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Low Angle Structure Factor of Liquid Alkali Metals Using One Component Plasma System

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We present results of calculations of the liquid structure factor $S(q)$ of the alkali metals by using an analytical form for the direct correlation function of the OCP reference system as well as the random phase approximation to consider the electronic screening. The treatment, which is based on the Baus and Hansen model, works well with two parameters Γ and x_0 . It is found out that the value $x_0^2 = 2.34$ is good to describe the low- q region of $S(q)$ but unable to reproduce the first peak while $x_0^2 = 3.2$ makes the situation reversed.

As an application, $S(0)$ values of fluid rubidium are calculated from melting temperature to critical point. The results reproduce experiments with good agreement without showing divergence up to the temperature $T = 1800$ K.

1 INTRODUCTION

There has been slow progress in the theory of one component plasma system in spite of considerable efforts made by several workers (Galam and Hansen,¹ Chaturvedi *et al.*,² Evans and Sluckin,³ Iyetomi *et al.*,⁴ Mon *et al.*,⁵ and Ono and Yokoyama⁶). This is a classical fluid of identical points like charges embedded in a rigid uniform background, thereby its direct use for real liquid metals includes the Coulomb repulsion between the bare ions but omits the indirect ion-ion attraction arising from electronic screening. Minoo *et al.*⁷ and subsequently other authors (Mon *et al.*⁵ and Ross *et al.*⁸) have shown

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that the structure factor of the OCP gives a good representation of $S(q)$ for alkali metals in the region of its main peak. The electronic screening, necessary to describe low- q region, can be included through random phase approximation (RPA) to treat the indirect ion-ion interaction. However, among perturbative theories of the liquid structure factor $S(q)$, RPA has been the subject of discussion and several authors have expressed a doubt to include indirect ion-ion interaction through RPA in the OCP system. With our numerical calculations we assess that such an approximation is sufficiently accurate to predict the structure factor of alkali metals, provided that the values of the parameters i.e. x_0 and Γ have to be judiciously chosen. For heavy alkali metals the repulsive part of the interionic repulsion is extremely soft so that OCP reference system should be conveniently used at all densities. Taking advantage of the accurate experimental data of the long-wavelength limit of expanded liquid rubidium, we have checked the validity of our statement. The aim of this paper is to present the results of the structure factor of low- q region by using RPA and to apply OCP system to the expanded rubidium. All the calculations in this paper are based on semi analytic theory proposed by Baus and Hansen.⁹

2 FORMULATION

The structure factor in the random phase approximation can readily expressed

$$S(q) = \frac{1}{1 - \rho[C_{\text{OCP}}(q) - \beta\mu_{\text{sc}}(q)]} \quad (1)$$

here $C_{\text{OCP}}(q)$ is the Fourier transform of the direct correlation function expressed by Baus and Hansen⁹ as

$$C_{\text{OCP}}(q) = -\frac{4\pi\Gamma a(2p+1)!!}{q^2} \frac{j_p(x)}{x^p} \quad (2)$$

where $j_p(x)$ being the spherical Bessel function of the order p and $x = qr_0$ is a dimensionless parameter depending on the scaling parameter r_0 . The second term in Eq. (1) is the indirect interaction between the ions which can be considered as a perturbation to the direct Coulomb repulsion and can be expressed in terms of normalized energy-wavenumber characteristic $F_N(q)$.

$$\mu_{\text{sc}}(q) = -\frac{4\pi z^2 e^2}{q^2} F_N(q) \quad (3)$$

Using the solution of Eq. (2) and combining with Eq. (3), we arrive at the following analytical expression for the static structure factor for $p = 3$ (Bretonnet and Khanna¹⁰)

$$S(q)^{-1} = 1 + \frac{3\Gamma x_0^2}{X^2} \left\{ \frac{105}{X^4} \left[\left(\frac{15}{X^2} - 6 \right) \frac{\sin X}{X} - \left(\frac{15}{X^2} - 1 \right) \cos X \right] - F_N(q) \right\} \quad (4)$$

where x_0 is a dimensionless parameter defined by $x_0 = \tau_0/a$. The scaling parameter r_0 represents an effective screening radius. Physically the direct correlation function $C(r)$ can be thought of as due to electrostatic potential of an effective ionic charge distribution inside a sphere of radius r_0 .

