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[18]Two of the sources of error in Monte Carlo calculations are the statistical error, associated with the fact that chains of finite length are used, and the statistical-mechanical error, associated with the fact that only a finite number of particles are used. A third source of error in our use of Monte Carlo hard-sphere data results from the empirical formulas employed to fit the data. Verlet and Weis (Ref. 6) estimated the statistical error of their hard-sphere calculation to be of the order of 0.01 in $g_d(r)$. Their empirical fit, Eq. (C1), differs from their Monte Carlo results by at most 0.03. An estimate of the statistical-mechanical error can be obtained by comparing Monte Carlo hard-sphere calculations of two groups of investigators using different numbers of particles. When we compare the Verlet and Weis empirical

$g_d(r)$ (calculated for 864 particles) with the results of Barker and Henderson (~ 100 particles) [Mol. Phys. (to be published)], we find that at high densities the Barker-Henderson peak heights are lower (by as much as 0.08 at $\rho d^3 = 0.85$) and that near $r = 1.5d$ the Barker-Henderson values for $g_d(r)$ are higher by around 0.03.

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X-Ray Determination of the Static Structure Factor of Liquid Na and K

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Highly accurate x-ray diffraction measurements are presented for the static structure factor $a(q)$ for liquid Na (at 100 and 200 °C) and liquid K (at 65 and 135 °C). A detailed error analysis is presented showing that the over-all root-mean-square error in $a(q)$ never exceeds 2.5% for any value of the momentum transfer q and the relative root-mean-square error in $a(q)$ between different temperatures is always less than 1.5%. We discuss and demonstrate the reliability of the tabulated values for the atomic form factor and the Compton-scattering correction. A brief discussion is included of the relative merits of x-ray vs neutron diffraction for obtaining the static structure factor.

I. INTRODUCTION

In recent years it has become recognized that one of the most important quantities characterizing a liquid metal is the static structure factor. A detailed knowledge of this quantity is essential for a quantitative understanding not only of the structure of the liquid, but also of numerous other properties of liquid metals and alloys. These include, for example, transport coefficients, electronic structure, and the dynamical properties of the ions.

There have been many previous measurements of the static structure factor $a(q)$ for a large number of liquid metals. However, the theory of liquid metals has now progressed to the point where a more precise determination of $a(q)$ is essential. To this end, we have made careful measurements of the x-ray diffraction pattern of liquid Na and K as a function of temperature,

and from these data we have obtained $a(q)$. We used a transmission geometry in order to achieve much higher accuracy than heretofore in the low-q region for q ($= 4\pi\lambda^{-1}\sin\theta$) down to 0.3 Å^{-1}. It is precisely this low-q region which is relevant to the current theory[1-4] of the transport coefficients of monovalent liquid metals.

Although there exist previous determinations[5-8] of $a(q)$ for Na and K, major emphasis had been concentrated on obtaining the structure of the peaks, and these previous data are not reliable in the low-q region. Even more serious is the fact that they disagree rather markedly with each other over the entire range of q.

In Sec. II, we present a discussion of the procedure employed to obtain $a(q)$ from the raw data. Two of the important steps in this procedure are the subtraction of the Compton scattering and the division by the square of the atomic form factor. There exists a controversy regarding the accuracy

of the calculated values of these two quantities. In Sec. III, we show that the calculated values are, in fact, in complete agreement with the latest experiments which are accurate to 1%. A comparison is made in Sec. IV of some of the relative advantages of x-ray diffraction over neutron diffraction as a means of determining $a(q)$. In Sec. V, the data for $a(q)$ are presented, together with a detailed error analysis. Finally, in Sec. VI, we compare our results to those of previous measurements.

II. TREATMENT OF DATA

It is important to recognize that $a(q)$ is not directly accessible through diffraction experiments. A number of important corrections must be applied to the raw data to obtain $a(q)$. These include corrections for empty-cell scattering, absorption, polarization, and Compton (incoherent) scattering, as well as normalization and division by the square of the atomic form factor. At each step in this process, care must be exercised to minimize errors. Indeed, it has been suggested[9,10] that it is not possible using x rays to obtain reliable data for $a(q)$, especially in the low-q region, because of the alleged large uncertainty introduced by the corrections which must be applied to the raw data. However, we shall show[11] that the error introduced thereby is negligible.

Our $a(q)$ data for Na were taken using monochromatic Cu $K\alpha$ radiation and Mo $K\alpha$ radiation in a transmission geometry. The experimental aspects have already been described in detail.[12] The use of two different wavelengths served as a check on the consistency of the data. For K, the absorption of Cu radiation is very high, even for our thinnest samples. Therefore, only Mo radiation measurements were carried out for K. Another check on the internal consistency of the data was obtained by the use of sample cells of differing thicknesses.

For both the full and empty cells, at each temperature data were taken at $\frac{1}{4}°$ intervals from $2\theta = 1.75°$ to $2\theta = 60°$. Empty-cell data were taken at constant time per point of typically 1500 sec. This provided a higher number of counts and greater accuracy at low angles where the empty-cell correction is proportionately larger and more important. Full-cell data for Na were taken at constant count per point of typically 40 000 counts up to $2\theta = 40°$ and 10 000 counts thereafter. For K, about $\frac{1}{3}-\frac{1}{2}$ as many counts per point were taken because of the lower intensity. Taking an equal number of counts per point gives equal counting statistics for both the low-intensity region below the first peak, as well as the much more intense region of the first three peaks. Several passes were made at each temperature.

