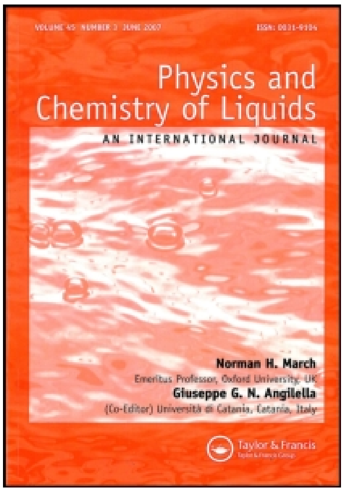

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Small Angle Scattering from Liquids: van der Waals Forces in Argon and Collective Mode in Na

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Because of discrepancies between recent estimates of van der Waals forces in liquid metals, we have examined available experimental data on the small angle scattering of X-rays from liquid Na, and have compared it with neutron scattering data on liquid argon. In the latter case, it follows from first principles that the liquid structure factor $S(k)$ has the small k expansion

$$S(k) = S(0) + a_2k^2 + a_3k^3 + \cdots \qquad \text{(i)}$$

Therefore we have plotted $(S(k) - S(0))/k^2$ from available data for both Na and Ar, and they are immediately found to be qualitatively different. For a given state of argon, a_2 and a_3 can be extracted and are quite consistent with theoretical estimates.

For Na, the small angle scattering does not have the form (i) and it is demonstrated that there is a term proportional to k at small k. This means that one of the leading terms determining the approach of the radial distribution function $g(r)$ to its asymptotic value of unity at large r is proportional to r^{-4}. It is shown that this behaviour arises from the dispersion of a collective mode, in which the density fluctuations oscillate independently with a well defined dispersion relation $\omega(k)$. This relation has the form, with v_s the velocity of sound,

$$\omega(k) = v_sk + dk^2 + \cdots \qquad \text{(ii)}$$

We have estimated the dispersion for Na, K and Rb from an approximate theory and have compared it with the experimentally observed collective mode for liquid Rb.

Finally, after extracting the k term discussed above, the magnitude of the k^3 term is estimated from experimental data on Na. It is quite consistent with the data to take the coefficient of k^3 as zero and possible reasons for this are discussed.

1 INTRODUCTION

Recently, there has been interest in the area of van der Waals forces in liquid metals. Chatterjee[1] has used some thermodynamic properties to establish approximate relations of the van der Waals constant c_6 in the form c_6/r^6, in

TABLE I

Estimates of the van der Waals coefficient c_6

	c_6 in units of 10^{-78} Jm^6		
Metal	Chatterjee	Upadhyaya *et al.*	Mahanty and Taylor
K	369.10	1.46	
Rb		2.99	
Cs	744.60	6.77	
Cu	36.30		1.00
Ag	63.74		4.39
Au	84.20		6.36

terms of the critical temperature and the van der Waals gas constants. His values for the alkali and noble metals are compared in Table I with the estimates made by Mahanty and Taylor[2] and Upadhyaya, Wang and Moore[3] from dielectric screening theory. They are seen to differ by a large factor, which is obviously disturbing.

We have therefore examined whether we could test these estimates by examining the small angle scattering data from liquid Na. In order to do this, it is instructive to compare and contrast the small angle scattering in liquid sodium with that in liquid argon. In this latter case, there is a precise theory of the small angle scattering, first given by Enderby, Gaskell and March[4] and leading to the form for the small k expansion of the liquid structure factor $S(k)$:

$$S(k) = S(0) + a_2 k^2 + a_3 k^3 + \cdots \tag{1.1}$$

The form of a_3 is given in terms of the van der Waals constant c_6 by

$$a_3 = \pi^2 \rho \{S(0)\}^2 c_6 / 12 k_B T \tag{1.2}$$

where $S(0)$ is given by the well-known result of fluctuation theory as

$$S(0) = \rho k_B T K_T \tag{1.3}$$

K_T being the isothermal compressibility and ρ the number density of atoms.