The screening function $\varepsilon(q)$ employed to determine $F_N(q)$ (Eq. 3) may generally be expressed in terms of the local field correction $G(x)$ as

$$\varepsilon(q) = 1 + \frac{4\pi}{q^2} \Pi(q) \quad (5)$$

where $\Pi(q)$ is the electron gas polarisation function

$$\varepsilon(q) = \frac{(K_F/\pi^2)f(x)}{1 - (4K_F/\pi q^2)G(x)f(x)} \quad (6)$$

$$f(x) = \frac{1}{2} + \frac{(x^2 - 1)}{4x} \ln \left| \frac{1 - x}{1 + x} \right| \quad x = q/2K_F$$

Many forms of the local field exchange and correlation function $G(x)$ have been suggested in the literature however we focus on two. The first one comes from Vashishta and Singwi¹¹ (VS) and is one of the easiest and most accurate form to handle. The second one recently proposed by Ichimaru and Utsumi¹² (IU) accurately reproduces the Monte Carlo results on electron gas and satisfies the self consistency conditions in the compressibility sum rule and the short range correction. The function $G(q)$ thus measures the extent to which the exchange and Coulomb correlations act to modify the effective interaction between the density fluctuations of the electrons. If one ignores such an effect by setting $G(x) = 0$, the Hartree screening function (ε_H) results.

3 RESULTS AND DISCUSSION

(i) The structure factor of liquid alkali metals in low- q region

It has been observed that the problem to reproduce the correct structure factor in low- q region and peak position depends on the choice of x_0 i.e. the

ratio of the effective screening radius r_0 to the mean ion sphere radius a . Such conclusion is drawn by calculating structure factor from Eq. (4). We construct $F_N(q)$ containing information about electron gas screening (Hartree, V.S. and I.U.) and the nonlocal model potential of Shaw¹³, with the procedure as one used by Bretonnet and Khanna.¹⁰ The results for two choices of x_0 are discussed as following. Firstly, we have used the value proposed by Evans and Sluckin³ i.e. $x_0^2 = 2.34$ with the proper choice of $\Gamma = 171$ (Slattery *et al.*¹⁴) at which fluid-solid transition occurs. We observe in Figure 1 (a-c) that the structure factors of liquid alkali metals obtained by Hartree dielectric function lie systematically smaller than with those obtained from V.S. or I.U. dielectric screening functions which are in good agreement with experiments (Waseda¹⁵). Nevertheless, Hartree screening may reproduce the same values with very low Γ for instance $\Gamma = 100$ for Na. It is due to the fact that Γ has also small effects on low- q region. Thus the choice of Γ as a variable parameter might improve the results for each element in low- q region, but can not reproduce the first peak position.

Secondly, the value of $x_0^2 = 3.2$ (Bretonnet and Khanna¹⁰), obtained by fitting the first peak of the structure factor, distorts low- q region. The role of exchange and correlation corrections can not be explained as the Hartree dielectric screening reproduces better results than those obtained from V.S. or I.U. screening functions. For same Γ and x_0 , the low- q region is mainly affected by screening functions but the structure factor attains approximately same value for higher- q region irrespective of the dielectric screening function. To summarize, we can say that the present modified Baus and Hansen scheme in RPA has the merit of yielding convenient analytical results in low- q region of $S(q)$ with the choice of the parameter $x_0^2 = 2.34$ whereas $x_0^2 = 3.2$, which is better to reproduce the first peak, makes the low- q region little distorted. This anomaly reflects a failure of the Baus and Hansen model and the origin of this defect has not yet been fully examined.

(ii) The calculations of $S(0)$ for expanded rubidium

This is the motivation for performing another theoretical investigation of the structure factor of expanded rubidium which is based on random phase approximation. Only a few attempts (Evans and Sluckin³) have been made theoretically to study the structure factor $S(0)$ of expanded liquid metals by using OCP system. For the fluid alkali metals, characteristic changes of the scattering behaviour and of the microscopic structure as a function of density by varying temperature and pressure have been observed experimentally (Pfeifer¹⁶ and Franz *et al.*¹⁷). Thermodynamic perturbation calculations elucidate the influence of the repulsive and attractive interactions on the microscopic structure of the liquid metals. The study of Evans and Sluckin³