The corrections for empty-cell scattering and absorption by the sample, as well as self-absorption of the sample scattering, were applied in the standard way for a flat transmission geometry using a thin-walled Be container. The product of the absorption coefficient times sample thickness was obtained by direct measurement of the sample *in situ*, rather than relying on handbook values for the absorption coefficient. Applying the absorption and empty-cell correction with the appropriate geometrical factor resulted in a fairly smooth curve even at the position of the main Be peaks. Moreover, the absorption and empty-cell corrections (which include the correction for low-angle air scattering) resulted in a curve which extrapolates smoothly towards the known value at $q = 0$. The fact that the same expressions for the absorption correction give good results both at the Be peaks as well as at the low-q values serves as a confirmation of the choice of absorption factor.

Normalization was carried out in the standard way by a computer iteration procedure. Even though small coherent oscillations persist out to high angles, the baseline of these oscillations and thus the normalization of the data could be unambiguously determined to within $\frac{1}{2}$%.

III. ATOMIC FORM FACTORS AND COMPTON SCATTERING

One of the important procedures which must be applied to all x-ray data is division by the square of the atomic form factor $f(q)$. This quantity is determined from calculations based on the electronic wave functions. Egelstaff[10] has contended that using the tabulated values[13] of $f(q)$ leads to significant errors of up to 20% in $a(q)$ as determined from x-ray diffraction data. To quote Egelstaff, "The theoretical uncertainty in $f(q)$ arises from three causes: (i) The free-atom values of $f(q)$ are uncertain to 5%, (ii) the free-atom value is modified in the liquid by several per cent, (iii) the thermal motion modifies $f(q)$ and in particular introduces a small temperature dependence." We shall examine in detail these three points and show that each is unfounded.

Although Egelstaff gives no reference for his first criticism, it is undoubtedly based on several experiments from the early 1960's. At that time, absolute measurements were made of $f(q)$ at the reciprocal-lattice vectors for aluminum,[14] copper,[14] iron,[14] and chromium.[15] The measured values were all 4—5% lower than the tabulated values.[13] However, it has since been shown[16] that these discrepancies were due to deterioration of the powder specimens and porosity effects. More recent experiments have been carried out for copper,[17] iron,[16] nickel,[18] and magnesium.[19] In each case, the agreement with the tabulated value[13] is excellent; the tabulated value always lies within the 1%

error of the experimental measurements[16-19] of $f(q)$.

The second criticism refers to what is commonly called the "solid-state effect." This effect arises from the fact that the electronic wave functions appropriate to a free atom are used for calculating the tabulated values for $f(q)$, whereas the proper electronic wave functions to use are those appropriate to the solid metal or, in our case, to the liquid metal. The core electrons are not affected in going from the free atom to the metallic phase. But, there are substantial changes in the valence- and d-electron wave functions. However, it has been shown both experimentally[16-19] and theoretically[17] that despite the substantial changes in the outer wave functions, the resulting change in $f(q)$ is always small. At $q = 0$, the solid-state effect is identically zero. A calculation of $f(q)$ using wave functions appropriate to metallic copper has shown that the solid-state effect is of order $\frac{1}{2}\%$, varying somewhat as a function of q (see Fig. 2 of Ref. 17). For q equal to a reciprocal-lattice vector, measurements of $f(q)$ have been carried out for Cu as well as for several other metals.[16-19] In each case, the solid-state effect is so small (much less than 1%) that deviations from the tabulated values have not been observed.

The calculation[17] predicting a solid-state effect of order $\frac{1}{2}\%$ was performed for Cu which has 10 d electrons in addition to the valence electron. When one considers Na and K which have no d shell at all and only a single valence electron, it is clear that the solid-state effect for Na and K is totally negligible for all q. Thus, the "several per cent" error in $f(q)$ mentioned by Egelstaff, again without reference, is not in accord with current theory or experiment.

The third criticism which concerns thermal effects on $f(q)$, if correct, would be of special importance to us. We are particularly interested in the detailed temperature dependence of $a(q)$, and even a relatively small temperature dependence of $f(q)$ could lead to a significant error in our results. Egelstaff bases this criticism on the shell model of Cochran[20] which treats the outer shells of the core electrons as polarizable and thus susceptible to thermal motion. On the basis of this model, Cochran and co-workers[21] have analyzed the phonon spectrum of NaI and found excellent agreement with experiment. However, examination of this paper[21] shows that the only polarization that need be considered is that of the iodide ion. As Cochran himself emphasizes, the Na^+ core electrons are so tightly bound that their polarizability is totally negligible and should be ignored. Thus, far from being a problem for x-ray diffraction of liquid metals,

the excellent agreement for NaI serves, if anything, as a confirmation that there is no thermal effect for the $f(q)$ of Na. In any case, the shell model of Cochran is specific to substances with ionic and/or covalent bonding. Therefore, to apply this model to metals is inappropriate.

In summary, we conclude that there is no reason to doubt the accuracy and reliability of the tabulated values of $f(q)$.

There are several important points to be noted regarding the application of the $f(q)$ tables.[13] For the usual measurements of Bragg peaks in the solid, one must multiply the tabulated $f(q)$ values by a temperature-dependent correction factor, usually expressed in the form $\exp(-B\lambda^{-2}\sin^2\theta)$. This takes into account the reduction of the ideal Bragg peaks due to the modest thermal disorder of the atoms in the solid. Moreover, there is a related temperature-dependent correction factor[22] $(1 + \alpha)$ which subtracts out the effect of thermal diffuse scattering. Both of these correction factors are to be applied *only* to measurements of the Bragg-peak intensity. Neither is to be applied to measurements of $a(q)$ for liquid metals. This is because for liquid metals it is precisely the thermal and structural disorder that one is measuring. Finally, one must, of course, take into account the small but by no means negligible dispersion corrections ($\Delta f'$ and $\Delta f''$) to $f(q)$, which are tabulated[13] for the commonly used x-ray wavelengths.

