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The structure factors of liquid alkali metals in the hard-sphere system

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Abstract. The structure factors $S(q)$ of liquid alkali metals are calculated using a fluid of hard spheres as a reference system together with the Cummings potential in a random-phase approximation. For the hard-sphere reference system the direct correlation function of Colot and co-workers is used to improve the Percus–Yevick approximation at liquid-metal densities. This leads to good agreement with experimental data, particularly at low q .

Recently, considerable interest has been focused on obtaining a better reference system for use in the calculation of static structure factors of liquid alkali metals. Such calculations usually make use of a perturbation theory together with the decomposition of an inter-atomic potential into reference and perturbation parts—in this, the hard sphere (HS) has played a dominant role (Young 1977, Ashcroft and Stroud 1978). However, for the softer core potentials, such as the alkali metals possess, the reference part, when replaced by the HS potential, was found to be inappropriate. Recently, it has been shown that the one-component plasma (OCP) yields a lower variational upper bound to the free energy than does the HS model (Mon *et al* 1981, Chaturvedi *et al* 1981a). Although the OCP enjoys this advantage its application to liquid metals still raises problems such as the interpretation of the plasma parameter (Bretonnet and Khanna 1985). Another reference system, of an intermediate character, is a system of charged HS in a homogeneous compensating background (Palmer and Weeks 1973). This system yields a higher variational upper bound to the free energy than either the HS or the OCP fluid and the structure factors are very similar to those obtained using the OCP. In both of these cases, unphysical behaviour of the structure factor $S(q)$ near its principal peak region in the random-phase approximation (RPA) resulted, and this was overcome by truncating the pseudopotential after its first node (Singh and Holz 1983, Lai 1985).

Now we return to the HS reference system: when a HS reference system potential is used one can soften the core by the method of Weeks *et al* (1971). McLaughlin and Young (1982) used this method together with the mean-density approximation to describe simple liquid metals in both the low- q and high- q regions of $S(q)$. The analytic solution of the Percus–Yevick equation for HS is normally used to describe the reference system. This solution needs to be corrected in the packing fraction range $0.4 \leq \eta \leq 0.74$ so that agreement with the HS Monte Carlo ‘experiments’ is achieved. The lower end of this range is, of course, that of the liquid-metal packing fractions. For this reason

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McLaughlin and Young (1982) employed the Verlet and Weis (1972) approach. Another method of obtaining improvement was introduced by Waisman (1973); this involved solving the mean-spherical integral equation to obtain a Yukawa form. However, this gave rise to a complex set of equations to solve. Colot *et al* (1986) proposed a semi-empirical HS direct correlation function (DCF) which was derived using the Yukawa form of the DCF together with the Verlet and Weis (vw) result. A simple analytic expression was obtained which depended only on the packing fraction. We use this expression to describe our HS reference system.

It should be noted that a HS Yukawa reference system has recently been introduced to study liquid metals (Hayter *et al* 1983, Li *et al* 1986, Hausleitner and Hafner 1988). In this reference system the Yukawa potential is repulsive and therefore gives rise to a 'softening' of the potential.

Hayter *et al* (1983) have maintained that the Friedel oscillations are not significant in determining the radial distribution functions of the liquid metals. However, in the evaluation of the structure factor, particularly for low q , the long-range oscillations are important. In fact, the recent work of Arlinghaus and Cummings (1987) suggests that both the softness of the core and the oscillatory tail are important in describing the structure factor of liquid metals such as rubidium. For this reason we have included the oscillatory tail through the Cummings potential (Cummings 1979) in the RPA together with the HSY procedure of Colot *et al* (1986) for the reference system. Bretonnet (1983) has used the Cummings potential but with the Percus–Yevick HS reference system to compare structure factors in the long-wavelength limit ($q = 0$) for a number of liquid metals and obtained reasonable agreement with experiment.

The structure factor $S(q)$ is related to the direct correlation function $c(q)$ by

$$S(q) = 1/(1 - c(q)). \quad (1)$$

Colot *et al* (1986) postulated a semi-empirical expression for c_{PYT} for HS fluid which they obtained by mixing the Percus–Yevick DCF with the DCF of the Yukawa tail, producing the simple Fourier-transformed DCF

$$c_{\text{PYT}}(q) = ac_{\text{PY}}(q) + [24\eta b/(q^2 + d^2)][\cos q + (d/q) \sin q] \quad (2)$$

where $a(\eta)$ and $b(\eta)$ are determined by requiring thermodynamic consistency with the Carnahan–Starling equation of state and the d -values are found from fitting the vw solution. c_{PY} is the Wertheim–Thiele solution (Wertheim 1963, Thiele 1963) of the PY equations for hard spheres. We use c_{PYT} for the solution of our reference system. The parameters $a(\eta)$, $b(\eta)$ and $d(\eta)$ are given by Colot *et al* (1986).

