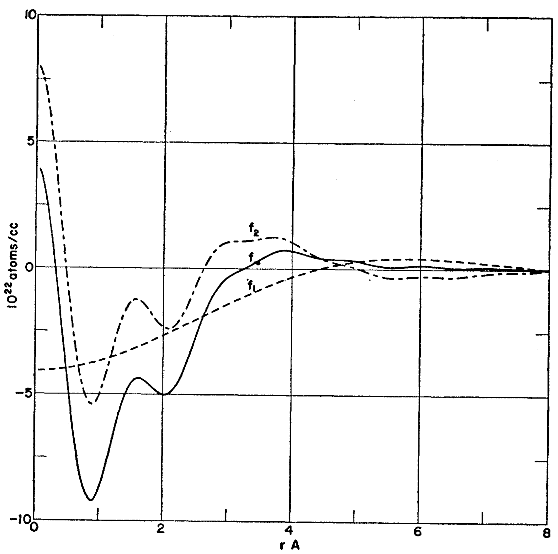

FIG. 2. Partial, $f_1(r,4.20°\text{K})$, $f_2(r,4.20°\text{K})$ and total interaction functions $f(r,4.20°\text{K})$, (atoms/cc), *vs* the interatomic separation r, (A).

We give in Figs. 1 and 2, the functions $f_1(r,T)$, $f_2(r,T)$, and their resultant, the actual interaction function $f(r,T)$, at 2.06°K and 4.20°K liquid temperatures, respectively. The graphs extend only to 8 A separation. At larger separations, these functions are only very small fractions of their values at closer separations, at 2 A, for instance. These functions, as representative of the low- and high-temperature functions, exhibit both qualitative and quantitative differences. At low temperatures, the $f(r,T)$'s have a deep and sharp minimum. At the higher temperatures, the principal minimum is less deep and less sharp. At larger separations, the low temperature i.f.'s remain negative, becoming quite small though; at the higher temperatures, they become positive at medium separations. It will be observed that the component functions f_1 and f_2 remain, numerically, relatively close at most distances r. This result is similar to the one obtained with the $g(r,T)$ functions[1] and underlines the importance of the small Δk-value structure factors in the determination of the $f(r,T)$ functions. The relatively short-range character of the $f(r,T)$ functions is apparent on the graphs.

It should be remembered here that, in contrast with the c.f.'s, which have to satisfy a physical condition at

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

vanishing r, the i.f.'s do not have as precise a physical meaning at $r \to 0$. Since the experimental structure factors are necessarily only approximate, above all at large Δk-values, they were found to lead[1] to $g(r,T)$ functions which did not satisfy the physical condition imposed on them at the origin. They thus had to be modified at close separations. On the basis of this result, it is also expected that the $f(r,T)$ functions here obtained be cruder approximations to their actual unknown values at the origin and at small distances than they are at medium and large distances. There are, in principle, two methods for improving the functions $f(r,T)$ somewhat. One of these consists in using in (2.1) the structure factors computed with the physically correct form of the $g(r,T)$ functions. In the other method, one might use the fundamental relation[2,4] with its integral extended over the whole space, essentially,

$$f(r,T)=g(r,T)-\int g(|r-r'|,T)f(r',T)dv(r'), \qquad (2.5)$$

and obtain with it the first iterated $f^{(1)}(r,T)$ by replacing in the folding integral $f(r,T)$ by its zero-order approximation, and so on. Neither of these methods of improving the interaction functions has been made use of here, and, hence, only their zero-order approximation has been derived here.

At large separations the functions $f(r,T)$, while becoming very small, are oscillatory. At 2.06°K, and $8\text{ A} \leqslant r \leqslant 20\text{ A}$, one finds the following zeros: 9.60, 14.70, 15.05, 15.65, and 17.70 A. The zeros in the range 8–20 A, at 4.2°K, are 11.05, 14.50, 14.95, 15.55, and 18.50 A. The absence of oscillations at medium separations assures the analytical simplicity of these functions when compared to the c.f.'s. At larger separations also, the number of zeros of the i.f.'s is less than that of the c.f.'s. Their analytical simplicity notwithstanding, the i.f.'s cannot be used alone in the all-important pair distribution functions, as the fundamental relation (2.5) excludes the simple substitution of $g(r,T)$ in the pair distribution functions by $f(r,T)$.

TABLE I. The space integrals $F(20\text{ A},T)$ of the interaction functions at various temperatures.

T °K	$-F(20\text{ A},T)$ calc.	$-F(T)$ exp.
1.25	19.6	20.3
1.50	15.8	15.7
1.75	13.1	13.3
2.06	11.1	11.2
2.25	9.03	9.20
2.50	7.55	7.62
2.75	6.08	6.14
3.01	4.99	5.02
3.25	4.15	4.02
3.50	3.09	3.12
3.75	2.33	2.30
3.97	1.68	1.69
4.20	1.17	1.18

As in the investigation of the c.f.'s in S.D., it was important to submit the i.f.'s obtained here to the important integral checks available for these functions. In spite of their probable crude character at small separations, it will be seen that they satisfy with good accuracy these integral tests. One of these concerns their space integral which is defined by a general statistical thermodynamic relation[2,4]:

$$\int_0^\infty f(r,T)4\pi r^2 dr = F(T) = 1-[\langle\Delta N^2\rangle_{\text{Av}}/N]^{-1}. \qquad (2.6)$$

