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On the Structure of Liquid Bismuth

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Accurate measurements on the static structure factor $S(Q)$ for liquid bismuth at 566 K are reported. The non-simple structure of bismuth is discussed in the light of existing theories for liquid metals. The pair distribution function is evaluated as well as the first order pair potential according to the procedure suggested by de Angelis and March. The results have been used to calculate the fourth energy moment of the dynamic scattering function and good agreement is obtained with recently published experimental results.

INTRODUCTION

The interest in non-simple liquids, i.e. semimetals like gallium, tin, and bismuth, and semiconductors in the fluid phase like silicon and germanium, has increased considerably during the latest years. It is well known that for these liquids the static structure factors $S(Q)$ measured by neutron and X-ray diffraction techniques¹ exhibit some particular anomalies as compared to those for ordinary liquid metals as for example lead. The anomalies consist of the presence of a more or less pronounced shoulder on the high Q side of the main diffraction peak of $S(Q)$ as well as in small asymmetries of the second and third peaks. Many attempts have been made in order to explain these features. The common approach has been to assume that two different structures are co-existing in the liquid. For example, several attempts to describe the structure of liquid bismuth in terms of two hard sphere

models^{2,3,4} have been made but the results are not convincing. Recently Davidovic *et al.*⁵ suggested that the subsidiary peak in liquid Ge could be associated with a certain type of vacancies in the liquid. Thus the liquid phase should be regarded as a combination of "regular" and "irregular" structures where the term "regular" is used to denote the structure of an ordinary liquid. The "irregular" structure, on the other hand, is associated to a certain degeneracy of the state of the liquid around single vacancies supposed to be randomly distributed over the whole liquid volume.

In recent years there has also been renewed interest in the determination of an effective inter-particle potential from liquid structure factors. In this connection the self-consistent method developed by Schommers⁶ should be mentioned as well as the use of the modified hyper-netted chain equation as recently demonstrated by Levesque *et al.*^{7,8} The results from these calculations indicate that there is a correlation between the shape of the effective pair potential, $U(R)$, and the existence of the hump in $S(Q)$. Thus Mon *et al.*⁹ and Schommers⁶ concluded that $U(R)$ in liquid Ga is of ledge type. These findings are confirmed by Olsson and Dahlborg¹⁰ who found that $U(R)$ for an ordinary liquid metal as liquid lead is of a simple oscillatory nature while for liquid Bi, a semimetal like gallium, it is of ledge type.

In this paper accurate measurements of $S(Q)$ for liquid bismuth close to the melting point will be reported. The structure of Bi has been studied both by neutron^{11,12} and by X-ray diffraction^{13,14,15} techniques earlier. However, there is a remarkable disagreement between the results of different experiments and thus we feel it worthwhile to take up the subject again. Recently also extensive neutron inelastic scattering measurements^{16,17,18} have been reported. From the results of these it is interesting to note that Dahlborg and Olsson¹⁶ concluded that the molecular motions in Bi cannot be described in the terms applicable to classical liquids.

EXPERIMENTAL RESULTS AND DATA REDUCTION

The neutron diffraction patterns were obtained using a two axis diffractometer at the R2 reactor in Studsvik. Two different incident neutron wave lengths were used, 0.95 Å and 1.22 Å. The Q resolution ($\hbar Q$ is the momentum transfer in the scattering process) around the main diffraction peak in the static structure factor $S(Q)$ was about 0.05 \AA^{-1} . The covered Q range was $0.3 \text{ \AA}^{-1} < Q < 9.3 \text{ \AA}^{-1}$ and the liquid bismuth sample was kept at $(566 \pm 2)\text{K}$ which is 22 K above the melting point.

The measured data were corrected for trivial experimental effects and normalized to absolute cross section units via vanadium calibration measure-

ments. However, special care was taken in order to correct for inelastic scattering (IS) and multiple scattering (MS) events in the sample. It has been shown^{8,19} that a brief knowledge of the dynamic scattering function $S(Q, \omega)$ ($\hbar\omega$ being the energy transferred to the system in the scattering process) is necessary if a measurement of $S(Q)$ is to be properly corrected for these two experimental effects. The $S(Q, \omega)$ for liquid bismuth is known from the measurements by Dahlborg and Olsson^{16,17} for $Q < 7 \text{ \AA}^{-1}$ and when complemented by a theoretical expression, based on generalized hydrodynamics, for larger Q values both the IS and the MS corrections were calculated on an absolute scale. As expected the MS is for bismuth almost completely isotropic while the IS exhibited some oscillations. The amplitude of these were rather small but in order to arrive at as an accurate $S(Q)$ as possible they have to be taken into account.