Using the RPA allows us to write the expression for the $c(q)$ of the system in terms of the reference potential and its perturbation $\varphi_1(q)$:

$$c(q) = c_{\text{PYT}}(q) - \beta\varphi_1(q) \quad (3)$$

where $\beta = 1/k_{\text{B}}T$ and $\varphi_1(q)$ is the Fourier transform of the Cummings potential (Cummings 1979).

$$\beta\varphi_1(q) = -\frac{12\eta}{q} \left[x_1 \left(\frac{a_1 \sin q + (a_2 + q) \cos q}{(a_2 + q)^2 + a_1^2} + \frac{a_1 \sin q - (a_2 - q) \cos q}{(a_2 - q)^2 + a_1^2} \right) + x_2 \left(\frac{a_1 \cos q + (a_2 - q) \sin q}{(a_2 - q)^2 + a_1^2} - \frac{a_1 \cos q - (a_2 + q) \sin q}{(a_2 + q)^2 + a_1^2} \right) \right] \quad (4)$$

Table 1. The Cummings potential parameters and long-wavelength limit of the structure factor.

Metal	T (K)	η	σ	x_1	x_2
Na	378	0.465	6.25	-0.275	0.442
K	343	0.460	7.76	-0.539	0.725
Rb	312	0.472	8.30	-0.539	0.772

Metal	a_1	a_2	$S(0)$	$S(0)$ (Bretonnet)	$S(0)$ (Experiment†)
Na	2.155	6.060	0.0242	0.0191	0.0240
K	3.176	6.015	0.0254	0.0213	0.0247
Rb	3.00	6.00	0.0228	—	0.0220

† Chaturvedi *et al* (1981b).

where $x_1 = \Lambda_1/k_B T\sigma$, $x_2 = \Lambda_2/k_B T\sigma$, $a_1 = z\sigma$, $a_2 = \mu\sigma$ and $q = Q\sigma$. The parameters Λ_1 , Λ_2 , z and μ are defined by Bretonnet (1983).

The structure factor is then obtained from (1). In the long-wavelength limit

$$S(0) = S_{\text{PYT}}(0) \{1 - [24\eta(x_1 a_1 + x_2 a_2)/(a_2^2 + a_1^2)] S_{\text{PYT}}(0)\}^{-1} \quad (5)$$

where

$$S_{\text{PYT}}(0) = [1 - ac_{\text{PY}} - (24\eta b/d^2)(1 + d)]^{-1}. \quad (6)$$

The DCF $c(q)$ from (3) is used in (1) for calculating the structure factor of the alkali metals Na, K and Rb at their melting points. The packing fraction η is used to adjust the position of the first peak—this essentially means an adjustment of the HS diameter σ . The values of η and σ are given in table 1. Minor adjustment is needed to the parameter values of Bretonnet (1983) to obtain an excellent fit to the experimental values—these are also listed in table 1. In figure 1 the experimental values from Waseda (1980) are compared with the computed values. The results are in good agreement for the first peak but not for the second peak. This phase shift in the second peak and beyond is a feature of all the HS approaches but is, in fact, improved for the OCP (Chaturvedi *et al* 1981a, Ono and Yokoyama 1984). In figure 2 the low- q values are shown using the same values of parameters and excellent agreement is obtained. In table 1 the long-wavelength limits $S(0)$ from (5) are compared with experiment and the values obtained by Bretonnet (1983). The results show better agreement with experimental results than with those given by Bretonnet. In figure 1(c) $S_{\text{PYT}}(q)$ is compared with the above result for Rb for the same value of η —the improvement due to the inclusion of the Cummings potential is evident. The value of η could be adjusted so that the first peak of $S_{\text{PYT}}(q)$ showed better agreement with experimental results but this would give rise to a poor agreement in the low- q region.