Here,

$$\langle\Delta N^2\rangle_{\text{Av}}/N = n(T)kT\chi_T \qquad (2.7)$$

is the isothermal mean square fluctuation of the number of atoms, N, per atom, $n(T)$ stands for the mean atomic concentration and χ_T is the isothermal compressibility of the liquid at the temperature T. The generating function of the interaction functions is essentially, by Eq. (2.1),

$$\Phi(\Delta k,T)=1-F_L^{-2}(\Delta k,T). \qquad (2.8)$$

With the rigorous formula[4]

$$\lim_{\Delta k\to 0} F_L^{-2}(\Delta k,T)=[n(T)kT\chi_T]^{-1}, \qquad (2.9)$$

one obtains

$$F(T)=\lim_{\Delta k\to 0}\Phi(\Delta k,T), \qquad (2.10)$$

in some analogy with the corresponding relation valid for the space integral $G(T)$ of the c.f.'s discussed in S.D.[1,4] The functions $F(T)$ and $G(T)$ of liquid He^4 have both been graphed previously.[4] These functions are complementary to each other, to some extent, as far as their qualitative behavior is concerned. They are both negative at low temperatures, defined by the characteristic temperature[1,4] T_0 or T_i, or at $T<T_0$. They vanish at T_0 and become positive at the high temperatures $T_0 \leqslant T \leqslant T_c$. In normal liquids, $F(T)$ decreases with decreasing temperature down to the normal melting point T_m, or

$$F(T_m)\leqslant F(T)\leqslant F(T_0)=0. \qquad (2.11)$$

In liquid He^4 a unique situation is realized, because when it is in equilibrium with its vapor, this liquid phase seems to extend, according to all evidence available at the present time, down to absolute zero. As a result, $F(T)$ tends to larger and larger negative values as the temperature tends toward very small values. Both $F(T)$ and $G(T)$ are monotonically increasing functions of the temperature. In liquid He^4, their complementary aspect is clearly expressed by the relations

$$\lim_{T\to 0} F(T)\to -\infty; \quad \lim_{T\to T_c} F(T)=1, \qquad (2.12)$$

and

$$\lim_{T\to 0} G(T)\to -1; \quad \lim_{T\to T_c} G(T)\to\infty. \qquad (2.13)$$

Their common zero is at T_0. The preceding relations indicate that the functions $f(r,T)$ may be expected to be more regular then the $g(r,T)$'s in the interval $T_0 \leqslant T \leqslant T_c$. In certain applications of these functions, the use of the $f(r,T)$'s, when alone, might become necessary in preference to the $g(r,T)$ functions.

Since the $f(r,T)$ functions are only available in tabular form over a necessarily finite separation range r, the complete space integrals $F(T)$ cannot be obtained with them. One has to calculate the generalized integrals

$$F(r,T)=\int_0^r 4\pi r^2 f(r,T)dr. \tag{2.14}$$

These have been computed at the various liquid temperatures over most of the r range over which the $f(r,T)$'s are available. We give in Table I, the values of $F(20\text{ A},T)$ together with their experimental values or $\{1-[n(T)kT\chi_T]^{-1}\}$. A glance at the table shows that the $f(r,T)$ functions satisfy rather well their space integral test. Clearly, since this is an integral test, it is not justified to infer from it the locally correct character of the functional behavior of the $f(r,T)$'s. On the other hand, these results lend some support to the likelihood that the $f(r,T)$ functions represent, at the present time, the best approximations to the unknown rigorous interaction functions. Clearly, if the space integral checks do not allow for any rigorous justification of the locally correct character of the derived i.f.'s, neither do they allow the drawing of the opposite conclusion. It seems to us that the results of Table I justify at least the not unreasonable conjecture on the fair degree of approximation to the unknown rigorous interaction functions achieved locally, by the results of the present analysis. As mentioned above, the functions derived here are probably worse at close separations.

A second type of integral test applied to the $f(r,T)$ functions consisted in the inversion of the Fourier integrals (2.1), or the calculation of $[1-\Phi(\Delta k,T)]$ or $F_L^{-2}(\Delta k,T)$, Eq. (2.8). Here, again, the generalized integrals

$$\Phi(r,\Delta k,T)=4\pi\int_0^r f(r,T)[\sin r\Delta k/r\Delta k]r^2dr, \tag{2.15}$$

had to be computed. These were obtained at intervals of 0.25 A^{-1} in Δk, from 0.25 to 6.0 A^{-1}, at the two liquid temperatures of 2.06 and 4.20°K. The calculated reciprocal structure factors are given by $[1-\Phi(20\text{ A},\Delta k,T)]$, they are denoted by $F_L^{-2}(\Delta k,T,20\text{ A})$, 20 A being the upper limit of the integrals (2.15). Table II gives the experimental and calculated reciprocal structure factors. The former result from those used in S.D. It will be observed that the interaction functions $f(r,T)$ reproduce fairly well the experimental structure factors, demonstrating the internal consistency and good accuracy of the numerical calculations.

TABLE II. Experimental $F_{L,\text{ exp}}^{-2}(\Delta k,T)$ and calculated $F_L^{-2}(\Delta k,T,20\text{ A})$ reciprocal structure factors at 2.06 and 4.20°K.

Δk, A^{-1}	F_{exp}^{-2} (Δk,2.06°K)	F_L^{-2} (Δk,2.06,20 A)	F_{exp}^{-2} (Δk,4.20°K)	F_L^{-2} (Δk,4.20,20 A)
0.25	11.4	11.4	2.62	2.62
0.50	8.62	8.59	3.33	3.32
0.75	5.81	5.81	3.77	3.78
1.00	3.92	3.94	3.19	3.18
1.25	2.61	2.62	2.23	2.24
1.50	1.74	1.75	1.50	1.50
1.75	1.10	1.06	0.980	0.975
2.00	0.758	0.770	0.781	0.780
2.25	0.787	0.785	0.813	0.813
2.50	0.885	0.879	0.917	0.924
2.75	0.962	0.962	0.990	0.993
3.00	1.00	1.00	1.03	1.03
3.25	1.02	1.02	1.04	1.04
3.50	1.02	1.02	1.03	1.03
3.75	1.00	0.998	1.01	1.01
4.00	0.962	0.957	0.990	0.999
4.25	0.917	0.920	0.952	0.957
4.50	0.901	0.901	0.935	0.934
4.75	0.909	0.907	0.926	0.926
5.00	0.926	0.922	0.926	0.927
5.25	0.943	0.943	0.935	0.930
5.50	0.962	0.966	0.943	0.946
5.75	0.980	0.984	0.980	0.980
6.00	1.000	0.995	1.01	1.01

Some additional properties of the interaction functions will be given in the next section.