RESULTS

The finally obtained structure factor is shown in Figure 1 where the circles represent a selection from the measured data and the full line is a cubical spline approximation to the entire experimental data set. These average values are given in Table I. It is seen that the specific feature of $S(Q)$ centered around 3 \AA^{-1} is very distinct, in fact much more pronounced than in earlier

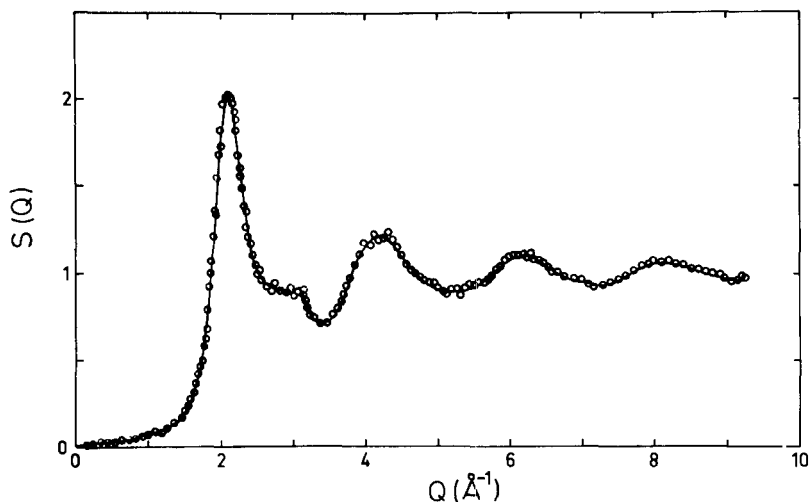


FIGURE 1 The structure factor $S(Q)$ for liquid bismuth at 566 K. Circles represent a selection of the measured points and the full curve is a cubical spline approximation to the complete experimental data set.

TABLE I
Measured $S(Q)$ for liquid bismuth at 566 K.

Q	$S(Q)$	Q	$S(Q)$	Q	$S(Q)$	Q	$S(Q)$
0.0	0.0093 [†]	2.5	1.020	5.0	0.912	7.5	0.954
.16	0.943	.1	0.900	.6	0.977
.2	0.010*	.7	0.915	.2	0.894	.7	1.002
.3	0.011*	.8	0.904	.3	0.894	.8	1.026
.4	0.013	.9	0.890	.4	0.901	.9	1.044
.5	0.015	3.0	0.889	.5	0.915	8.0	1.054
.6	0.018	.1	0.915	.6	0.939	.1	1.059
.7	0.022	.2	0.794	.7	0.972	.2	1.057
.8	0.028	.3	0.724	.8	1.009	.3	1.051
.9	0.035	.4	0.718	.9	1.045	.4	1.042
1.0	0.042	.5	0.731	6.0	1.074	.5	1.031
.1	0.050	.6	0.780	.1	1.094	.6	1.020
.2	0.062	.7	0.872	.2	1.099	.7	1.007
.3	0.083	.8	0.981	.3	1.092	.8	0.994
.4	0.123	.9	1.081	.4	1.073	.9	0.981
.5	0.185	4.0	1.157	.5	1.046	9.0	0.970
.6	0.270	.1	1.204	.6	1.016	.1	0.963
.7	0.400	.2	1.217	.7	0.990	.2	0.963
.8	0.684	.3	1.199	.8	0.974		
.9	1.174	.4	1.160	.9	0.964		
2.0	1.745	.5	1.108	7.0	0.954		
.1	2.012	.6	1.053	.1	0.943		
.2	1.857	.7	1.002	.2	0.933		
.3	1.464	.8	0.961	.3	0.929		
.4	1.174	.9	0.932	.4	0.937		

† from compressibility data.

* from reference 10.

measurements.¹² The present data compare well in the small Q region with earlier results¹⁰ and also to the measured zeroth moment of $S(Q, \omega)$ ¹⁶ over the whole Q region.

