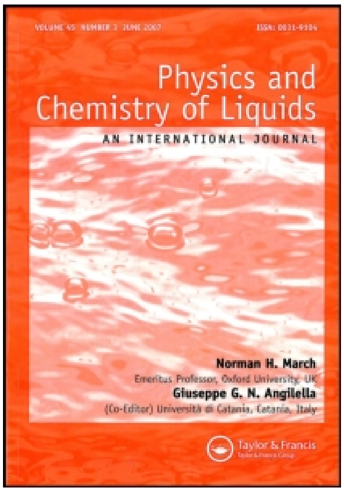

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Letter

Dispersion Forces and Small-angle Neutron Scattering from Liquid Noble Metals

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Maggs and Ashcroft have re-opened the question of the analogy between the cohesion of a molecular crystal, in which dispersion forces play a major role, and that in a metal crystal with polarizable ion cores. It is pointed out that small-angle neutron scattering from liquid noble metals could be used to test their predictions.

Key Words: Dispersion forces, small-angle neutron scattering, liquid noble metals.

Maggs and Ashcroft[1] have recently re-opened the question of the analogy between the cohesion of an insulating crystal such as argon, in which dispersion forces that are dynamic in origin play a major role, and cohesion in a metal crystal with polarizable ion cores. These workers make predictions as to the long-range form of the interatomic interaction $\phi(r)$ in such metals which, using conventional notation employed in insulating crystals, is argued in Ref. 1 to take the form

$$\phi(r) = -\frac{c_6}{r^6} \tag{1}$$

Earlier estimates of c_6 for monovalent metals can be found in the work of Matthai and March.[2] Whereas for the noble metals, Chatterjee[3] has used some thermodynamic properties to establish approximate relations for c_6 in terms of the critical temperature and the van der Waals gas constants, his estimates are a factor of 15 to 30 greater than the first principles estimates of Mahanty and Taylor,[4] whose work used the earlier treatment of Rehr *et al.*[5]

Because of the current interest generated by Maggs and Ashcroft[1] in the noble metals, as having ions with polarizable cores, we want to re-emphasize here the importance of measuring the small-angle neutron scattering from the noble metals in the liquid phase near their melting temperatures.

Let us set out the argument first for liquid argon. At sufficiently large r, and far from the critical point, one has the asymptotic relation

$$c(r) = -\frac{\phi(r)}{k_B T} \tag{2}$$

for the Ornstein-Zernike direct correlation function $c(r)$. Its Fourier transform, $\tilde{c}(k)$ say, is related to the liquid structure factor $S(k)$ by

$$\tilde{c}(k) = \frac{S(k) - 1}{S(k)}. \tag{3}$$

Use of Eqs (1) and (2), plus the relation (3), has been known[6] for more than twenty years to yield the small angle scattering from the liquid insulator as

$$S(k) = S(0) + a_2 k^2 + a_3 k^3 + \cdots \tag{4}$$

The form of a_3 is given in terms of c_6 in Eq. (1) as

$$a_3 = \frac{\pi^2 \rho \{S(0)\}^2 c_6}{12 k_B T} \tag{5}$$

where $S(0)$ is determined by fluctuation theory as

$$S(0) = \rho k_B T K_T, \tag{6}$$

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

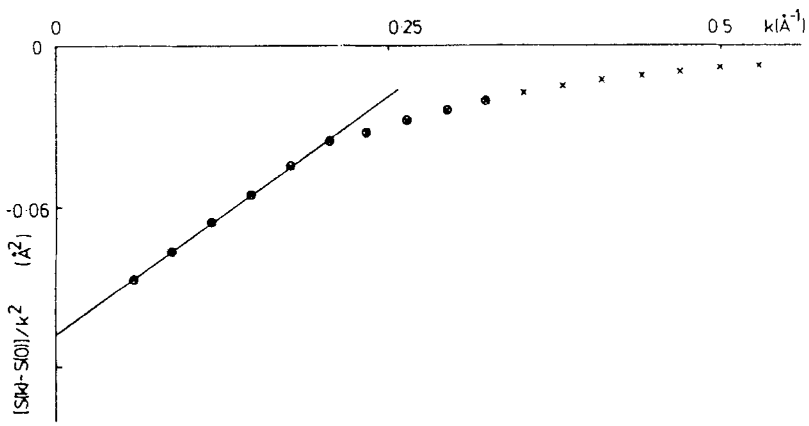

Figure 1 $(S(k) - S(0))/k^2$ against k from neutron scattering data of Yarnell *et al.*[7] The straight line is the fit[2] to the form (4).

Figure 1 shows the way the measured small-angle neutron scattering data of Yarnell *et al.*[7] from liquid argon was analyzed by Matthai and March.[2] The calculated value of a_3 from Eq. (5) was 0.375 Å^3. It is of interest here to note that Robinson and March[8] have shown that 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.

Turning to liquid metals Matthai and March[2] analyzed the small-angle X-ray scattering data[9] of Greenfield *et al.*[10] on both liquid Na and K. While they proposed, as a result of their analysis, that a term proportional to k, namely a_1k, had to be inserted in Eq. (4) in order to make sense of the X-ray scattering data on these two metals, their analysis, and especially their Figure 5 for liquid Na, could then be well fitted by an expansion

$$S(k) = S(0) + a_1k + a_2k^2;$$

i.e. without a k^3 term.

Of course, Maggs and Ashcroft[1] have stressed that their theoretical work is only appropriate to ions with polarizable cores. Therefore, it would now be of considerable interest if accurate small-angle neutron scattering data could be obtained for the liquid noble metals. It has to be stressed, though, that in Figure 1 for liquid argon, it is k values less than about $\frac{1}{4}$ Å^{-1} which are needed to extract a_3 in Eq. (4), and though $S(k)$ has been measured on liquid noble metals we know of no really accurate data in this range of wavenumber k.

In summary, such a small-angle neutron scattering experiment on, say, liquid Cu just above its melting temperature would be of considerable interest to test the validity of an analogy between the insulating liquid Ar, for which Eq. (4) is directly applicable, and liquid Cu, with polarizable ion cores. If the neutron data on liquid noble metals can be analyzed in terms of the small k expansion (4), then a_3 and hence, using (5), c_6 can be extracted and brought into contact with the predictions of Maggs and Ashcroft.[1] If, as in the work of Matthai and March,[2] a term a_1k has to be introduced into Eq. (4) for the liquid noble metals, analysis leading to a_3 should still prove possible by means of their procedure.

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