3. INTERFERENCE PROPERTIES OF STATIC ATOMIC DISTRIBUTIONS IN LIQUID He^4

Neglecting all effects arising from the relative motion of the atoms of the scattering medium and the incident neutrons, as well as all specific atomic binding effects, the total slow-neutron scattering cross section per liquid atom, in units of the isolated stationary free-atom total scattering cross section σ_f, may be written as[7]

$$\begin{aligned}\sigma_L(k,T)/\sigma_f &= 1+[(1+\mu^{-1})^2/4\pi] \\ &\quad \times\int_0^{\pi/2}[F_L^2(\Delta k,T)-1]2\pi\sin(2\theta)d(2\theta) \\ &= 1+(1+\mu^{-1})^2 I_d(k,T).\end{aligned} \tag{3.1}$$

I_d, the static direct interference integral written in terms of the correlation function $g(r,T)$, becomes the indirect static interference integral, or

$$\begin{aligned}I(k,T) &= \int_0^\infty (\sin kr/kr)^2 g(r,T)4\pi r^2 dr \\ &= I(\lambda,T).\end{aligned} \tag{3.2}$$

Here μ is the mass of the spinless scattering atom in units of the neutron mass. For not too light atoms, $\mu \gg 1$, the bound-atom total scattering cross section σ_∞ or $\sigma_f(1+\mu^{-1})^2 \sim \sigma_f$, and (3.1) reduces to the form con-

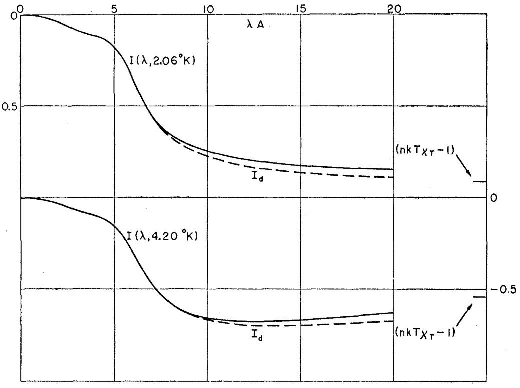

FIG. 3. The direct and indirect interference integrals, $I_d(\lambda,T)$ and $I(\lambda,T)$ as a function of the wavelength λ(A), at 2.06 and 4.20°K.

sidered by us previously.[4] The transformation leading from $I_d(k,T)$, defined in terms of the structure factor F_L^2, to $I(k,T)$ is elementary, requiring simply the expression of the static structure factor[4] $F_L^2(\Delta k,T)$ in terms of the static correlation function $g(r,T)$.

With the exception of neutrons of relatively short wavelength, to be defined more closely below, the interference term in (3.1) is an important element of the total scattering cross section. With the analysis of the liquid He^4 x-ray scattering data of Reekie[3] performed in S.D., we are now in a position to study the interference term in detail. The results which will thus be obtained are, however, of interest not only for liquid He^4 but for any monatomic liquid, as well as for polyatomic liquids, insofar as their intermolecular interference properties are concerned.

The physical assumptions underlying the interference term in (3.1) correspond to neglecting the energy change of the neutron in the scattering as well as to the frozen or static character of the local concentration deviations from the mean concentration. These assumptions are evidently the better justified, the faster are the incident neutrons. With decreasing neutron velocities, the static interference term becomes an increasingly cruder approximation to the actual interference term. Nevertheless, an investigation of the interference integrals is still of great interest for several reasons. One of these stems from the fact that the very long wavelength asymptotic limit of the static interference integral is given by the space integral $G(T)$. If the correct asymptotic behavior is obtained, then an additional integral check has also been achieved on the correlation functions $g(r,T)$. The physical justification of the evaluation of the integrals $I(\lambda,T)$ at medium wavelengths λ will be considered below.

Since terms arising from the neutron-atom relative motion effect cannot but increase the total scattering cross section, (3.1) represents its lower limit, as long as small specific binding effects are neglected.

At sufficiently short wavelengths, replacing $\sin^2 kr$ by its mean value of $\frac{1}{2}$, one obtains with (3.2),

$$\lim_{\lambda\ \mathrm{small}} I(\lambda,T)=\lambda^2 r_G^{(-2)}(T)/8\pi^2, \tag{3.3}$$

where

$$r_G^{(-2)}(T)=\int_0^\infty r^{-2}g(r,T)4\pi r^2 dr \tag{3.4}$$

is the second negative moment of the correlation function. The interference integral vanishes parabolically with neutron wavelength.

We have discussed on various occasions[1,4] the positive even moments of the correlation function. With the known details of $g(r,T)$, it may be expected that $r_G^{(-2)}(T)$ be negative over most of the temperature range, both in liquid He^4 and in normal liquids. However, the possibility that $r_G^{(-2)}(T)$ vanishes at some temperature T_{-2} such that $T_0<T_{-2}<T_c$, and becomes positive in the range (T_c-T_{-2}), cannot be ruled out. There might thus be a small though finite and accessible temperature interval (T_c-T_{-2}), where $I(\lambda,T)$ would be positive at short wavelengths, leading thus to a total scattering cross section per liquid atom larger than the isolated free-atom cross section. Such an effect, if observed, would be a manifestation of the longer-wavelength critical neutron opalescence phenomenon discussed by us some time ago.[5] Using the previously obtained[1] $g(r,T)$ functions, we have calculated the second negative moments $r_G^{(-2)}(T)$ at a series of liquid temperatures. These are given in Table III. They all correspond to the integrals (3.4) extended to the upper limit of 20 A. These integrals converge rapidly so that their limiting values are already achieved at about 10 A. The slight jump in the values of these moments between 2.75 and 3.01°K is associated with the approximate character of the correlation functions in passing from the low-temperature region, $T\leqslant 2.75$°K, to the high-temperature region, $T\geqslant 3.01$°K, as discussed in S.D., where the preceding division of the explored temperature interval is fully defined.