Because of the well-defined theory of the small-angle scattering from, say, liquid argon, we have plotted in Figure 1 the measured small-angle scattering from the data of Yarnell, Katz and Wenzel,[5] in the form suggested by Eq. (1.1), namely a plot of $(S(k) - S(0))/k^2$. This plot allows us to estimate a_2 and a_3. It is true that Yarnell *et al.*[5] have had to extrapolate their measured data to join on to the compressibility data for $S(0)$ in Eq. (1.3). We indicate in Figure 1 the points that are measured and those that are the extrapolated values of Yarnell *et al.*[5] While, ideally, the measured points need extending down to smaller angles, we have extracted from the work of Yarnell *et al.*

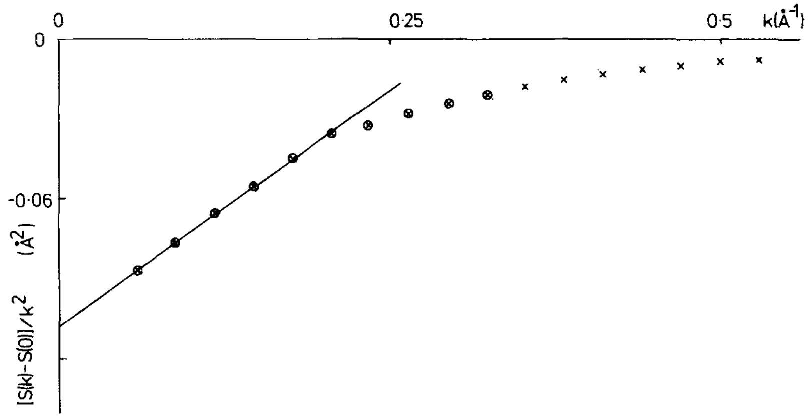

FIGURE 1 $(S(k) - S(0))/k^2$ against k for argon from data of Yarnell *et al.*, × denote measured points while ⊗ are extrapolated values given by Yarnell *et al.* The straight line is the fit to the form (1.1).

the coefficients a_2 and a_3 and these are recorded in Table II. Though these values depend on the extrapolated data, one can have confidence in this when the values are compared with the theoretical estimate of a_3 given in Eq. (1.2). As Robinson and March[6] have shown, the constant c_6 in liquid argon is expected to be reduced from its free space value by some few per cent only, due to the van der Waals interactions occurring in the condensed dielectric liquid medium. As for a_2, Woodhead-Galloway, Gaskell and March[7] have estimated the coefficient for various thermodynamic states. These theoretical estimates of a_2 and a_3 are also recorded in Table II. We conclude from Table II that the data of Yarnell *et al.*[5] for argon is in accord with the small angle scattering theory embodied in Eqs. (1.1) and (1.2).

At this point, we turn to compare and contrast the small angle X-ray scattering data for Na, as observed by Greenfield, Wellendorf and Wiser[8] with that discussed above for argon. Figure 2 immediately shows then that the situation is qualitatively different and that it makes no sense to try to

TABLE II

Constants a_1, a_2 and a_3 appearing in expansions (1.1) and (1.4)

	a_1 (Å)	a_2 (Å)^2	a_3 (Å^3)
Ar (calc.)	—	-0.08	0.375
Ar (expt)	—	-0.12	0.35
Na	0.002	0.0184	0
K	0.0095	0.025	0

