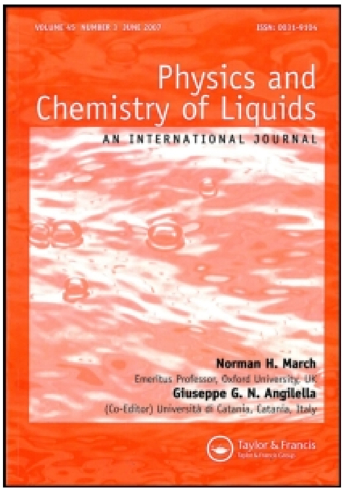

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Structure Factor of Liquid Alkali Metals in a Charged Hard Sphere System

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The structure factors of liquid alkali metals are calculated by treating a system of charged hard spheres (CHS), embedded in a rigid, uniform and neutralizing background. With the use of this model as a reference, the effects of responding electrons are taken into account in random phase approximation. The results obtained for the static structure factor of alkali metals are in good agreement with the experimental data.

Key Words: Structure factors, liquid alkali metals, charged hard sphere system.

1 INTRODUCTION

There has been much interest in the study of the static structure factor $S(q)$ of liquid alkali metals. Earlier attempts to calculate $S(q)$ of liquid alkali metals had the systems of neutral hard spheres (NHS)[1-3] and the classical one component plasma (OCP)[4-6] as their reference systems. The reason for general inadequacy of NHS models in the case of alkali metals seems to lie in the fact that their repulsive cores are comparatively soft. Although OCP is generally superior over a system of NHS in the sense of predicting lower free energy[5], it has the practical disadvantage of not being analytically available. In this model the positive ions are considered as point charges which is not so in actual alkali metals whose ionic diameters are of the same order of magnitude as the Coulomb hole in the corresponding OCP. Recently a new reference system is introduced. It is a system of charged hard spheres embedded in a rigid, uniform and neutralizing background. This model is attractive since it has the advantages that a NHS system and an OCP system possess besides the analytical expressions, solved by Palmer and Weeks[7] within a mean spherical approximation, are available. The model has also been examined very recently against machine calculations[8]. Theoretically, CHS model has been adopted by Singh and Holz[9] and Lai[10]. Singh and Holz used this model as the reference system, the effect of responding electrons was taken into account in a linear-response approximation, which adopts a local model potential of Ashcroft. They obtained unphysical values of $S(q)$ near its principal peak region which was overcomed by truncating pseudopotential after its first node. Lai has calculated the reference liquid structure factors which adopts the variational calculations, the parameters correspond to minimum of the Helmholtz free energy. These authors[9,10] have used the disposable parameter to be the HS diameter. In principle we have two free parameters, the HS diameter and the plasma parameter. However, as a reasonable approximation, we choose η and Γ are two disposable parameters for a complete specification of the CHS system. The purpose of this paper is to determine the structure factor of alkali metals by using the results of Palmer and Weeks for the direct correlation function combined with indirect ion interaction in random phase approximation (RPA), we shall present numerical results and show that the height and the position of the first peak can be accurately measured without implying empirical cut-off by introducing a non-local model potential.

2 THE CHARGED HARD SPHERE MODEL

We employ the charged hard sphere model proposed by Palmer and Weeks in which the interacting pairwise potential is given by

$$V(r) = \begin{vmatrix} \infty & r < \sigma \\ Z^2e^2/r & \gamma > \sigma \end{vmatrix} \tag{1}$$

here Z and σ are, respectively, the valence and HS diameter. Their results for the direct correlation function, appropriate for an CHS system in a uniform background of electrons, can be written as

$$C(x) = \begin{vmatrix} A + BX + CX^2 + DX^3 + EX^5 & \text{for } X < 1 \\ -\gamma/X & X > 1 \end{vmatrix} \tag{2}$$

where $X = r/\sigma$, σ being the effective hard core diameter of the charged spheres. The coefficients A, B, C, D and E are defined in the text of