Replacing (3.3) in (3.1), one obtains

$$\lim_{\lambda\to 0}\sigma_L(\lambda,T)/\sigma_f=1+[(1+\mu^{-1})^2/8\pi^2]\lambda^2 r_G^{(-2)}(T), \tag{3.5}$$

the asymptotic short-wavelength total scattering cross section. It is, of course, of evident interest to compare the asymptotic cross-section formula with the rigorous one, Eq. (3.1), where the interference term is computed exactly. This comparison, whose details need not be given here, shows that the asymptotic formula is quite acceptable out to λ equal to about 4 A at all the liquid temperatures here investigated, or at $1.25\leqslant T\leqslant 4.20$°K. It should be noted that for heavier liquids, where μ^{-1} becomes small, the asymptotic formula may become valid out to somewhat longer wavelengths.

We give in Fig. 3 two indirect interference integrals as a function of the wavelength at the two representative temperatures of 2.06 and 4.20°K. The interference integral vanishes, of course, in the limit of vanishing wavelength. It decreases from this limit slowly at first, in the range of about $\lambda \leqslant 2$ A, and at an increasing rate for somewhat larger λ. The slight wiggles at short wavelengths can be traced essentially to the approximate angular shape of the $g(r,T)$ functions, at small separations, which was discussed in detail in S.D. It will be seen that in the range $5 \leqslant \lambda \leqslant 9$ A there is a rather rapid drop in the value of the integral, reminiscent of the Bragg edge anomaly. It is connected, of course, to the main peak of the structure factor curves, which were given in S.D. The characteristic rapid drop of $I(\lambda,T)$ will be seen to be sharper at the low rather than at the higher temperature as might have been expected. Beyond the sharp drop, the interference integrals flatten out and reach their asymptotic long wavelength range. We will return below to the discussion of this range of large λ.

We give in the same Fig. 3, the direct interference integrals I_d, beyond about 4 A. These two integrals coincide to about 8–9 A, and deviate slightly from each other at longer wavelengths.

From Eq. (3.1), the direct interference integral is, changing the integration variable,

$$I_d(k,T) = (1/2k^2)\int_0^{2k} [F_L^2(\Delta k,T)-1](\Delta k)d(\Delta k). \quad (3.6)$$

Identifying this with $I(k,T)$, Eq. (3.2), and going over to the limit $\lambda \rightarrow 0$ or $k \rightarrow \infty$, one obtains the theorem

$$r_G^{(-2)}(T) = \int_0^{2k\rightarrow\infty} [F_L^2(\Delta k,T)-1](\Delta k)d(\Delta k), \quad (3.7)$$

which is an expression of the second negative moment of the correlation function $g(r,T)$ in terms of its generating function which is $F_L^2(\Delta k,T)$. A more direct proof of (3.7) can be obtained at once by replacing in the definition (3.4) the c.f., or $g(r,T)$ by its expression in terms of the Δk Fourier integral of the structure factor,[4,1] and integrating over r. Also, the definition of the second negative moment of the interaction function

$$r_F^{(-2)}(T) = \int_0^\infty r^{-2} f(r,T) 4\pi r^2 dr, \quad (3.8)$$

with Eq. (2.1), yields in this way the rigorous relation

$$r_F^{(-2)}(T) = \int_0^\infty [1-F_L^{-2}(\Delta k,T)](\Delta k)d(\Delta k). \quad (3.9)$$

The knowledge of the second negative moment $r_G^{(-2)}(T)$, Eq. (3.7), directly through the structure factor is, in principle, a great advantage for the use of the asymptotic short wavelength limit (3.5) of the interference integral. Actually, the problem is more complicated. The complication arises from the empirical character of the structure factor, the precision of which decreases with increasing Δk values. With the physical condition[1,4] imposed upon the $g(r,T)$ functions at small separations r, and above all at $r \rightarrow 0$, one, indirectly, modifies the empirical structure factors at large Δk values. Hence, the second negative moments obtained with carefully derived correlation functions should be, under these conditions, more satisfactory than those calculated directly with the uncorrected structure factors using (3.7). If the experimental structure factors had been obtained with precision over a large Δk interval, one might have expected to verify with them the correct limit of $g(r,T)$ as $r \rightarrow 0$, and also to derive with them the fairly well approximated second negative moments $r_G^{(-2)}(T)$ or $r_F^{(-2)}(T)$. At the present time, the indirectly obtained moments given in Table III are more accurate than those which result from the theorems expressed by (3.7) or (3.9).

TABLE III. Second negative moments $r_G^{(-2)}(20\text{ A},T)$ of the correlation functions $g(r,T)$ at various temperatures.

T°K	$-r_G^{(-2)}(20\text{ A},T)$ A^{-2}
1.25	0.633
1.50	0.633
1.75	0.633
2.06	0.634
2.25	0.634
2.50	0.629
2.75	0.620
3.01	0.625
3.25	0.613
3.50	0.597
3.75	0.577
3.97	0.559
4.20	0.539

In comparing now the direct interference integral $I_d(k,T)$, Eq. (3.6) and the indirect interference integral $I(k,T)$, Eq. (3.2), the former is, evidently, to be preferred to the latter, with the exception of the region of the short wavelengths or large k values, as we have just shown. Since $I_d(k,T)$ is preferable, with the above exception, to $I(k,T)$, the question arises as to the usefulness of the latter. It is, however, easy to see that the studies of $I(k,T)$ lead to two different types of results concerning the correlation function. One of these concerns an additional integral check on $g(r,T)$ as expressed by (3.2). In Fig. 3 we have a graphical illustration, at two liquid temperatures, of the over-all correct character of the c.f.'s. It will be seen that at the longer wavelengths, the largest deviations between I_d and I amount to at most five percent. Below 4 A, I_d becomes unreliable as discussed above. In view of the multiple uses[1] of the $g(r,T)$'s in the evaluation of various properties of the liquid, such an additional check on the correlation function is of evident interest. It will be noted that the indirect interference integrals tend to approximate (but to be somewhat greater than) the more correct direct interference integrals at the longer wavelengths.