Another important correction consists of subtracting the Compton scattering from the normalized x-ray data. As in the case for $f(q)$, Compton scattering is also determined[13] from calculations based on the free-atom electronic wave functions. Adams and Ashcroft[9] have questioned the validity of these calculations. They point out that measurements by Laval[23] for Al show discrepancies of the order of 50%. The most disturbing aspect of this claim is that the percentage discrepancy is largest precisely in the important low-q region below the first peak in $a(q)$. However, the 1942 measurements of Laval were subsequently repeated by Walker.[24] Walker's detailed measurements of Compton scattering for Al are in *excellent* agreement with the tabulated values.[13] Moreover, his measurements extrapolate smoothly to the known value at $q = 0$. In contrast to these more recent data, the few, widely separated points measured by Laval do not appear to exhibit consistent behavior between the high- and low-q region. In view of the later, more detailed measurements by Walker, we conclude that there is no evidence for a discrepancy between the tabulated values for Compton scattering and the experimental data.

IV. X-RAY SCATTERING VS NEUTRON SCATTERING

As is well known, there is another widely used

experimental method for obtaining $a(q)$, namely, neutron diffraction. The primary advantage of using neutron diffraction is that a knowledge of the atomic-form-factor correction is unnecessary. However, there are two important correction factors which are important for neutron-diffraction data but are negligible for x-ray diffraction data. The first is the correction necessitated by departures from the static approximation, which assumes that all the neutrons are scattered elastically. The early work of Placzek[25] predicted negligible changes[26] in $a(q)$ due to the static approximation. However, Ascarelli and Caglioti[27] have recently contended that the Placzek analysis seriously underestimates the effect of the static approximation for neutron-diffraction data. By using the dynamical structure factor appropriate to a classical liquid, they were able to obtain a quantitative estimate of the errors resulting from the static approximation. They found that these errors introduced significant distortions in $a(q)$, tending to wash out structure.

Applying the Ascarelli-Caglioti correction formula to the case of Na, we find that conventional neutron diffraction distorts the shape of the true $a(q)$ curve, leading to a 7% overestimate of $a(q)$ at the leading edge of the main peak $(q = 1.8 \text{ Å}^{-1})$ and a 2% underestimate of the peak height. It should be noted that the neutron-diffraction data[5] for Na and K ignore this correction. In contrast to the difficult situation for neutron scattering, the static approximation is excellent for x-rays, leading to the negligible error in $a(q)$ of order 10^{-5}.

The second correction which must be applied to neutron data is to subtract contributions resulting from multiple scattering. The common procedure in neutron-diffraction work is to assume that the multiple scattering is isotropic. The justification for this assumption is based on the work of Vineyard,[28] of Cocking and Heard,[29] and of Blech and Averbach.[30] They present approximate formulas for the multiple-scattering correction as a function of q, and in fact, in some of the more recent neutron work,[31] these correction formulas are indeed applied. The over-all conclusion from these papers is that multiple scattering is roughly isotropic for neutron scattering from liquid metals. Thus, the common procedure of subtracting a q-independent constant from the measured intensity is generally satisfactory. However, at low-q, where $a(q)$ itself is very small, multiple scattering is many times larger than $a(q)$. Therefore, even a relatively modest angular dependence in the multiple scattering will lead to a significant percentage error in $a(q)$. In contrast, multiple scattering is unimportant[11] for x-ray diffraction of liquid metals.

For the low-q region, the small value of $a(q)$

presents special experimental difficulties. Our data demonstrate that x-ray diffraction in a transmission geometry can yield much better results for $a(q)$ in this region than neutron diffraction. We illustrate this point in Fig. 1 by comparing the quality of our low-q results for $a(q)$ of Na with one of the most careful neutron-diffraction measurements available. We have chosen for comparison the measurement of Pb by Egelstaff et al.[31] because reliable neutron-diffraction measurements of Na in the low-q region do not exist. For neutron data, there is a much larger counting error at low q because of the very large multiple- and incoherent-scattering contributions which must be subtracted from the observed neutron intensity. The remaining intensity, representing $a(q)$, is several times smaller than the total observed intensity, leading to a large statistical error. Egelstaff et al.[31] report a statistical error ranging from about 50% at $q = 0.4 \text{ Å}^{-1}$ to about 15% at $q = 1.4 \text{ Å}^{-1}$.
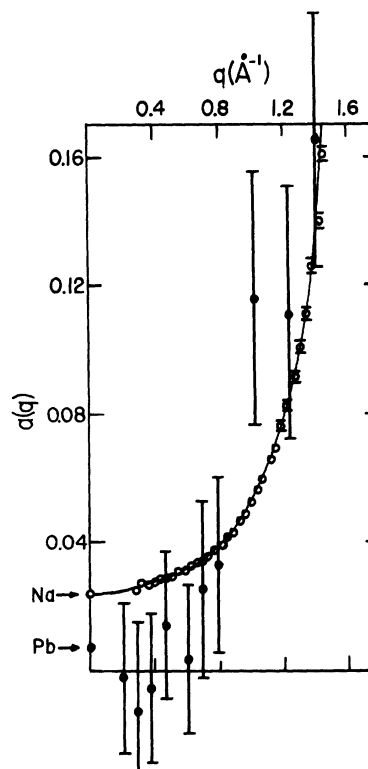

FIG. 1. Comparison of the quality obtainable by x-ray vs neutron-diffraction measurements of $a(q)$ at low q. The open circles refer to our unsmoothed x-ray data points for $a(q)$ for Na at 100°C. The solid circles refer to the unsmoothed neutron data points for Pb measured at 340°C (Ref. 31). The error bars indicate the total error, random plus systematic. For the lowest-q x-ray data points, the error is less than the size of the open circles. The values of $a(0)$, designated by arrows, were obtained from the compressibility sum rule, Eq. (1).