Singh and Holz[9]. The Fourier transform of Eq. (2) is given by

$$\begin{aligned}\rho C(q) = \frac{24\eta}{q^6}\{&Aq^3(\sin q - q\cos q) + Bq^2[2q\sin q\\ &-(q^2-2)\cos q - 2] + Cq[(3q^2-6)\sin q - (q^2-6)q\cos q]\\ &+ D[(4q^2-24)q\sin q - (q^4-12q^2+24)\cos q + 24]\\ &+ E[6(q^4-20q^2+120)q\sin q - (q^6-30q^4+360q^2\\ &-720)\cos q - 720]/q^2 - \gamma q^4\cos q\}\end{aligned} \tag{3}$$

here q is expressed in units of σ^{-1}. We calculate $\gamma = \Gamma a_0/\sigma$; $a_0 = (\frac{3}{4}\pi n)^{1/3}$ and σ is determined by the relation $\eta = \pi\sigma^3/6\Omega$. The structure factor in the RPA can be readily expressed by

$$S(q) = \frac{1}{1 - \rho[C(q) - \beta\mu_{Sc}(q)]} \tag{4}$$

here $C(q)$ is the Fourier transform of the direct correlation function expressed by Eq. (3), $\beta = (K_B T)^{-1}$ and $\rho = N/V$ is the number density of the ions. The second term in the bracket of Eq. (4) is the indirect interaction between the ions, which can be expressed in terms of normalized energy wave number characteristic $F_N(q)$

$$\mu_{Sc}(q) = -\frac{4\pi Z^2 e^2}{q^2} F_N(q) \tag{5}$$

3 RESULTS AND DISCUSSION

The main aim of this investigation is to present our results for the static structure factor of Na, K and Rb and to compare them with the experimental data. We have to point out that the choice of $F_N(q)$ plays a significant role in the determination of the structure factor. It is generally recognized that Ashcroft's model is a good local model pseudopotential involving only one core-radius parameter. However, all the physical contents of the pseudopotential theory may not emerge through a single empirical fit of this parameter. Bretonnet and Regnaut[11] have shown that the liquid structure is sensitive to the nonlocality involved in pseudopotential. The practical disadvantage of a local model pseudopotential is that the values of $S(q)$ near its principal peak region becomes large and the height of the first peak cannot be adjusted with reasonable choice of parameters. This needs an empirical cut off near its principal peak as adopted by Singh and Holz[9] and Chaturvedi *et al.*[12]. Here we choose to work with the non-local shaw model potential as used in the work of Bretonnet and Khanna[6]. It produces the smoothest pseudo wavefunction, in the spirit of Cohen and Heine[13]. We therefore construct $F_N(q)$ by using nonlocal model potential of Shaw taking into account the electron gas response function of Vashishta and Singwi[14].

We present our results for $S(q)$ of Na at the melting temperature in the Figure 1. The structure factor $S(q)$ obtained with $\eta = 0.434$ and