Another type of result included in the indirect interference integrals consists in their yielding the extension of the spatial regions, around the origin atom, which contribute effectively to the scattering process through their concentration deviations from the mean. In the numerical calculations here performed, one indeed obtains the generalized interference integrals

$$I(\lambda,T,r)=\int_0^r\left[\frac{\sin(2\pi r/\lambda)}{2\pi r/\lambda}\right]^2 4\pi r^2 g(r,T)dr, \qquad (3.10)$$

as a function of the variable upper limit r. The very form of the indirect interference integrals proves that their destructive character, over the whole temperature range here investigated, results predominantly from the existence of the hole in the atomic distribution around any atom within the liquid, which atom was chosen arbitrarily to be at the origin of the coordinate system. Of course, the positive concentration deviations from the mean, or the hills in the atomic distribution, tend at larger separations to minimize, through their constructive interference effects, the large destructive effects arising from the density defects at close separations. At a given temperature, the shorter the wavelength the smaller is the spatial region, around the origin atom, the atoms of which take an active part in the scattering process. This region is seen to increase in size with increasing wavelengths. In the limit of λ very large, or k very small, one has from (3.10),

$$\lim_{\lambda\text{ large}} I(\lambda,T,r)=G(r,T), \qquad (3.11)$$

which was shown to oscillate[1] out to quite large separations r. Clearly, the preceding spatial properties of the indirect interference integral do not appear in their direct evaluation through $I_d(k,T)$.

We should like to discuss briefly the behavior of the interference integrals in the asymptotic long-wavelength or small wave-vector region. Remembering the parabolic approach[1,4] of $F_L{}^2(\Delta k,T)$ in Δk toward its limit $F_L{}^2(0,T)$ or $n(T)kT\chi_T$, (3.6) leads to

$$\begin{aligned}\lim_{k\to0} I_d(k,T)&\cong[F_L{}^2(0,T)-1](1/2k^2)\int_0^{2k}(\Delta k)d(\Delta k)\\ &=n(T)kT\chi_T-1, \end{aligned}\qquad (3.12)$$

showing that $I_d(k,T)$ has the same limit at vanishing k as $[F_L{}^2(\Delta k\to 0,\, T)-1]$. The same result obtains, of course, with (3.2), since

$$\begin{aligned}\lim_{k\to0} I(k,T)&=\int_0^\infty 4\pi r^2 g(r,T)\\ &=G(T)\\ &=n(T)kT\chi_T-1. \end{aligned}\qquad (3.13)$$

In order to obtain now the more detailed behavior of the interference integrals at small k, one has but to expand $(\sin x/x)^2$ in $I(k,T)$, Eq. (3.2), and keep the first two terms. This yields

$$\begin{aligned}\lim_{k\text{ small}} I(k,T)&=G(T)-\tfrac{1}{3}k^2 r_G{}^{(2)}(T)\\ &=n(T)kT\chi_T-1-\frac{4\pi^2}{3}(r_G{}^{(2)}(T)/\lambda^2), \end{aligned}\qquad (3.14)$$

where the first equation, expressing the parabolic approach of $I(k,T)$ in k toward its limit $I(0,T)$, is quite similar to the parabolic approach of the difference $F_L{}^2(\Delta k,T)-1$ in Δk toward its limit $[F_L{}^2(0,T)-1]$ or $[n(T)kT\chi_T-1]$, according to

$$\lim_{\Delta k\text{ small}}[F_L{}^2(\Delta k,T)-1]=G(T)-\tfrac{1}{6}(\Delta k)^2 r_G{}^{(2)}(T). \qquad (3.15)$$

Since, as shown in S.D., at $T\leqslant T_2$, $r_G{}^{(2)}(T)<0$, and at $T\geqslant T_2$, $r_G{}^{(2)}(T)>0$, it will be seen that as a function of λ, for instance, $I(\lambda,T)$ approaches its limit from above at $T\leqslant T_2$, while the approach is from below at $T\geqslant T_2$. But since $I(\lambda,T)$ vanishes parabolically from below at $\lambda\to0$, and since it approaches its very long wavelength limit $\lambda\to\infty$ from below also, it must have at least one minimum in the wavelength interval, at $T\geqslant T_2$. This is exhibited clearly in Fig. 3. The characteristic temperature T_2 was shown[1] to be in the range 2.25–2.50°K.

A special discussion of the interference integral is now needed in the vicinity of the critical temperature. Because of the anomalous behavior of the correlation function, it is indicated here to use the expression of the structure factor in terms of the interaction function whose behavior is normal at the approach of the critical temperature. One has here[4]

$$\begin{aligned}\lim_{T\to T_c,\ \Delta k\text{ small}} F_L{}^2(\Delta k,T)-1&\sim\lim F_L{}^2(\Delta k,T)\\ &=n(T)kT\chi_T[1+\tfrac{1}{6}n(T)kT\chi_T(\Delta k)^2 r_F{}^{(2)}(T)]^{-1}. \end{aligned}\qquad (3.16)$$

Replacing (3.16) in (3.1) or (3.6) and integrating, one finds

$$\begin{aligned}\lim_{T\to T_c,\ k\text{ small}} I_d(k,T)\\ =(\tfrac{3}{2}k^2 r_F{}^{(2)}(T))^{-1}\ln[1+\tfrac{2}{3}n(T)kT\chi_T k^2 r_F{}^{(2)}(T)]. \end{aligned}\qquad (3.17)$$

However, the full use of the preceding result[8] to obtain the k or λ behavior of $I_d(k,T)$ could be misleading. This is so because (3.16) is valid only under the assumption that the $(\Delta k)^2$ term in its denominator is large in comparison with the next term, which is proportional to $(\Delta k)^4$, in an alternating infinite series.[4] The $(\Delta k)^2$ term is assumed to be large compared to the sum of the terms of order higher or equal to the fourth in (Δk). Hence, (3.17) is actually valid only up to terms in k^2, or one has to