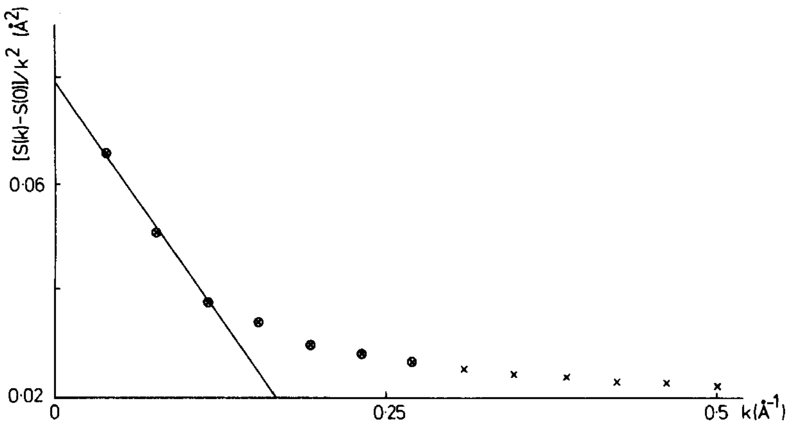

FIGURE 2 Same as Figure 1 but for liquid Na, from data of Greenfield *et al.*

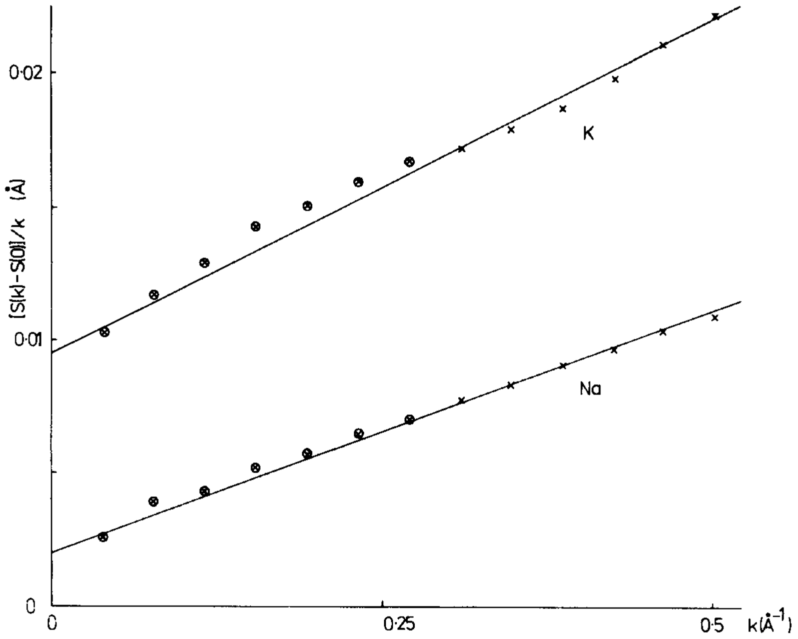

FIGURE 3 $(S(k) - S(0))/k$ against k for liquid Na and K. Straight lines show best fit to Eq. (1.4).

interpret this data on Na with the formula (1.1), because the overall slope is not constant as for Ar and is of the opposite sign. Replotting the data, it emerges that what is omitted from Eq. (1.1) as applied to Na is a term linear in k. Therefore, we shall write, to $0(k^2)$,

$$S(k) = S(0) + a_1 k + a_2 k^2 + \cdots \tag{1.4}$$

The question then arises as to the magnitude of the linear term in k required to fit the experimental data, and equally important, how to interpret it. We have extracted from the plot of $(S(k) - S(0))/k$ in Figure 3 the value $a_1 = 2 \times 10^{-3}$ Å, and we turn immediately to discuss the interpretation in Section 2 below. However, it is of interest to note from Figure 3 that X-ray measurements on liquid potassium[8] also reveal a linear term in k.

2 SMALL ANGLE SCATTERING AND COLLECTIVE OSCILLATIONS IN LIQUID METALS

As has been emphasized by Bratby, Gaskell and March,[9] and more recently by Young and coworkers,[10] the specific heat properties of simple liquid metals like Na near their freezing points are very simple, namely that the specific heat at constant volume c_v is near to $3R$, R being as usual the gas constant, while the ratio of the specific heats γ is near to unity. The simplest way to understand this is to liken the liquid metal to a collection of independent harmonic oscillators. These oscillators are to be thought of as associated with independent oscillations of the density fluctuations $\rho_{\mathbf{k}}$, defined by

$$\rho_{\mathbf{k}}(t) = \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \tag{2.1}$$

the sum being over the positions $\mathbf{r}_i(t)$ of all the ions at time t. Roughly, the above experiments on specific heats prompt one to write that $\rho_{\mathbf{k}}(t)$ oscillates according to

$$\rho_{\mathbf{k}}(t) = \rho_{\mathbf{k}}(0) \exp(i\omega(k)t) \tag{2.2}$$

where $\omega(k)$ is the frequency of the collective mode as a function of k. The simplest theory,[11] based essentially on Eq. (2.2), is to write the van Hove function, or dynamical structure factor, $S(k, \omega)$ as

$$S(k, \omega) = 2\pi S(k)\delta(\omega - \omega(k)). \tag{2.3}$$

Assuming that the collective mode exhausts the sum rule, with m being the ionic mass,

$$\int \omega^2 S(k, \omega) \frac{d\omega}{2\pi} = \frac{k^2 k_B T}{m}, \tag{2.4}$$

an assumption we test below by comparing its consequences with experiment, then it follows that

$$\omega^2(k) = \frac{k^2 k_B T}{mS(k)} \tag{2.5}$$

Using the form (1.4) for small k in Eq. (2.5), it follows that, with the ratio of the specific heats taken as unity in accord with the above discussion

$$\omega(k) = v_s k + \mathrm{d}k^2 + \cdots \tag{2.6}$$

Clearly, the dispersion of the collective mode at small k is then the origin of the k term in Eq. (1.4) and in the above simplest theory of the collective mode one notes that

$$d = -\frac{v_s a_1}{2S(0)}. \tag{2.7}$$

3 ESTIMATE OF DISPERSION OF COLLECTIVE MODE FOR LIQUID ALKALI METALS

Though we have given the above specific heat evidence in favour of collective modes in small core metals like liquid Na, to our knowledge the only simple metal in which collective modes have been directly demonstrated by measur-