TABLE I. Experimental values of $a(q)$ for Na and K, each at two temperatures.

2θ	q	$a(q)$ (Na) 100°C	200°C	$a(q)$ (K) 65°C	135°C	2θ	q	$a(q)$ (Na) 100°C	200°C	$a(q)$ (K) 65°C	135°C
0.00	0.000	0.0240	0.0322	0.0247	0.0312	18.25	2.80	0.605	0.675	1.125	1.10
0.25	0.039	0.0241	0.0323	0.0251	0.0316	18.50	2.84	0.61	0.675	1.155	1.13
0.50	0.077	0.0243	0.0325	0.0256	0.0321	18.75	2.88	0.62	0.68	1.18	1.145
0.75	0.116	0.0245	0.0328	0.0262	0.0327	19.00	2.92	0.635	0.685	1.195	1.15
1.00	0.154	0.0248	0.0330	0.0269	0.0334	19.25	2.96	0.65	0.70	1.195	1.155
1.25	0.193	0.0251	0.0333	0.0276	0.0342	19.50	3.00	0.67	0.715	1.19	1.155
1.50	0.232	0.0255	0.0336	0.0284	0.0351	19.75	3.03	0.695	0.735	1.185	1.155
1.75	0.270	0.0259	0.0340	0.0292	0.0361	20.00	3.07	0.72	0.755	1.175	1.15
2.00	0.309	0.0264	0.0345	0.0300	0.0371	20.25	3.11	0.75	0.775	1.155	1.145
2.25	0.347	0.0269	0.0350	0.0309	0.0382	20.50	3.15	0.785	0.80	1.135	1.135
2.50	0.386	0.0275	0.0356	0.0319	0.0394	20.75	3.18	0.82	0.825	1.115	1.125
2.75	0.425	0.0281	0.0363	0.0331	0.0408	21.00	3.22	0.86	0.855	1.095	1.11
3.00	0.462	0.0288	0.0371	0.0344	0.0424	21.25	3.26	0.90	0.885	1.07	1.085
3.25	0.501	0.0295	0.0380	0.0358	0.0442	21.50	3.30	0.94	0.92	1.04	1.055
3.50	0.540	0.0304	0.0389	0.0373	0.0462	21.75	3.34	0.985	0.955	1.015	1.03
3.75	0.578	0.0313	0.0399	0.0390	0.0483	22.00	3.37	1.025	0.98	0.99	1.005
4.00	0.617	0.0323	0.0411	0.0409	0.0506	22.25	3.41	1.06	1.01	0.97	0.985
4.25	0.656	0.0334	0.0425	0.0430	0.0532	22.50	3.45	1.095	1.04	0.95	0.965
4.50	0.694	0.0346	0.0441	0.0453	0.0562	22.75	3.49	1.12	1.065	0.935	0.95
4.75	0.733	0.0359	0.0459	0.0479	0.0596	23.00	3.53	1.145	1.085	0.92	0.935
5.00	0.772	0.0374	0.0479	0.0510	0.0635	23.25	3.56	1.165	1.105	0.91	0.925
5.25	0.809	0.0391	0.0501	0.0546	0.0680	23.50	3.60	1.185	1.115	0.90	0.92
5.50	0.848	0.0411	0.0526	0.0588	0.0734	23.75	3.64	1.195	1.125	0.89	0.91
5.75	0.887	0.0434	0.0554	0.0635	0.0799	24.00	3.68	1.205	1.135	0.885	0.905
6.00	0.925	0.0461	0.0585	0.0692	0.0876	24.50	3.75	1.205	1.15	0.875	0.895
6.25	0.964	0.0492	0.0619	0.0764	0.0967	25.00	3.83	1.20	1.15	0.88	0.895
6.50	1.00	0.0526	0.0658	0.0856	0.108	25.50	3.90	1.175	1.14	0.90	0.91
6.75	1.04	0.0564	0.0703	0.0970	0.122	26.00	3.98	1.145	1.12	0.925	0.93
7.00	1.08	0.0606	0.0755	0.112	0.139	26.50	4.05	1.105	1.085	0.955	0.95
7.25	1.12	0.0652	0.0815	0.130	0.161	27.00	4.13	1.065	1.05	0.985	0.98
7.50	1.16	0.0702	0.0884	0.155	0.192	27.50	4.20	1.025	1.01	1.015	1.01
7.75	1.19	0.0760	0.0962	0.187	0.229	28.00	4.28	0.98	0.975	1.04	1.03
8.00	1.23	0.0828	0.105	0.226	0.277	28.50	4.35	0.94	0.955	1.045	1.04
8.25	1.27	0.0908	0.115	0.279	0.338	29.00	4.43	0.905	0.935	1.05	1.04
8.50	1.31	0.100	0.127	0.352	0.43	29.50	4.50	0.88	0.92	1.055	1.04
8.75	1.35	0.111	0.141	0.45	0.56	30.00	4.58	0.875	0.91	1.05	1.04
9.00	1.39	0.125	0.157	0.62	0.74	30.50	4.65	0.875	0.915	1.04	1.035
9.25	1.43	0.141	0.175	0.87	0.98	31.00	4.73	0.885	0.92	1.025	1.025
9.50	1.46	0.161	0.198	1.20	1.29	31.50	4.80	0.895	0.93	1.01	1.02
9.75	1.50	0.185	0.228	1.61	1.67	32.00	4.87	0.91	0.935	0.99	1.01
10.00	1.54	0.216	0.267	2.11	2.06	32.50	4.95	0.935	0.94	0.975	0.995
10.25	1.58	0.256	0.316	2.55	2.36	33.00	5.02	0.955	0.95	0.965	0.985
10.50	1.62	0.308	0.376	2.73	2.51	33.50	5.10	0.98	0.965	0.96	0.98
10.75	1.66	0.374	0.458	2.62	2.38	34.00	5.17	1.00	0.98	0.955	0.975
11.00	1.70	0.469	0.578	2.32	2.14	34.50	5.24	1.02	0.99	0.955	0.975
11.25	1.73	0.588	0.740	1.92	1.83	35.00	5.32	1.035	1.00	0.96	0.98
11.50	1.77	0.761	0.940	1.61	1.58	35.50	5.39	1.05	1.01	0.965	0.98
11.75	1.81	0.992	1.18	1.34	1.37	36.00	5.46	1.055	1.02	0.975	0.985
12.00	1.85	1.30	1.48	1.14	1.19	36.50	5.54	1.055	1.03	0.99	0.995
12.25	1.89	1.71	1.75	1.00	1.05	37.00	5.61	1.05	1.035	1.00	1.00
12.50	1.93	2.14	2.05	0.90	0.94	37.50	5.68	1.04	1.035	1.005	1.00
12.75	1.96	2.52	2.33	0.81	0.855	38.00	5.76	1.03	1.03	1.01	1.005
13.00	2.00	2.80	2.46	0.735	0.785	38.50	5.83	1.02	1.025	1.01	1.005
13.25	2.04	2.80	2.37	0.68	0.74	39.00	5.90	1.01	1.02	1.015	1.005
13.50	2.08	2.65	2.23	0.645	0.71	39.50	5.98	1.00	1.015	1.015	1.005
13.75	2.12	2.40	2.05	0.62	0.685	40.00	6.05	0.99	1.01	1.015	1.005
14.00	2.16	2.07	1.82	0.61	0.67	40.50	6.12	0.98	1.005	1.015	1.005