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[8] This was also obtained in reference 6 in an entirely different way.

expand (3.17) and write

$$\begin{aligned}\lim_{T\to T_c,\ k \text{ small}} & I_d(k,T)\\ &= n(T)kT\chi_T[1-\tfrac{1}{3}n(T)kT\chi_T k^2 r_F^{(2)}(T)]\\ &= n(T)kT\chi_T-\tfrac{1}{3}k^2 r_G^{(2)}(T), \qquad (3.18)\end{aligned}$$

which is identical to what one obtains directly with (3.15), provided one uses the rigorous relation,

$$r_G^{(2)}(T)=r_F^{(2)}(T)n(T)kT\chi_T, \qquad (3.19)$$

between the second positive moments[4,9] of the correlation and interaction functions. In the limit, $k\to[1/r_G^{(2)}(T)]^{\frac{1}{2}}\to 0$, (3.18) reduces to $n(T)kT\chi_T$, which may be called the optical or radiation limit. Hence, as far as the static interference integral is concerned, its approach toward the limit $k\to 0$ is strictly parabolic at all temperatures. At the approach of the critical temperature the slope dI/dk at $k\to 0$ becomes very large because $r_G^{(2)}(T)\to\infty$ at $T\to T_c$. To the approximation of the static interference integral, the critical opalescence of very slow neutrons[5] is expressed essentially by the first term on the righthand side of Eq. (3.18) or the isothermal mean square fluctuation per atom of the total number of atoms of the system, that is, $\langle\Delta N^2\rangle_{\text{Av}}/N$.

We have to discuss finally the limitations on the validity of the static interference integral at decreasing wave numbers k or increasing wavelengths λ of the slow neutrons. As far as the collective portion of the slow-neutron scattering process is concerned, the assumption of the frozen or static atomic concentration deviations from the mean $n(T)$, defined by $g(r,T)$, is equivalent to neglecting completely the energy exchange between the neutron and the collection of the scattering atoms forming the scattering system. For short collective interaction times of the neutron and the liquid τ, which might be estimated to be of the order of l/v, l being some length over which $g(r,T)$ is appreciable, the use of a frozen or static correlation function is equivalent to assuming the existence of a group of rigidly connected atoms. Hence, in the collective part of the scattering process, the energy transferred to this massive system is indeed negligible. With decreasing neutron velocities, τ increases and when it becomes of the same order of magnitude or larger than some characteristic time of the liquid which is a measure for the time needed for the concentration deviations to be built up or to disappear, the apparent "rigidity" of the interatomic correlations loses its significance. As a result, the energy change of the neutrons in the collision becomes more and more significant and affects now the collective or interference part of the scattering cross section. The effect of the energy change of the neutrons on the interference integral may be expected to decrease the numerical value of the static interference integral. At liquid temperatures such that $T\lesssim T_0$, the static interference integral is likely to be negative, at not too short neutron wavelengths, and will tend to underestimate the collective part of the total scattering cross section. At $T>T_0$, at the same neutron wavelengths, the opposite situation might be expected to prevail. At any rate, slower and slower neutron scattering processes, in liquids for instance, involve relaxation type of time effects in their formal description, as first pointed out by Van Hove.[6] A method of evaluating the generalized dynamic or time dependent correlation function $g(r,T,t)$ has also been given. However, a correct evaluation of the characteristic liquid times, which are expected to be temperature dependent, presents a problem as yet unsolved. Hence to find, for a given liquid at a given temperature, that critical neutron velocity below which the static approximation to the interference integral starts to lose its validity, is itself a problem whose correct solution is closely tied to the liquid characteristic relaxation time problem. The length l mentioned above may be taken approximately to be the square root of the second positive moment $[r_G^{(2)}(T)]^{\frac{1}{2}}$ of the static correlation function, at least at those liquid temperatures where this quantity is reasonably well defined. We have seen that this is not the case in the vicinity of the characteristic temperature T_2. In a temperature interval containing T_2, the approximate definition of the length l is to be completed possibly with the help of some other moments of $g(r,T)$, such as $r_G^{(-2)}(T)$ or $r_G^{(4)}(T)$, for instance.

A particularly interesting situation arises at the approach of the critical temperature. Here, the order of magnitude of the momentum change of the neutron on scattering arising from the collective effect of the liquid atoms is defined essentially by the characteristic structural length $[r_G^{(2)}(T)]^{\frac{1}{2}}$, through $\hbar[r_G^{(2)}(T)]^{-\frac{1}{2}}$ or, in virtue of (3.19), by $\hbar[r_F^{(2)}(T)n(T)kT\chi_T]^{-\frac{1}{2}}$, which quantity is small and tends to vanish as $T\to T_c$. As a result the neutron energy change on scattering is considerably reduced, which circumstance reestablishes the validity of the static approximation to the interference integrals at all wavelengths. However, this situation is claimed[6] to be valid only in an extremely small temperature interval near the critical temperature. Hence the static interference integral coincides with the dynamic one at short and medium wavelengths, it deviates from the latter at longer wavelengths, at all temperatures, with the exception of the point-like interval near T_c, where the two expressions are always identical. This result suggests that the static interference integral might be at least a crude approximation to the dynamic one at those wavelengths and temperatures where the latter is the only one which is physically justified.

4. AVERAGE KINETIC ENERGIES AND ROOT MEAN SQUARE FORCES PER ATOM IN LIQUID He^4

We should like now to further exploit the results obtained in S.D. on the approximate evaluations of the

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[9] L. S. Ornstein and F. Zernike, Physik. Z. **19**, 134 (1918). The relation between the even positive moments $r_G^{(2n)}$ and $r_F^{(2n)}$ is given in reference 4.