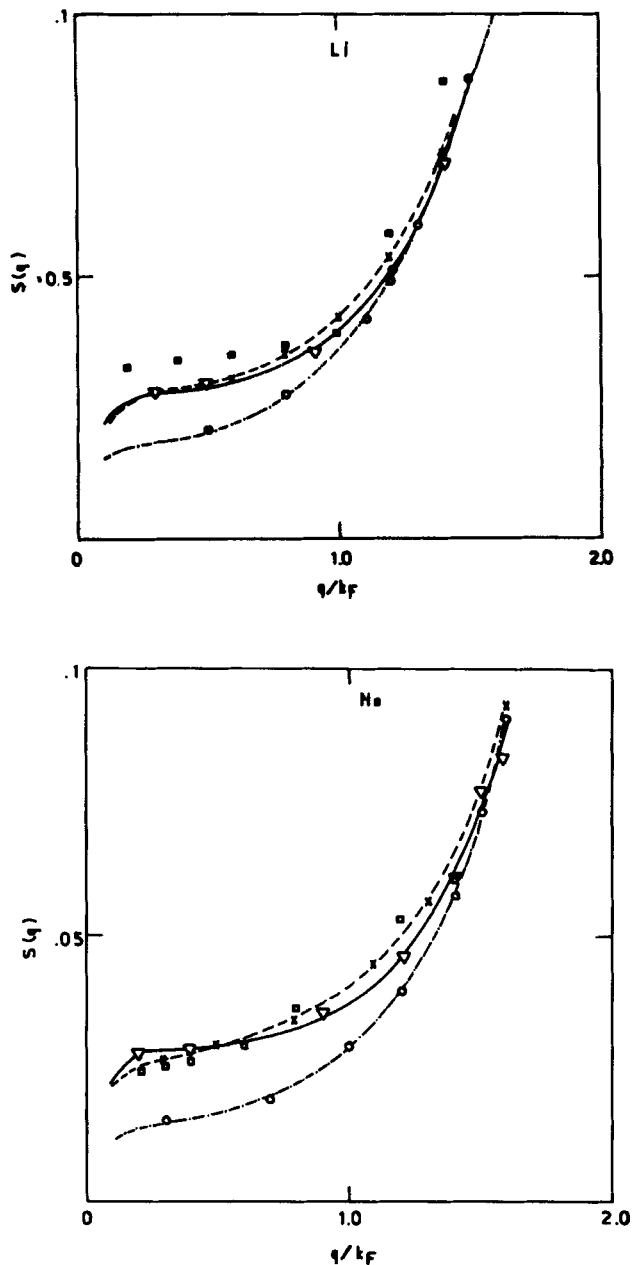


FIGURE 1 (a-c) The structure factor of Li, Na and K using $x_0^2 = 2.34$ for three dielectric functions H (○○○), VS (▽▽▽) and I. U. (×××). Experimental points (□□□): Waseda (1980).

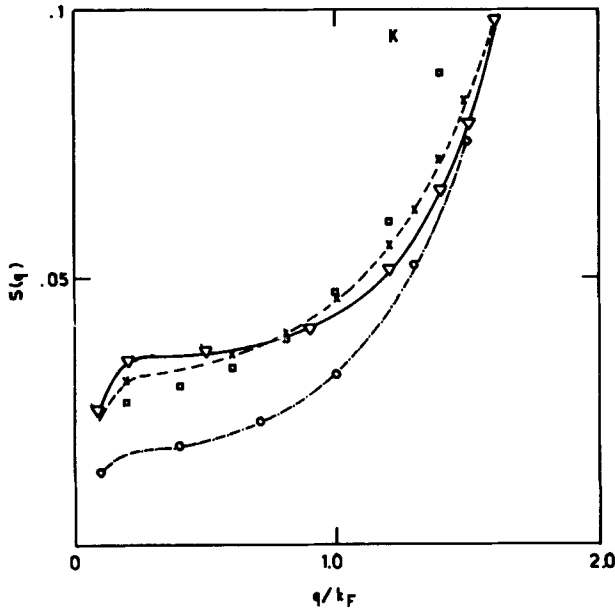


FIGURE 1 (continued).