TABLE I. (*Continued*)

2θ	q	a(q) (Na) 100°C	200°C	a(q) (K) 65°C	135°C	2θ	q	a(q) (Na) 100°C	200°C	a(q) (K) 65°C	135°C
14.25	2.19	1.78	1.60	0.605	0.66	41.00	6.19	0.975	1.00	1.01	1.005
14.50	2.23	1.52	1.45	0.61	0.66	41.50	6.26	0.97	0.995	1.01	1.005
14.75	2.27	1.30	1.30	0.615	0.67	42.00	6.34	0.965	0.995	1.005	1.005
15.00	2.31	1.13	1.16	0.625	0.68	43.00	6.48	0.96	0.99	1.00	1.00
15.25	2.35	1.00	1.035	0.64	0.695	44.00	6.62	0.965	0.985	1.00	1.00
15.50	2.38	0.90	0.955	0.665	0.71	45.00	6.77	0.97	0.985	1.00	1.00
15.75	2.42	0.83	0.895	0.695	0.725	46.00	6.91	0.98	0.985	0.995	1.00
16.00	2.46	0.78	0.845	0.725	0.75	47.00	7.05	0.99	0.99	0.995	1.00
16.25	2.50	0.74	0.795	0.765	0.785	48.00	7.19	1.00	0.995	0.995	1.00
16.50	2.54	0.70	0.755	0.80	0.82	49.00	7.33	1.005	1.00	1.00	1.00
16.75	2.58	0.67	0.73	0.84	0.855	50.00	7.47	1.01	1.005	1.005	1.00
17.00	2.61	0.645	0.71	0.88	0.895	51.00	7.61	1.01	1.005	1.005	1.00
17.25	2.65	0.625	0.695	0.93	0.94	52.00	7.75	1.01	1.005	1.00	1.00
17.50	2.69	0.615	0.685	0.975	0.98	54.00	8.03	1.005	1.00	1.00	1.00
17.75	2.73	0.605	0.68	1.02	1.02	57.00	8.44	1.00	1.00	1.00	1.00
18.00	2.77	0.605	0.675	1.075	1.06	60.00	8.84	1.00	1.00	1.00	1.00

By contrast, we find for our x-ray data a statistical error of only 1% at $q = 0.4$ Å^{-1}, decreasing to about $\frac{1}{2}$% at $q = 1.4$ Å^{-1}. We conclude from this and other similar comparisons that x-ray data are vastly superior to neutron data in the low-q region.

V. RESULTS AND ERROR ANALYSIS

Some authors present only the Fourier transform of the $a(q)$ data, but we believe that it is most useful to the reader to present the function $a(q)$ itself. Moreover, although it is most common to present the data in the compact form of a figure, only a table provides the accuracy needed for quantitative numerical applications of the data. In Table I, we present[32] our results for $a(q)$ for Na at $T = 100°$ and 200 °C and for K at $T = 65$ and 135°C. The first two columns give the angles 2θ at which the data were taken using Mo radiation and the corresponding values of $q = (4\pi/\lambda)\sin\theta$. In the following four columns, the data for $a(q)$ are presented. We display in Fig. 2 one of the curves of our $a(q)$ data, namely, Na at $T = 100°C$.

An important source of possible error is the particular choice of smoothing procedure applied to the data. In fact, a popular smoothing procedure involves taking Fourier transforms of the data. However, Schlup[33] has shown by a detailed statistical analysis that the very process of taking Fourier transforms introduces significant errors. We have therefore chosen to smooth our data by simply drawing a smooth curve through the data points.