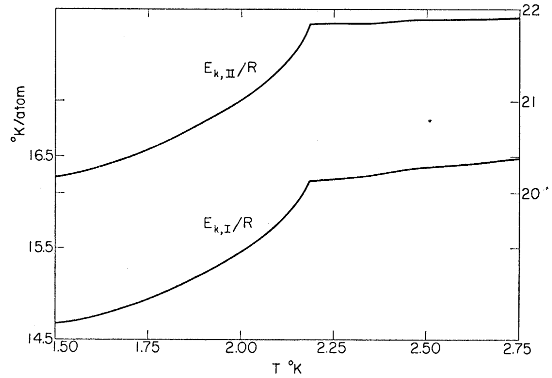

FIG. 4. Mean kinetic energies $E_{k,\mathrm{I}}(T)/R$ and $E_{k,\mathrm{II}}(T)/R$, (°K/atom), as a function of the liquid temperature (°K).

average potential energies per atom at the various liquid temperatures. With the rather well founded expression of the total energy per atom,

$$E(T)=E_k(T)+\Phi(T), \qquad (4.1)$$

where $\Phi(T)$ is the ensemble average of the potential energy per atom, exchange energy included, based on the pair approximation, it becomes possible to compute the mean kinetic energies $E_k(T)$. Here, the liquid energies $E(T)$, or the binding energies taken with the negative sign, are available experimentally, omitting the small pressure-liquid volume product, through

$$E(T)=-L(T)+\epsilon(T), \qquad (4.2)$$

where $L(T)$ is the latent heat per atom and $\epsilon(T)$ the total enthalpy, per atom, of the saturated vapor in equilibrium with the liquid at the temperature T. Keeping only the second virial coefficient in the thermal equation of state of the He^4 vapor, a procedure largely justified by Keller[10] at least below about 4°K, one obtains therefrom the vapor volume $V(T)$, with

$$pV=RT[1+(B(T)/V)], \qquad (4.3)$$

which volume is then introduced into the enthalpy equation

$$\epsilon(T)=kT[5/2-(T/V)(dB/dT)+(B/V)]. \qquad (4.4)$$

In (4.3) and (4.4) the second virial coefficients measured recently by Keller[10] in this Laboratory, as well as the empirical function $B(T)$ and its extrapolation[11] below 2°K have been used. In contrast with the vapor energies per atom $\epsilon(T)$, the latent heats at $T\leqslant 2.50$°K are of questionable accuracy, above all around the lambda point. In this low-temperature range the calculated latent heats[12] have been made use of. These calculated latent heats seem to reproduce well the experimental ones.[13] Above 2.75°K, more accurate latent heats became available recently.[14] The energies $\Phi(T)$ depend on the analytical approximation of the mutual potential energy of a pair of isolated stationary He^4 atoms as well as on the pair distribution functions $n(r,T)$ derived in S.D. In the vicinity of the lambda point, both the latent heats and the energies $\Phi(T)$ correspond to interpolated values. The kinetic energies thus calculated are quite approximate and carry automatically the uncertainties in the energies $\Phi(T)$ and $L(T)$. We give in Fig. 4 these average kinetic energies in the interval 1.50–2.75°K. The energies $E_{k,\mathrm{I}}(T)$ and $E_{k,\mathrm{II}}(T)$ are associated with the two approximations to the mean potential energies $\Phi_{\mathrm{I}}(T)$ and $\Phi_{\mathrm{II}}(T)$ which were discussed in detail in S.D.

It will be observed that these approximate kinetic energies per atom of the saturated liquid exhibit the expected angular point at the normal lambda temperature. This provides a quantitative sharpening of the qualitative proof given previously,[1] for the kinetic energy origin of the lambda transition in liquid He^4. The crude lambda discontinuities of both kinetic heat capacities $(dE_{k,\mathrm{I}}/dT)$ and $(dE_{k,\mathrm{II}}/dT)$ amount to about $5.5-6.0R$. It seems reasonable to expect that while the kinetic energies themselves, for a given potential energy set $\Phi(T)$, are quite approximate, their temperature derivatives be cruder approximations to the correct kinetic heat capacities. It turns out that the two types (I) and (II), of kinetic heat capacities are quite close to each other below the lambda point; their differences above T_λ are larger, as was to be expected from the previously[1] calculated potential heat capacities at these temperatures.

The very large values of both approximate kinetic energies $[E_{k,\mathrm{I}}(T)/R]$ and $[E_{k,\mathrm{II}}(T)/R]$ in comparison with the liquid temperatures T prove that they are essentially zero-point kinetic energies. Only a relatively small fraction of these kinetic energies appears to be of thermal excitation origin, in agreement with the values of the small empirical thermal energies $\int^T c(T)dT$, evaluated with the total heat capacity $c(T)$. Although only semiquantitative and indirect, the kinetic energies here obtained provide an interesting demonstration of the existence of a large zero-point kinetic energy at all the liquid temperatures investigated $1.25\leqslant T\leqslant 4.20$°K. Improved values of pair distribution functions, a decision on the best pair potential energy approximation as well as better latent heat values should lead, of course, to a unique and closer approximation of liquid He^4 kinetic energies.

The estimated zero-point kinetic energies per atom, resulting from extrapolating the kinetic energy curves toward low temperatures, are about 13 and 18°K, associated, respectively, with the potential energies $\Phi_{\mathrm{I}}(T)$ and $\Phi_{\mathrm{II}}(T)$.

In analogy with the calculation of the mean potential energies per atom in terms of the pair distribution functions $n(r,T)$, it appears interesting to evaluate the

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[10] W. E. Keller, Phys. Rev. **90**, 1 (1955).

[11] Kilpatrick, Keller, and Hammel, Phys. Rev. **97**, 9 (1955).

[12] J. Kistemaker, Physica **12**, 281 (1946).

[13] W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), pp. 229–232.

[14] R. Berman and J. Poulter, Phil. Mag. [7], **43**, 1047 (1952).

mean forces per atom. This will be done here through the calculation of the mean square force, yielding the root mean square force.[15] Beside being of intrinsic interest, this quantity is of some importance in a direct analysis of slow-neutron scattering processes in liquids in general, and in liquid He^4 in particular.