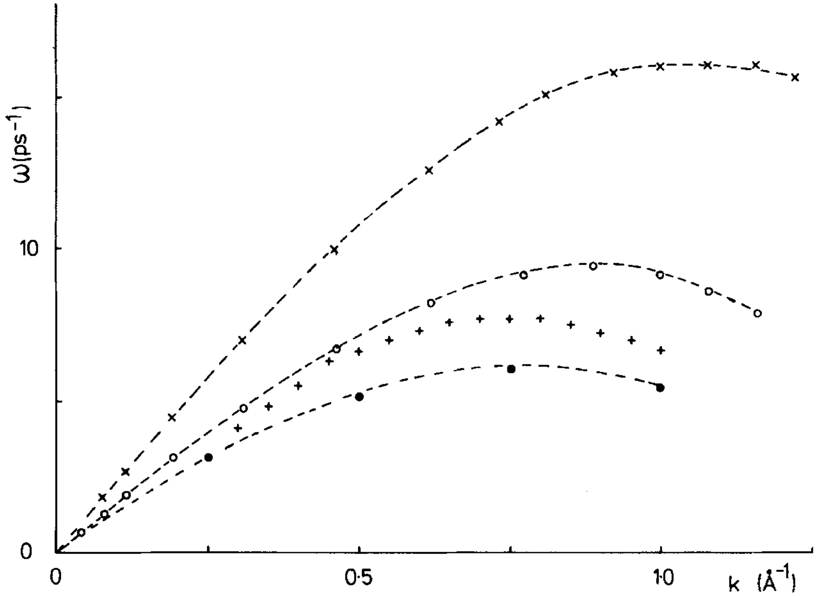

FIGURE 4 Dispersion relation $\omega(k)$ against k. × Na from Eq. (2.5); ○ K from Eq. (2.5); ● Rb from Eq. (2.5); + Rb from data of Copley and Rowe.

ing the peaks in $S(k, \omega)$, and plotting out the dispersion relation, is in liquid Rb. In Figure 4, we have plotted $\omega(k)$ against k from the data of Copley and and Rowe[12] for Rb. Also plotted in Figure 4 are the results obtained using Eq. (2.5) for Na, K and Rb. While we have used the $S(k)$ data of Greenfield *et al.*[8] for Na and K, for the structure factor of Rb we have used the results obtained in the molecular dynamics study of Rahman.[13]

We see for Rb that the simple theory of the collective mode used above is successful in reproducing the position of the maximum in $\omega(k)$. The quantitative discrepancy between theory and experiment in the numerical values of $\omega(k)$ for Rb shows that the approximations (2.3) and (2.4), while useful to get the main features of the dispersion relation, are not fully quantitative. From Figure 4, it is worth noting that the position of the maximum in $\omega(k)$, which occurs at 0.75 Å^{-1} for Rb, shifts to around 0.9 Å^{-1} for K and 1.1 Å^{-1} for Na.

4 IS THERE A VAN DER WAALS INTERACTION IN SIMPLE LIQUID METALS?

In addition to the small-angle scattering, one expects that the so-called Kohn anomaly around the diameter of the Fermi sphere $k = 2k_f$, will also affect the long range behaviour of $g(r)$ in liquid metals. As was suggested earlier,[14] this would give the leading asymptotic term in $g(r)$ to be of the form

$$g(r) \sim \frac{\cos(2k_f r)}{r^3} \tag{4.1}$$

though it was recognized that the finite mean-free path will eventually require a damping factor of the form $\exp(-r/l)$ where l is of the order of the electronic mean-free path, multiplying Eq. (4.1). The suggestion was also made[14] that the van der Waals forces would be screened out by the electron gas.