The smallness of the scatter of the data points in the low-q region is evident from Fig. 1. To demonstrate the extent of the scatter of the data points in the high-q region, we display the last few

peaks of $a(q)$ in Fig. 3 with a very expanded vertical scale. The points and solid line represent the smoothed and unsmoothed data, respectively. It is evident that the scatter of the unsmoothed data points is very small, except at high-q where fewer
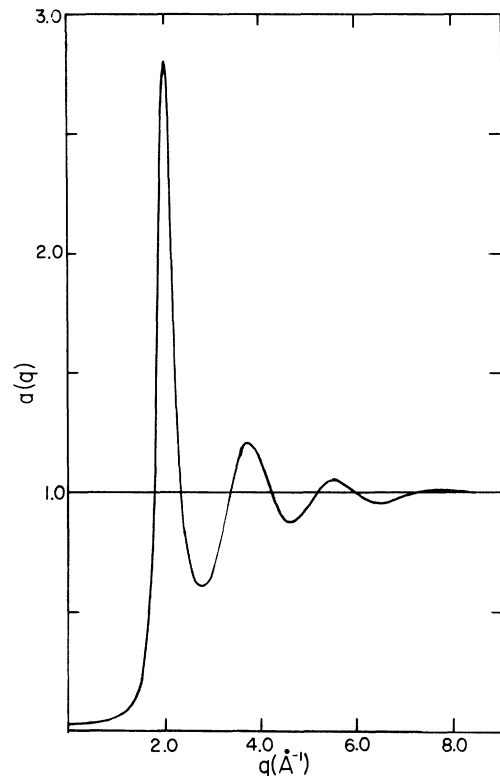

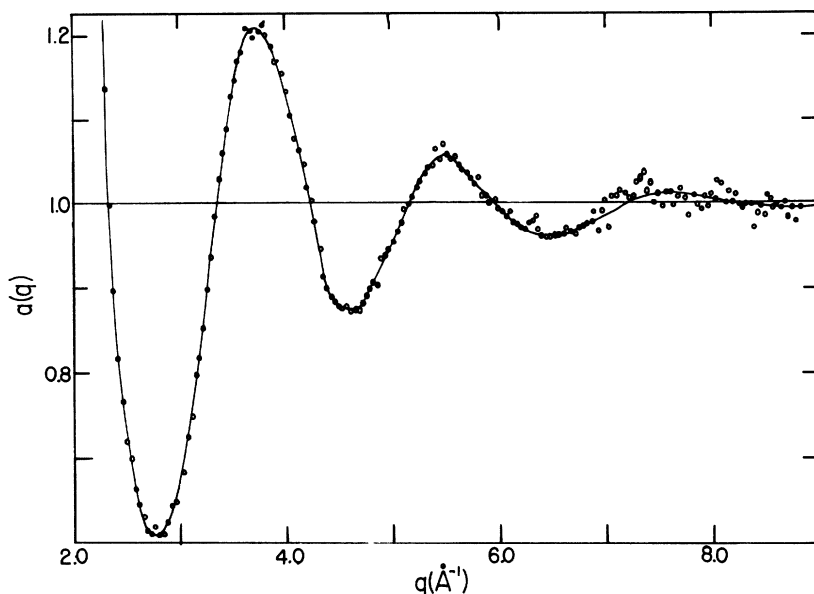FIG. 2. Graph of $a(q)$ as a function of q for liquid Na at 100 °C.

FIG. 3. Graph of $a(q)$ on an expanded vertical scale for the high-q region beyond the first peak. The points and the solid line represent unsmoothed and smoothed data, respectively. Note that the main peak has not been included in order to permit expansion of the vertical scale.

counts were taken. A careful statistical analysis shows that the counting error associated with both the full- and empty-cell data leads to a combined random error of typically $\frac{1}{2}\%$ for the data points in the low-q region of Fig. 1. Even on the expanded scale of the figure, this random error is in all cases smaller than the size of the open circles. Furthermore, the data extrapolate smoothly to the value of $a(0)$ given by the compressibility sum rule

$$a(0) = N_0 k_B T \chi_T , \qquad (1)$$

where N_0 is the density of atoms and χ_T is the isothermal compressibility. However, it should be recognized that smooth extrapolation to $a(0)$ is not a sensitive test of the data. In fact, one could vary the value of $a(0)$ by about 10% and the data would still appear to extrapolate smoothly to this new value.

For normalization of the data, the high-q region beyond the first peak is of central importance. For $q \gtrsim 6$ Å^{-1}, the over-all random error is about $\frac{1}{2}\%$. For the region $q \gtrsim 6$ Å^{-1}, where fewer counts per point were taken, the random error is about 1%. As can be seen by inspection of Fig. 3, a shift of the normalization by more than 1% is clearly inconsistent with the data.