As is well known the pair distribution function $g(R)$ is related to $S(Q)$ by

$$g(R) = 1 + (2\pi^2 R n)^{-1} \int_0^\infty dQ Q \sin(QR)(S(Q) - 1) \quad (1)$$

where n is the number density. In order to calculate $g(R)$ the present data have to be extended both for small and large Q . For small Q a parabolic variation $S(Q) = S(0) + bQ^2$ was used, where $S(0)$ is given by the macroscopic compressibility. The value on b was chosen to 0.03.¹⁰ For large Q the analytic expression

$$S(Q) = c_1 \cos(c_2 Q - c_3) \exp(-c_4 Q^2)/Q \quad (2)$$

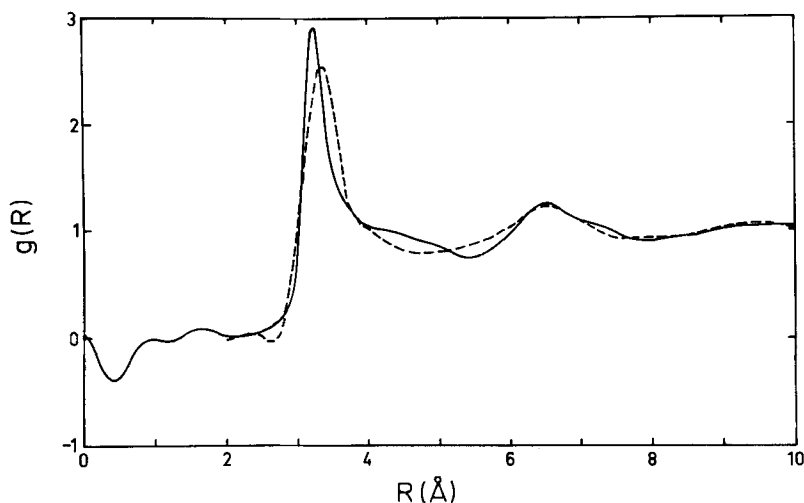


FIGURE 2 The pair correlation function for liquid bismuth at 566 K. Full curve is the present result and the dashed one shows the tabulated data of Waseda.¹

was fitted by least squares methods to the measured data for $Q > Q_{\min} = 4.6 \text{ \AA}^{-1}$ and Eq. (2) was then used to extend the integration in Eq. (1) from the largest measured Q value to infinity. The resulting $g(R)$ is shown in Figure 2. It is very satisfactory to note that the oscillations in the calculated $g(R)$ at small R is small, a fact which indicates that the correction procedure applied on the measured data is accurate. The choice of Q_{\min} is arbitrary but its value influences the amplitude of the oscillations to some extent. Thus it was chosen so that the oscillations were as small as possible. It should be realized that no renormalization of the data has been done and that all corrections have been calculated on an absolute scale. Also shown in Figure 2 are the tabulated results of Waseda.¹ There are considerable discrepancies between the two data sets but both exhibit a more or less pronounced irregularity in the region $4 < R < 5 \text{ \AA}$. The nature of this structure anomaly has been discussed by Davidovic *et al.*²¹ They suggest that there in a liquid showing such an anomaly two different structures are co-existing, one with the interatomic distance R (corresponding to the "regular" structure) and another one with the interatomic distance R' (the "irregular" structure), around structure imperfections which can be considered as single vacancies. The situation around the vacancy V is sketched in Figure 3. The distance R' is smaller than or equal to R at temperatures close to the melting point. It should be noted that bismuth contracts on melting and this fact can, from the crystallographic structure in the solid phase and from the shape of the measured $g(R)$ in the liquid, be interpreted so that the coordination number changes from $3 + 3$ in

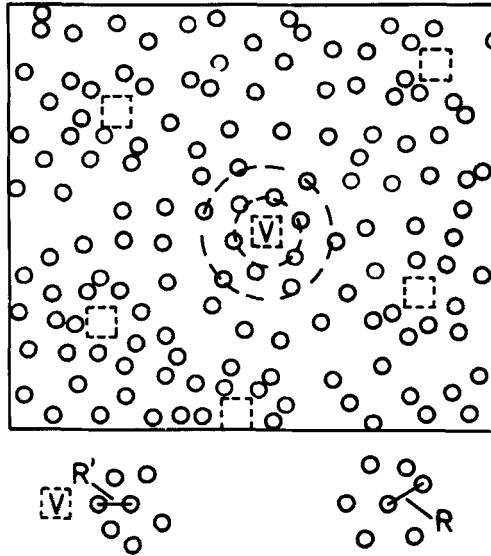


FIGURE 3 Two-dimensional sketch of the liquid bismuth structure with randomly distributed single vacancies (V).