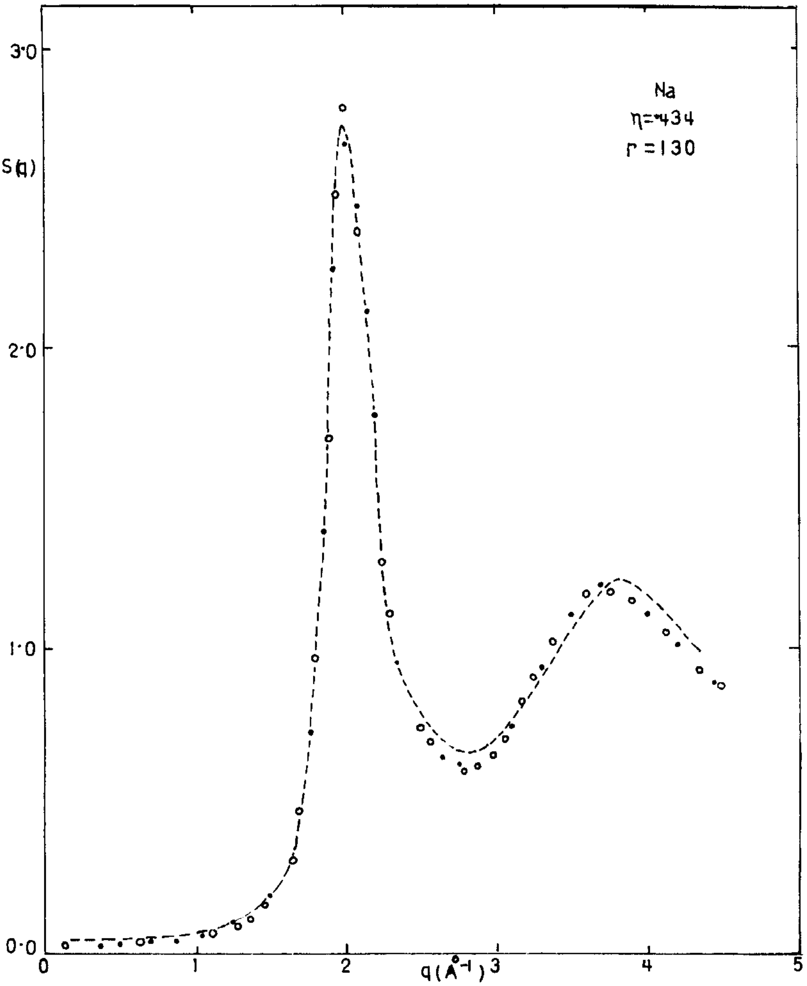

Figure 1 Liquid structure factor for Na calculated at $T = 100$°C using CHS reference system. Ours (- - - -). Experimental results; Waseda (solid circles), Greenfield *et al.* (open circles).

$\Gamma = 130$ is in reasonably good agreement with the experimental data of Waseda[15] and Greenfield *et al.*[16] However, the height of the first peak in Greenfield *et al.* is higher than Waseda value which further improves the agreement with experiment in low q region. This is encouraging results in view of the simplicity of RPA. The advantage of two disposable parameters η and Γ is that it is easy to fit the position and height of the first peak. Results of $S(q)$ for K are displayed and compared with experiments[15–16] in Figure 2. The common feature in Na and K is that the second peak of $S(q)$ is obtained at little higher

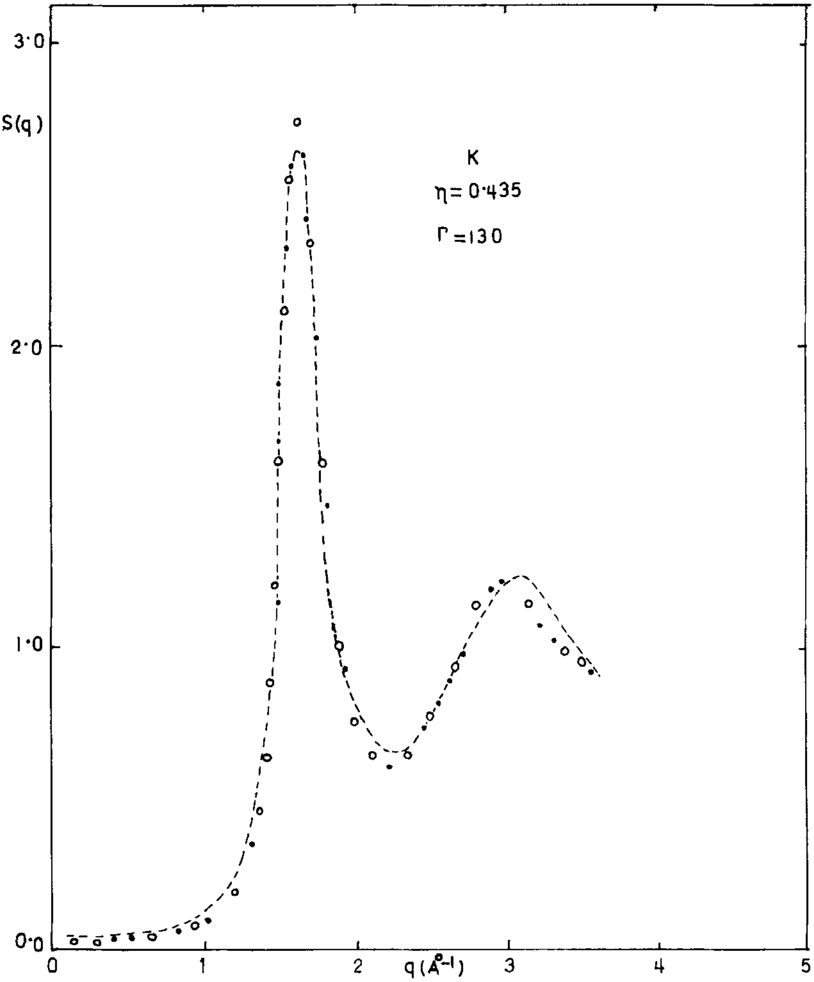

Figure 2 Liquid structure factor for K calculated at $T = 63.5°C$. See Figure 1 for notation.