shows an early divergence in the behaviour of $S(0)$ with density. This discrepancy is assigned by them to RPA. We use the same P-V-T data of Pfeifer¹⁶ as used by Evans and Sluckin³ to estimate the compressibility at a pressure of 150 bar for each temperature. However, we have used the Geldart and Vosko¹⁸ and Ichimaru and Utsumi dielectric functions. We derive the expressions of the long-wavelength limit of the structure factor in the Baus and Hansen model for $p = 3$

$$S(0)^{-1} = 1 - \frac{\Gamma x_0^2}{6} + \frac{3\Gamma}{a^2} \left[r_c^2 + \frac{\pi}{4K_F} - \left(\frac{1}{4K_F^2} + \frac{0.153}{4\pi K_F^3} \right) \right] \quad (\text{G.V.}) \quad (7)$$

$$S(0)^{-1} = 1 - \frac{\Gamma x_0^2}{6} + \frac{3\Gamma}{a^2} \left[r_c^2 + \frac{\pi}{4K_F} - \frac{\gamma_0}{K_F^2} \right] \quad (\text{I.U.}) \quad (8)$$

where $\rho = 3/4\pi a^3$; $K_F^3 = (3\pi^2 z \rho)$ and $\Gamma = \beta z^2 e^2/a$; $\gamma_0 = 0.25 + \gamma_1 \gamma_2 / \gamma_3$, γ_1 , γ_2 and γ_3 are the density dependent parameters defined in text of Ichimaru and Utsumi,¹² r_c is the core radius of the Ashcroft model potential. Our calculations also differ to that of Evans and Sluckin³ by using a density dependent pseudopotential core radius. These authors did not vary the core radius with density and it seems reasonable to suppose that such a procedure could be the cause of the major disagreement of their work with experiment. In fact, the simple relationship $r_c = 2.1 a_0 + 0.07 r_s$ (McLaughlin

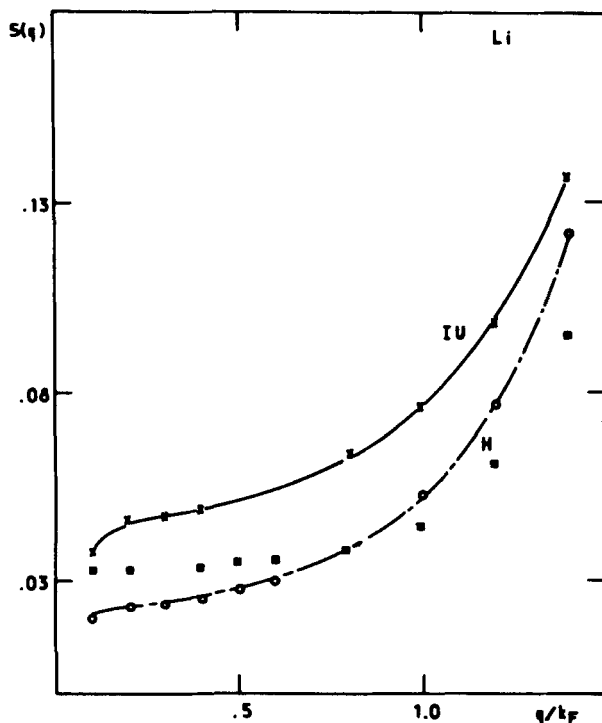


FIGURE 2 (a-c) The structure factor of Li, Na and K using $x_0^2 = 3.2$; H (○ ○ ○) and I.U. (× × ×) dielectric functions; Experimental points (■ ■ ■); Waseda (1980).

and Young¹⁹) leads a satisfactory fit which also leads to $r_c = 2.476 a_0$ at the melting temperature in essential agreement with $2.45 a_0$ given by Evans and Sluckin³. Our results (Table I) are in good agreement with experiments up to about 1400 K beyond that $S(0)$ values marginally deviate from experiments. The density dependent core radius has an advantage of describing $S(0)$ at very high temperatures while fixed core radius leads to divergence at critical temperature $T = 1823$ K. Further, density dependent pseudopotential decreases the long-wavelength scattering while fixed core radius increases the long-wavelength scattering at high temperatures and two results bracket the experiments up to $T = 1700$ K. The magnitude of $S(0)$ depends very sensitively on the cancellation between the OCP term and $F_N(q = 0)$ term for these expanded states. It appears that Geldart and Vosko dielectric screening¹⁸ is more suited like I.U. screening than V.S. screening for the OCP system. The thermodynamic instability is not the signature of phase transition but it is intimately related to the extremely unphysical description of the short range correlation afforded by RPA. We find that our results do not show thermodynamical instability leading to validity of the RPA approach