the solid to somewhere between 7 and 8 in the liquid. Some structure deformation may also occur due to the increase of the charge density in the vicinity of the vacancy and this will in turn manifest itself through the polarization effects discussed by Mon *et al.*⁹

As was mentioned above several different schemes exist in order to derive an effective pair potential from an experimentally determined $S(Q)$. Here we will indicate a route which according to our knowledge not has been exploited to its full capacity earlier. This route is based on the formalism developed by de Angelis and March²² who in a systematic way obtain the higher order correlation functions for a liquid metal from the Born-Green-Yvon hierarchy. Thus the theory provides a systematic iterative approach to the derivation of an effective pair potential.

To second order de Angelis and March obtains

$$U(R) = U(R)_0 + U(R)_I + U(R)_{II} \quad (3)$$

with

$$U(R)_0 = -k_B T \ln(g(r)) \quad (4)$$

and

$$U(R)_I = k_B T (2\pi^2 n R)^{-1} \int_0^\infty dQ Q \sin(QR) (S(Q) - 1)^2 \quad (5)$$

$U(R)_0$ is usually called the potential of mean force and $k_B T$ is the temperature in energy units. The second order term $U(R)_{II}$ is also possible to express in terms of $S(Q)$ but in a very complicated way and it will not be included in the discussion below. However, work in order to calculate also this term is in progress.

The effective pair potential for liquid bismuth is shown in the left part of Figure 4. The difference between the zeroth and the first order approximations (broken and full curves, respectively) is surprisingly small and the first order term in Eq. (3) seems to affect only the attractive or the long-range part of the potential. It is of considerable interest to compare the results on bismuth with the ones on an ordinary liquid metal as lead. Using the data of Dahlborg *et al.*²³ and of Olsson and Dahlborg¹⁰ the results shown in the right part of Figure 4 are obtained. In this case the amplitude of the long-range part is much larger and also the influence of the first order term is considerable as compared to bismuth. Thus it might be conjectured that the higher order terms in Eq. (3) also will have a great impact in the case of lead. A general conclusion from Figure 4 is that the pair potential for liquid bismuth very probably is of ledge type while for lead it is of a more oscillatory nature. This is in conformity with the results of Olsson and Dahlborg.¹⁰ It should also be mentioned that Schommers⁶ for another semimetal, gallium, from a measured $S(Q)$ derived a potential of very similar shape to the one shown for bismuth in Figure 4.

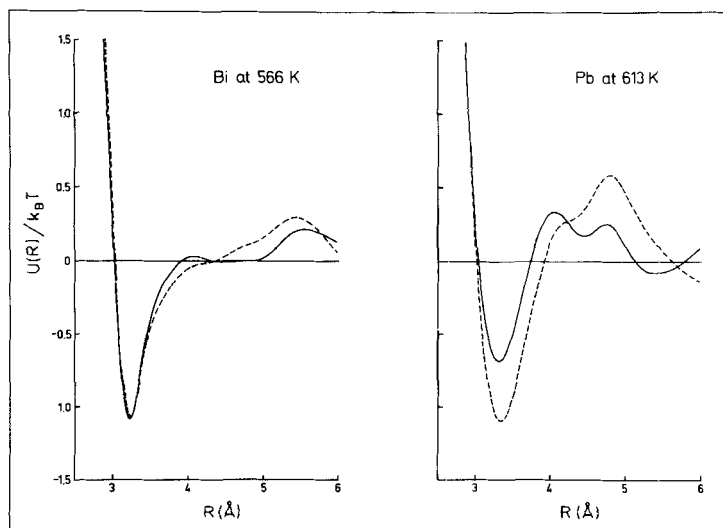


FIGURE 4 Effective pair potentials for liquid bismuth at 566 K (left) and for liquid lead at 623 K (right). The dashed curves are the zeroth order terms in Eq. (3) while the full one is the sum of the zeroth and the first order terms.