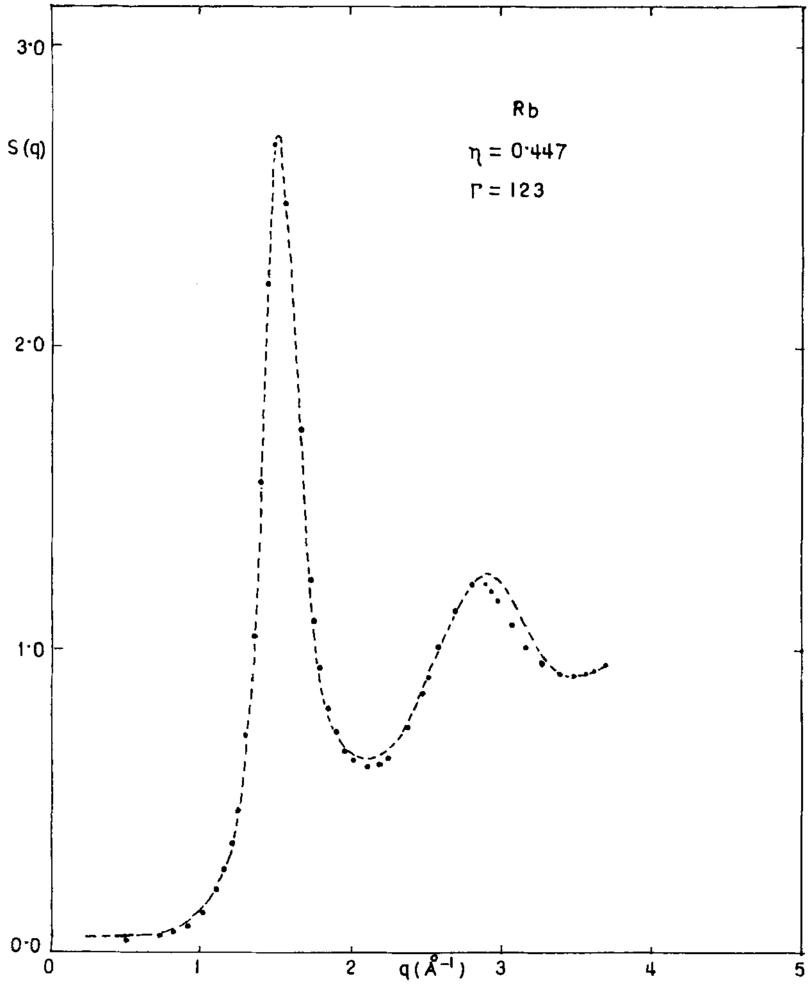

Figure 3 Liquid structure factor for Rb calculated at $T = 38.9°C$. Ours (- - - -). Experimental results of Waseda shown by solid circles.

value of q although it has the same amplitude as obtained by experiments. Such deviations were also observed by Lai[10] which were pronounced for neutral hard sphere system. The pair potential $v(R)$ is separated into a short-range, $v_0(R)$ and long-range part $v_1(R)$. The former corresponds to the short-range repulsive forces. The latter contribution is considered a perturbation of $v_0(R)$. In the liquid alkali metals, $v_0(R)$ is assumed to be sufficiently soft to also be subject to perturbation expansion from the reference fluid. Our results indicate that to study the structural properties of alkali metals for which the

Table 1 Hard-sphere diameters σ determined for CHS system using Vashishta-Singwi dielectric function. All in atomic units.

σ	Na	K	Rb
Singh and Holz	6.199	7.743	8.266
Lai	6.162	7.562	8.068
Ours	6.13	7.61	8.20

repulsive cores are comparatively soft, the CHS is a good reference system. Our results for Rb are of better quality than that of Singh and Holz[9] and Lai[10]. This may be due to the use of nonlocal model potential and considering η and Γ are two disposable parameters. To explore further, we compare our values of hard sphere diameter with those obtained by Singh and Holz[9] and Lai[10] in Table 1. Our values lie inbetween the values quoted by these authors. The smaller value of HS diameter is preferred for metals with soft pair potential. Lai values are smaller than our values due to the fact that they have determined HS diameter for which Helmholtz energy is minimum. It is also appropriate to mention that our values of Γ are almost same as obtained by Lai[10] which corresponds to the minima of each Helmholtz free energy. These values of Γ are significantly different from the one predicted by Slattery *et al.*[17] at the melting temperature.

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