Having seen above that there is a long-range term in $g(r) \sim r^{-4}$ in liquid Na, K and Rb, arising from the dispersion of the collective mode, we finally turn to enquire, in the light of the evidence presented in the Introduction, whether there is a van der Waals term in these liquid alkalis. This would mean a k^3 term to be added in Eq. (1.4). To examine this point, we have extracted the k term from Eq. (1.4), and then in liquid Na and K we have plotted the data in Figure 5 in a suitable form to reveal the k^3 term. From this figure, it can be clearly seen that it is consistent with the experimental data to argue that there is no k^3 term in liquid Na, though we have demonstrated its presence conclusively for liquid argon by similar methods of analysis of

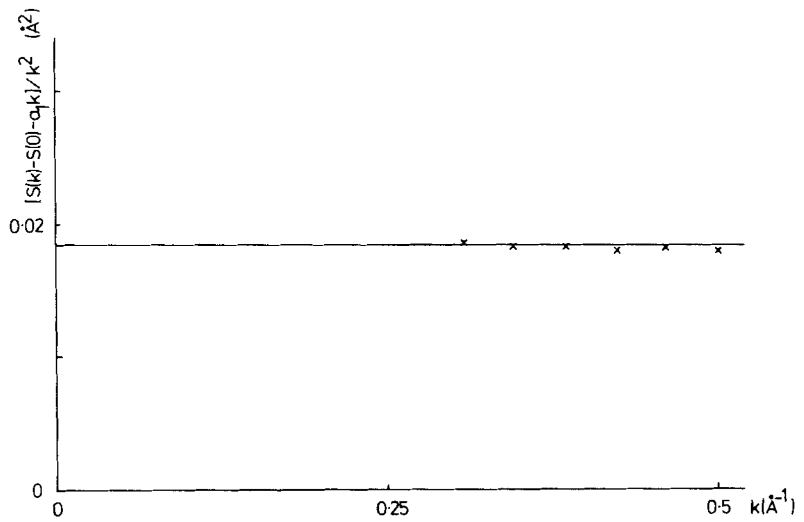

FIGURE 5 $(S(k) - S(0) - a_1 k)/k^2$ against k from data on Na. The straight line which is the best fit is made to have an intercept consistent with slope in Figure 3.

the small-angle data. In Figure 6, we demonstrate that the low k measurements on liquid Na can be fitted very well with an expansion of the type given in Eq. (1.4); that is without a k^3 term.

In the light of this conclusion as to the absence of the k^3 term in liquid Na, we want finally to re-examine the dielectric screening theory to see how such a conclusion might be compatible with that theory. Rehr, Zaremba and Kohn[15] examined the forces between ions immersed in an electron gas and found that the interaction could be expressed in terms of the ionic polarizability $\alpha(\omega)$ as

$$U(r) = -\frac{\hbar}{2\pi}\int_0^\infty \mathrm{d}u\,\alpha^2(iu)\left[\left(\frac{\partial^2 V(r, iu)}{\partial r^2}\right)^2 + \frac{2}{r^2}\left(\frac{\partial V(r, iu)}{\partial r}\right)^2\right]. \tag{4.2}$$

The screened coulomb interaction, $V(r, iu)$ is given by

$$V(r, iu) = \frac{2}{\pi}\int_0^\infty \mathrm{d}k\,\frac{\sin kr}{kr}\,\frac{1}{\varepsilon(k, iu)}, \tag{4.3}$$

where the frequency dependent dielectric function $\varepsilon(k, iu)$ describes the dynamic response of the electron gas. Mahanty and Taylor,[2] using a linear response theory, also obtained Eq. (4.2).

We see that for $\omega = 0$, the screened coulomb interaction between ions gives rise to the long-range behaviour of $g(r)$ as given by Eq. (4.1). Although the asymptotic limit of $\omega = 0$ in the random phase approximation may be