Recently the fourth energy moment, $\langle \omega^4(Q) \rangle$, of the dynamic scattering function, $S(Q, \omega)$, was determined experimentally.²⁴ This is defined as

$$\langle \omega^4(Q) \rangle / \langle \omega^2(Q) \rangle = 3\langle \omega^2(Q) \rangle + \Omega^2(Q) \quad (6)$$

where

$$\langle \omega^2(Q) \rangle = (k_B T/M)Q^2 \quad (7)$$

M is the atomic mass. The first term on the right hand side in Eq. (6) is entirely determined by the free motion of the atoms and usually this comprises the main component of the total fourth moment. However, the most interesting term from a physical point of view is the second one as it contains all the interaction effects. It can explicitly be written

$$\Omega^2(Q) = (n/M) \int_0^\infty dR g(R)(1 - \cos(Qz))(\partial^2 U(R)/\partial z^2) \quad (8)$$

Using the results presented above on $g(R)$ and $U(R)$ the curve in Figure 5 is calculated via Eq. (8). The circles are experimental points from Dahlborg *et al.*²⁴ The agreement between the two sets of data shown in Figure 5 is

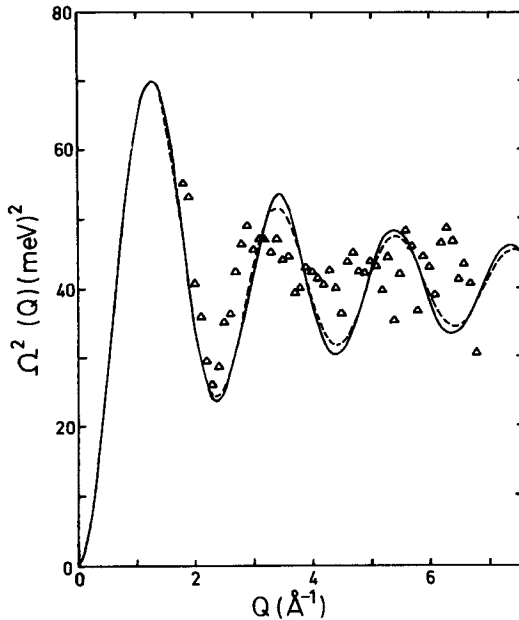


FIGURE 5 $\Omega^2(Q)$ for liquid bismuth. The full curve is calculated from Eq. (8) and the dashed one is obtained from a least squares fit of Eq. (9). The circles are the experimental results of Dahlborg *et al.*²⁴

surprisingly good in view of the very large difficulties to determine the fourth moment experimentally. Dahlborg *et al.* do not assign any errors to their results but instead state that the scatter of the points show the uncertainty in their values. Thus the agreement might be fortuitous but it nevertheless indicates that some confidence can be put in the de Angelis and March procedure to derive an effective pair potential for a liquid like bismuth. For liquid lead a much poorer agreement with the experimental results of Dahlborg *et al.* was obtained. This might have been expected from the fact that higher order terms obviously have to be included in Eq. (3) in order to arrive at a reliable pair potential for lead.

Under certain assumptions²⁵ $\Omega^2(Q)$ can be approximated by

$$\Omega^2(Q) = \omega_E^2(1 - 3 \sin(X)/X - 6 \cos(X)/X^2 + 6 \sin(X)/X^3) \quad (9)$$

where $X = QR_0$. ω_E is called the Einstein frequency and is of the order of the maximum phonon frequency in the solid. R_0 is a characteristic length in the liquid. A fit of Eq. (9) to the results calculated via Eq. (8) is shown as the dashed curve in Figure 5. The parameter values were found to be $\omega_E = 6.4$ meV and $R_0 = 3.15$ Å. The difference between the two curves is small and it is obvious that Eq. (8) can, with realistic values on the parameters, in most cases safely be used to estimate the fourth energy moment of $S(Q, \omega)$.

CONCLUSIONS

The static structure factor $S(Q)$ for liquid bismuth at 566 K is found to exhibit a more pronounced shoulder on the high Q side of the main diffraction peak than seen earlier both by neutron and X-ray diffraction measurements. The Q value for this particular feature is smaller than $2*k_F$ where k_F corresponds to the Fermi radius. It is also found that this shoulder has an important impact on the irregularity found between 4 and 5 Å in the pair distribution function and it is conjectured that this irregularity is a consequence of the simultaneous existence of two types of structures in the liquid. The effective pair potential seems to be of ledge type contrary what is the case in an ordinary liquid metal as lead. In order to test the obtained $U(R)$ molecular dynamics simulations will be performed in the near future and compared to experimental results on the dynamic structure factor.

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