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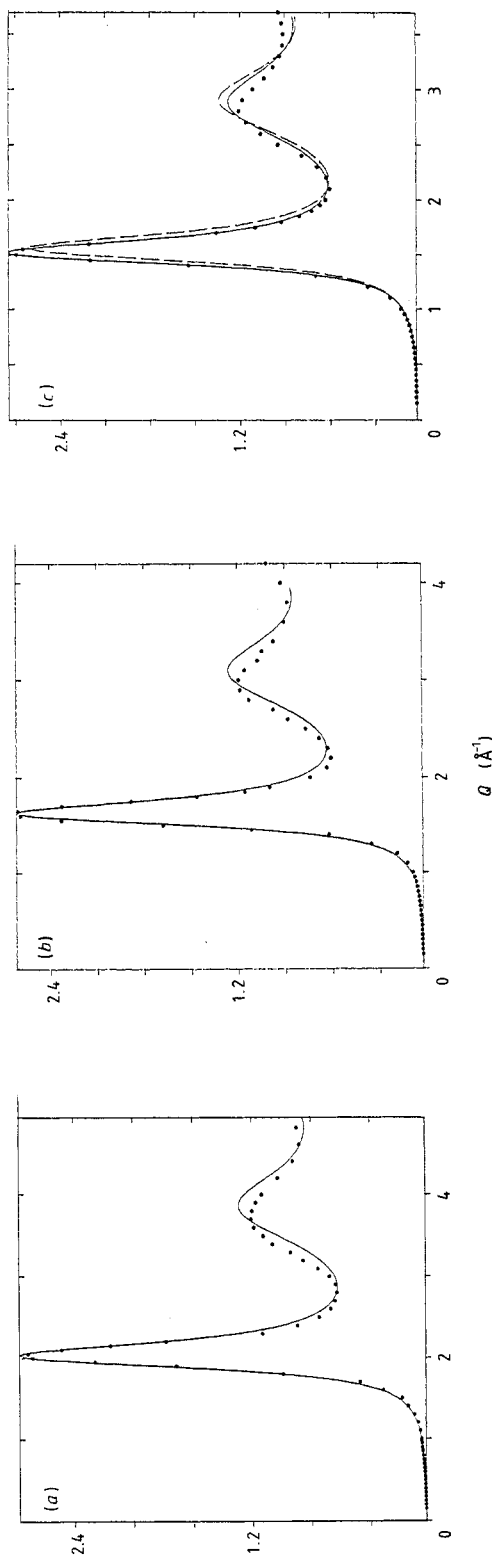


Figure 1. Structure factors for (a) Na, (b) K and (c) Rb. The full curves are theoretical results and the full circles are experimental ones (Waseda 1980). The broken curve is for hard spheres with a Yukawa tail (Cotot *et al* 1986).

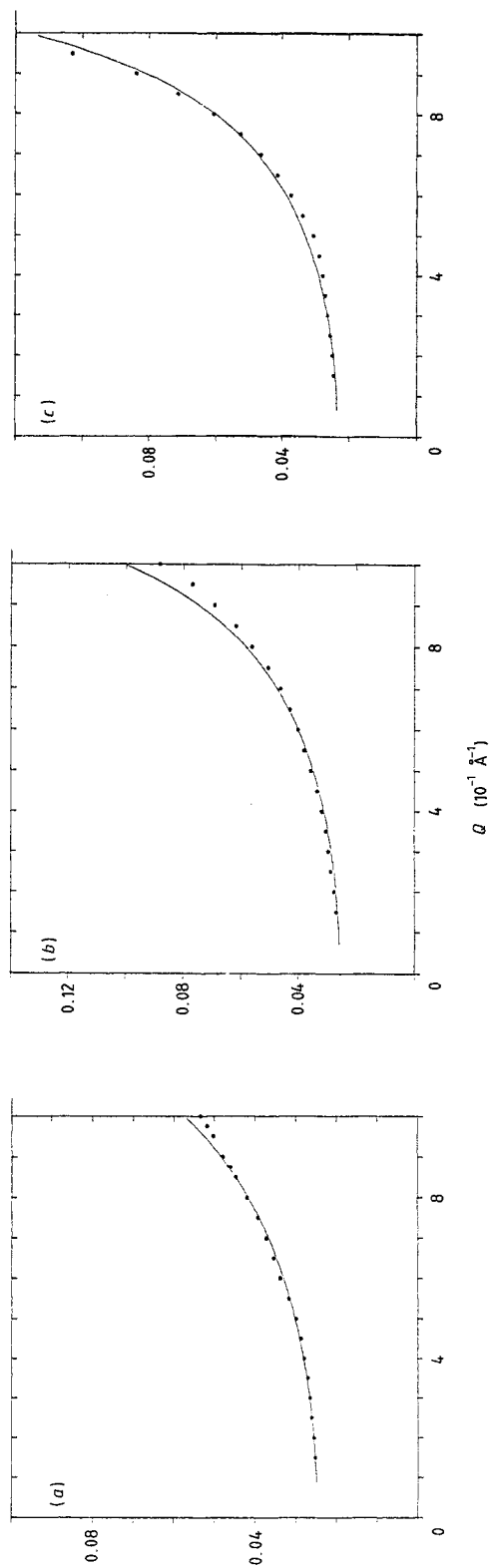


Figure 2. Low-angle structure factors for (a) Na, (b) K and (c) Rb. The full (theoretical) curves are calculated using ζ_{PYT} and the Cummings potential. The full circles are experimental results (Waseda 1980).

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