Let $f(r)$ be the force acting on an atom of a pair of isolated stationary atoms separated by the distance r. Assuming that this force originates in the pair potential energy $\varphi(r)$, of purely central character, we have, by definition,

$$\begin{aligned} f(r) &= -\operatorname{grad}\varphi(r) \\ &= -d\varphi/dr. \end{aligned} \tag{4.5}$$

The differential mean square force in the liquid due to the distribution existing at a distance r from the origin atom is, omitting the cross term depending on the unknown three-atom distribution function $n(r,r',T)$,

$$dF^2(r,T) = 4\pi r^2 f^2(r) n(r,T) dr, \tag{4.6}$$

and the total mean square force, in the pair representation approximation, is

$$F^2(T) = 4\pi \int f^2(r) n(r,T) r^2 dr, \tag{4.7}$$

the integral being extended over the whole volume of the system. Since the pair distribution functions $n(r,T)$ include exchange effects, the mean square forces $F^2(T)$ also include these effects. With the $n(r,T)$ functions available in tabular form, out to the extreme separation of $r = 20$ A, only the generalized square force integrals $F^2(r,T)$ can be obtained. These are functions of the upper limit r in the integrals (4.7). Using the two analytical approximations to the pair potential energies $\varphi_{\mathrm{I}}(r)$ and $\varphi_{\mathrm{II}}(r)$, defined previously,[1] we have obtained the mean square forces $F^2(20\text{ A},T)$ at a series of liquid temperatures. The effective ranges of the square forces $f_{\mathrm{I}}^2(r)$ and $f_{\mathrm{II}}^2(r)$ being moderate, the integrals (4.7) converge very rapidly, indicating that these mean square forces are determined, for all practical purposes, by the details of their fields extending over separations of the first neighbor atoms, at most. We give in Table IV, the root mean square forces $[F_{\mathrm{I}}^2(20\text{ A},T)]^{\frac{1}{2}}$ and $[F_{\mathrm{II}}^2(20\text{ A},T)]^{\frac{1}{2}}$. These two series of root mean square forces differ from each other as expected from the shapes of the potential energy functions $\varphi_{\mathrm{I}}(r)$ and $\varphi_{\mathrm{II}}(r)$. The former, being higher than the latter, gives rise to steeper gradients than the latter. The origin of the slight jumps in the values of these forces in passing from the low, $T \leqslant 2.75$°K, to the high temperature group, $T \geqslant 3.01$°K, has been discussed in S.D., and was already referred to above. Over the temperature range 1.25–4.20°K, the forces $(F_{\mathrm{I}}^2)^{\frac{1}{2}}$ and $(F_{\mathrm{II}}^2)^{\frac{1}{2}}$ first increase up to the lambda point, and then decrease beyond it with increasing temperatures, if the jump at 2.75–3.01°K is disregarded as it should be. The forces $(F_{\mathrm{I}}^2)^{\frac{1}{2}}$ are close to about 110 cal/mole×A, and the $(F_{\mathrm{II}}^2)^{\frac{1}{2}}$ forces are grouped around 80 cal/mole×A.

TABLE IV. Root mean square forces in liquid He^4 at various temperatures.[a]

T °K	$(F_{\mathrm{I}}^2(20\text{ A},T))^{\frac{1}{2}}$ cal/mole ×A	$(F_{\mathrm{II}}^2(20\text{ A},T))^{\frac{1}{2}}$ cal/mole ×A
1.25	115.0	83.3
1.50	115.2	83.6
1.75	115.2	83.6
2.06	117.3	85.1
2.25	117.3	85.1
2.50	115.5	83.8
2.75	113.4	82.3
3.01	125.4	89.8
3.25	122.2	87.6
3.50	118.8	85.2
3.75	115.0	82.5
3.97	111.0	79.5
4.20	105.3	75.6

[a] These are evidently approximate because of the omission of the cross term $\int f(r) f(r') n(r,r',T) dv(r) dv(r')$ in Eq. (4.7). Lack of information on $n(r,r',T)$ prevents one from estimating the value of the cross term, at the present time.

The problem of the closeness of either series of forces to the actual root mean square forces is of course similar to the corresponding problem of the potential energies $\Phi_{\mathrm{I}}(T)$ and $\Phi_{\mathrm{II}}(T)$. At the present time, no well-justified decision is available on the degree of fitness of the original analytical approximations to the pair potential energies of two isolated He^4 atoms, $\varphi_{\mathrm{I}}(r)$ and $\varphi_{\mathrm{II}}(r)$. There appear to be indications,[11] as far as the helium vapor second virial coefficient is concerned, that $\varphi_{\mathrm{II}}(r)$ tends to overestimate, in absolute value, the pair potential energy. The problem of the degree of approximation achieved on the pair forces, $[-\operatorname{grad}\varphi_{\mathrm{I}}(r)]$ and $[-\operatorname{grad}\varphi_{\mathrm{II}}(r)]$, was not raised so far, because the intervention of the forces, in the rather fragmentary status of the theory of liquids, seemed to be remote. However, as first shown by Placzek,[7] the investigation of slow neutron scattering phenomena in liquids may put the force problem to the fore, adding thus a new elementary physical quantity to be probed in liquids.

In concluding, I should like to thank Mr. Max Goldstein for his kind cooperation in coordinating the various numerical calculations. Thanks are due to Mr. P. E. Harper for his work on the "701" IBM Electronic Calculator, to Miss M. L. Johnson and Mrs. J. E. Powers for the many hand calculations, to Mrs. A. M. Snowden and Mrs. L. E. Moss for the preparation of the graphs.

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[15] These calculations originated in the discussions with Dr. H. S. Sommers, Jr., of the Los Alamos slow-neutron scattering data in liquid He^4. See Sommers, Dash, and Goldstein, Phys. Rev. **97**, 855 (1955).