An independent test of the normalization was carried out according to the method proposed by Rahman.[34] He has shown that $a(q)$ must satisfy the following relation:

$$4\pi^2 N_0 L j_1(\mu L) = \int_0^\infty dq \, q[a(q) - 1]$$

$$\times [j_0(qL + \mu L) - j_0(qL - \mu L)] , \qquad (2)$$

where $j_n(x)$ is the nth spherical Bessel function, μ is an arbitrary parameter, and L must be less than the effective hard-core diameter of the screened ion. To test our experimental results, we have performed the integration for the $a(q)$ data for Na at 100 °C for a variety of values of μ and L (see

TABLE II. Test of the normalization of the $a(q)$ data for Na at 100°C by the Rahman method. The first two columns list values for μ and L. The last column lists the factor by which the experimental $a(q)$ should be multiplied to obtain perfect agreement between the experimental (third column) and the theoretical values (fourth column) of Rahman's integral.

| L (Å)	μ(Å^{-1})	Integral Expt.	Theor.	Correction factor to $a(q)$
1.0	0.5	0.096	0.099	0.995
1.0	1.0	0.090	0.092	0.997
1.0	1.5	0.080	0.080	1.000
1.0	2.0	0.068	0.066	1.003
1.0	2.5	0.055	0.051	1.005
1.0	3.0	0.042	0.035	1.009
2.0	0.5	0.718	0.734	0.980
2.0	1.0	0.524	0.530	0.993
2.0	1.5	0.281	0.281	1.000
2.0	2.0	0.080	0.071	1.011
2.0	2.5	−0.034	−0.046	1.011
2.0	3.0	−0.057	−0.068	1.010
3.0	0.5	2.138	2.163	1.017
3.0	1.0	0.938	0.949	–
3.0	1.5	0.008	−0.002	1.009
3.0	2.0	−0.215	−0.231	1.013
3.0	2.5	−0.022	−0.031	1.010
3.0	3.0	0.102	0.097	1.006
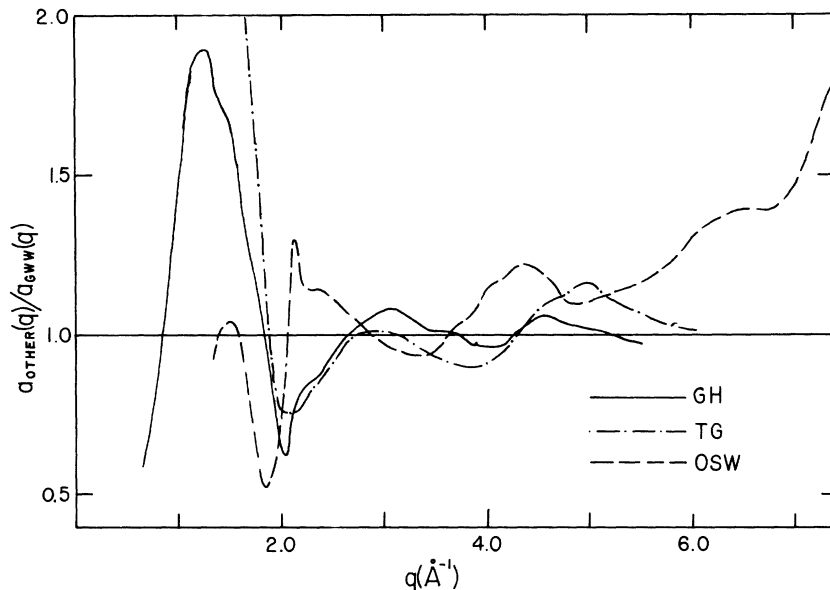
FIG. 4. Comparison of all the data for Na at about 100 °C. The curves represent the ratio of other data $a_{\mathrm{OTHER}}(q)$ to our data $a_{\mathrm{GWW}}(q)$. The notations GH, TG, and OSW denote, respectively, the neutron data of Gingrich and Heaton (Ref. 5), the x-ray data of Trimble and Gingrich (Ref. 7), and the x-ray data of Orton, Shaw, and Williams (Ref. 6).

Table II) to obtain the experimental values listed in the third column of the table. For each μ and L, we list in the fourth column the corresponding theoretical values obtained from the left-hand side of Eq. (2).

The magnitude of the error in $a(q)$ may be inferred by calculating the factor by which the experimental $a(q)$ must be multiplied to make the experimental value equal to the theoretical value. These factors are listed in the last column of Table II. From the table, we see that for typical values of μ and L, $a(q)$ need be changed by less than 1% to satisfy Eq. (2) exactly. This is consistent with our finding that the normalization used to obtain $a(q)$ is in error by less than 1%.

The largest source of systematic error in our results for $a(q)$ arises from the uncertainty of the tabulated values[13] for $f(q)$. On the basis of the discussion given in Sec. III, we ascribe a maximum error of 1% to $|f(q)|^2$. A second source of systematic error is the incoherent Compton scattering. Although this correction is probably not reliable to better than 1%, the resulting error in $a(q)$ is very small. For Na, it never exceeds $\frac{1}{2}$%; for K, it is even smaller.

The product of the absorption factor μ times the sample thickness was measured directly. This avoided the necessity of relying on the tabulated values[13] for μ and on an independent measurement of sample thickness, both of which are difficult to determine accurately. We instead measure directly the product of μ times sample thickness and our estimated error for this product is 1%. This leads to a negligible error in $a(q)$ for Na (less than 0.1% for all q) and about 0.3% for K except at the very lowest q values where the error

for K rises to about 1%.

Another significant source of error arises from drifts of the intensity of the x-ray beam. Although precautions were taken to minimize errors from such drifts, there remained an error of about 1%. This particular error is especially important when considering the temperature dependence of $a(q)$ because the direction of such intensity drifts is random between different temperature runs.

Since there are no other appreciable errors in the experiment, we can now summarize the over-all error in $a(q)$. For both Na and K, the over-all root-mean-square (rms) systematic error ranges from 0.5—2.0% depending on the value of q and the over-all random error ranges from 0.3—1.0%. Therefore, the total rms error in $a(q)$ does not exceed 2.5% for any value of q.