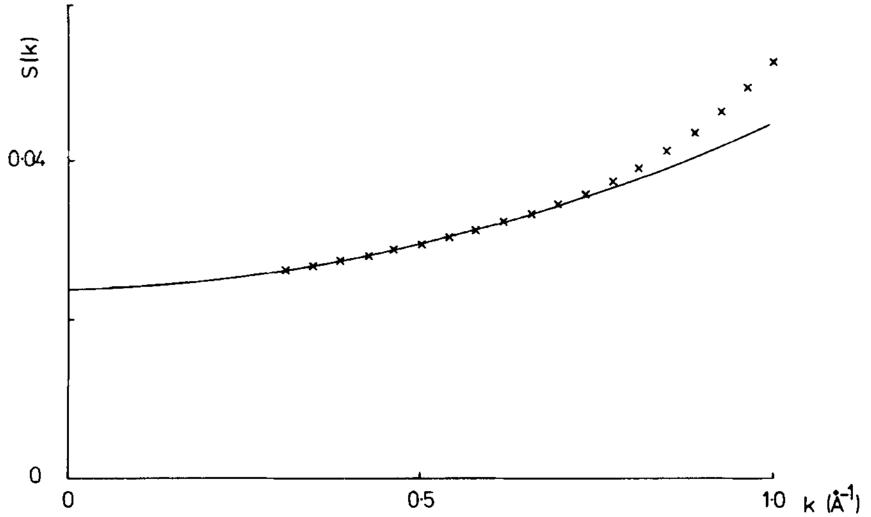

FIGURE 6 $S(k)$ against k for Na from Eq. (1.4), with coefficients from Table II. × indicate experimental points.

obtained analytically, this is not the case when the frequency dependence is included. Mahanty and Taylor, in an effort to obtain the asymptotic form of $U(r)$ from Eq. (4.2), used the hydrodynamic approximation to $\varepsilon(k, \omega)$:

$$\varepsilon_H(k, \omega) = 1 - \frac{5\omega_p^2}{(5\omega^2 - 3\hbar^2 \mathrm{k}_f^2 k^2)}, \tag{4.4}$$

with ω_p the usual plasma frequency, which then, in the limit k tends to zero, gives the van der Waals form

$$U(r) = \frac{c_6}{r^6} \tag{4.5}$$

where

$$c_6 = \frac{3}{2\pi} \int_0^\infty \left(\frac{u^2}{\omega_p^2 + \mu^2} \right)^2 \alpha^2(iu)\, \mathrm{d}u. \tag{4.6}$$

However, to obtain the form (4.5), there is the assumption that the long-range behaviour of $U(r)$ arises from $\varepsilon(0, iu)$. Since we find that, for liquid Na and K, the analysis of the $S(k)$ measurements for small k indicate the absence of a term in the interaction potential between ions which falls off as r^{-6}, this assumption needs to be investigated further.

We add that in the case of Ar, where there is no electronic screening, i.e. $\varepsilon(k, \omega) = 1$, the van der Waals coefficient c_6 extracted from the $S(k)$ measurements agrees well with that obtained from thermodynamic arguments, giving

TABLE III

Dielectric function $\varepsilon(q, iu)$ in the random phase approximation (RPA) and in the hydrodynamic approximation in the limit $q \to 0$ for a typical metal (Al)

$\frac{u}{\omega_p}$	$\varepsilon_{\mathrm{RPA}}(q, iu)$ as $q \to 0$	$\varepsilon_H(0, iu)$
2	1.20	1.25
1	1.47	2
0.5	2.9	5
0.1	48	101

confidence in our analysis of the $S(k)$ measurements. Also, it is relevant to mention that we have calculated $\varepsilon(q, iu)$ in the random phase approximation for some values of the arguments and these are compared in Table III with the hydrodynamic approximation (4.4). There are substantial differences, and this is enough to point to the fact that Eq. (4.4) should be transcended in future theoretical work on long-range forces in liquid metals.

5 CONCLUSION

Using the experimental scattering data of Yarnell *et al.*[5] on liquid argon the small-angle scattering theory embodied in Eqs. (1.1) and (1.2) is fully confirmed. But turning to liquid Na just above the freezing point, the data of Greenfield *et al.*[8] exclude the small k expansion (1.1) for Na and are in favour instead of the form (1.4). This form is shown to follow from the simplest theory of the collective oscillations of the density fluctuations. The order of magnitude of the dispersion observed, admittedly for liquid Rb, and not presently directly for Na, is consistent with the order of magnitude required to explain the small angle scattering.

It is clear from the present work that there is now a very worthwhile experimental program on small angle scattering that should clarify our understanding of the way collective modes, when they exist, will modify the small angle scattering. We have emphasized here that only when the collective modes can be extracted from the small angle scattering will it be possible to answer the question of whether van der Waals terms of the form c_6/r^6 really exist in simple liquid metals, or whether they are wholly screened out by the response of the electron gas to the oscillating dipoles on the liquid metal ions.

Present indications, which we have argued are not inconsistent with dielectric screening theory, are that in Na there is no term in c_6/r^6, but neither theory nor experiment is completely conclusive on this point and further work is needed.

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