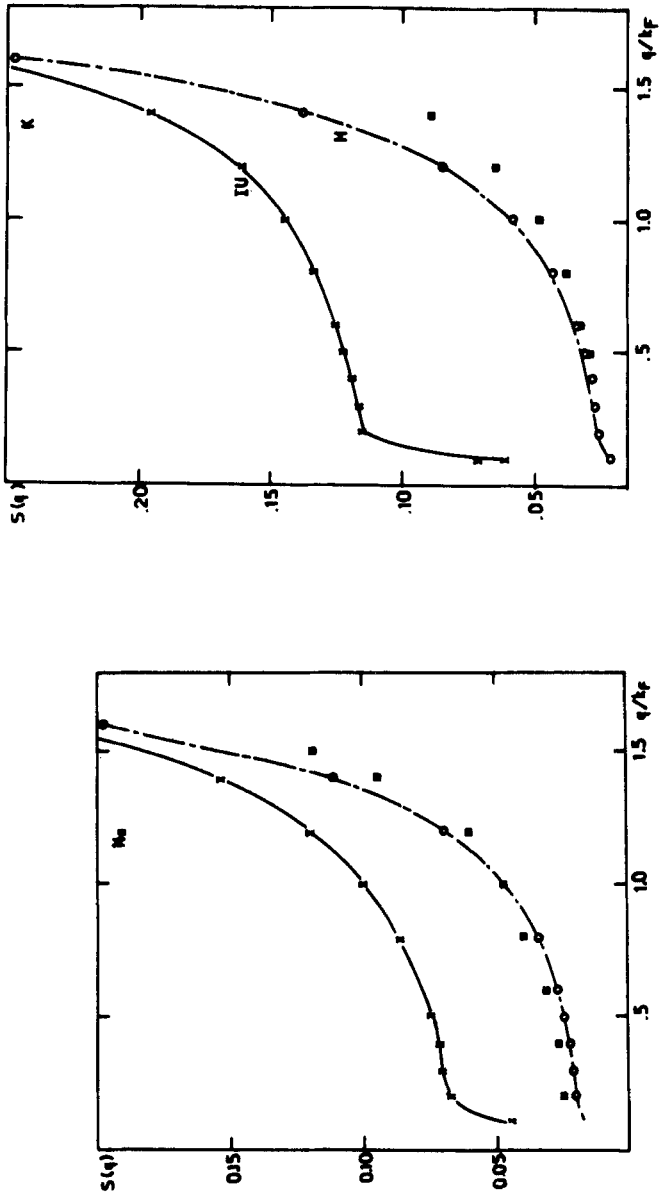


FIGURE 2 (continued).

TABLE I

$S(0)$ for expanded Rb as calculated from Eqs (7) and (8). $S^*(0)$ corresponds to the pseudopotential parameter $r_c = 2.1 a_0 + 0.07 r_s$ and $S(0)$ corresponds to $r_c = 2.476$. The suffixes represent the dielectric screening. $\Gamma = 172$ (at the melting temperature) varies with density at higher temperatures. $x_0^2 = 2.34$ remains constant for all calculations.

T (K)	ρ ($\text{\AA}^{-3} \times 10^3$)	$S_{G.V.}^*(0)$	$S_{G.V.}(0)$	$S_{I.U.}^*(0)$	$S_{I.U.}(0)$	$S(0)$ experiment
312	10.40	0.0232	0.0232	0.0235	0.0235	0.023
573	9.74	0.048	0.049	0.048	0.049	0.045
723	9.27	0.067	0.069	0.068	0.070	0.07
873	8.80	0.090	0.095	0.092	0.097	0.10
1023	8.32	0.120	0.129	0.122	0.132	0.13
1173	7.81	0.160	0.179	0.163	0.183	0.18
1323	7.29	0.217	0.255	0.220	0.260	0.24
1473	6.73	0.307	0.394	0.313	0.404	0.37
1573	6.34	0.405	0.575	0.413	0.592	0.51
1623	6.12	0.481	0.747	0.491	0.772	0.57
1673	5.90	0.584	1.036	0.598	1.078	0.67
1723	5.66	0.748	1.708	0.767	1.808	0.72
1773	5.42	1.013	4.326	1.043	4.90	0.79
1823	5.14	1.656	—ive	1.717	—ive	0.94

for the density dependent model potential. Thus we conclude that x_0 , whose the physical significance is still not well understood, becomes an important quantity to describe the whole structure factor of the alkali metals as well as their surface properties (Hasegawa and Watabe²⁰).

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