VI. COMPARISON WITH PREVIOUS RESULTS

Although there have been several previous determinations[5—8] of $a(q)$ for Na and K (two using x rays and one using neutrons), rather wide discrepancies exist between the various sets of data data. To illustrate these differences, we plot in Fig. 4 a comparison of all the data for Na at approximately 100 °C. In order to see in detail the extent of the differences, we plot as a function of q the ratio of each previous measurement of $a(q)$ to our values for $a(q)$. Good agreement would be indicated by a line lying close to unity for all q.

Gingrich and Heaton[5] normalized their neutron data (labeled GH in Fig. 4) such that $a(q)$ extrapolated to zero at $q = 0$, rather than to the correct value of $a(0) = 0.024$, as given by Eq. (1). However, inserting this correction would not markedly improve the data, even at low-q values. We believe
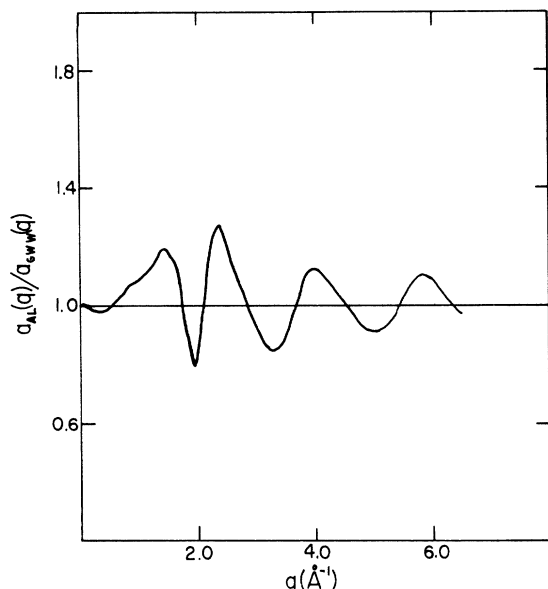
FIG. 5. Comparison between the Ashcroft-Lekner (Ref. 35) hard-sphere model $a(q)$ and our measured $a(q)$.

that the primary source of deviations between this neutron data and our x-ray data results from the inadequacy of both the static approximation and multiple-scattering correction for neutron scattering. The early x-ray measurements[7] (labeled TG in Fig. 4) were hindered by the inadequacy of the experimental techniques that were available over 30 years ago. The more recent x-ray data[6] (labeled OSW) clearly suffer from some significant systematic error since no choice of normalization makes $a(q)$ approach unity at large-q values. We have chosen Na for comparison between our data and previous results because the previous results were best for Na. For K, the quality of the previous data is considerably poorer.

In addition to the comparison with the measured values of $a(q)$, we have also included in Fig. 5 a curve based on the widely used Ashcroft-Lekner[35] model for $a(q)$, with their choice of 0.456 for the packing fraction of Na at 100 °C. It is ironic that this simple model, based on the unphysical assumption of a hard-sphere interatomic interaction, gives better over-all agreement than any previous

experimental measurements. Therefore, it is not unreasonable to use this model for those metals for which highly accurate data for $a(q)$ are not available.

VII. CONCLUSION

The major contribution of this work lies in providing, for the first time, highly accurate $a(q)$ data for Na and K for all values of q, including the important but experimentally difficult low-q region. We believe that it is not sufficiently recognized that one cannot carry out meaningful quantitative calculations using $a(q)$ data for which important details are in error.

We have presented the results of our x-ray diffraction measurements for $a(q)$ for liquid Na and K as a function of temperature. By exercising care, we have kept the over-all rms error to a maximum of 2. 5%. The error analysis has been described in detail. The rms relative error between data for $a(q)$ at different temperatures, including random error plus drifts, does not exceed 1. 5% for any value of q.

It has been suggested that one cannot escape from large inherent errors in x-ray determinations of $a(q)$ because of uncertainties in the atomic form factor and the correction for Compton scattering. We have shown that recent experiments, as well as calculations, confirm the tabulated values for these two quantities.

Neutron diffraction is an alternative experimental method for the determination of $a(q)$. We have pointed out the advantages enjoyed by x rays, especially in the low-q region. In particular, the static approximation and multiple scattering remain serious difficulties for evaluating $a(q)$ from neutron scattering.

We shall show in a subsequent publication how the availability of this highly accurate $a(q)$ data permits the reliable calculation of a variety of properties of liquid Na and K.

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Generalized Hydrodynamics and Analysis of Current Correlation Functions*†

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A generalization of the Navier-Stokes equation, valid for wavelengths and times of a molecular order of magnitude, is discussed on the basis of viscoelastic behavior of simple classical liquids. In this theory, transport coefficients are replaced by appropriate viscoelastic memory functions. The theory is verified by analyzing the data on current-correlation functions obtained from computer experiments. Three different models for the time dependence of the viscoelastic memory are investigated, namely, a single-exponential decay, a modified-exponential decay, and a Gaussian decay. It is observed that the memory functions are approximately Gaussian, at least for times of the order of one or two relaxation times. This is in agreement with a conjecture of Forster, Martin, and Yip. The wave-number dependence of the half-width of the Gaussian decay, and of the longitudinal- and shear-viscosity coefficients, are found from computer experiments. The extrapolated values of these transport coefficients, in the limit $k \to 0$, are in good agreement with experiments on liquid argon.

I. INTRODUCTION

In recent years, the dynamics of density fluctuations in simple classical liquids has been a subject of considerable interest. In particular, several theoretical attempts[1-4] have been made to reproduce the data obtained from computer experiments on fluctuations of the current density in liquid argon.[5,6] Our reasons for presenting still another article on the same topic are twofold: (i) We provide a simple heuristic argument leading to the generalized hydrodynamic equations that have been derived previously by more elaborate statistical-mechanical methods; and (ii) we present a more detailed and