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Temperature dependence of low angle structure factors of liquid alkali metals using electron-ion plasma model

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Abstract. The analytic solution of EIP model in the MSA via the OCP criterion yields temperature dependent results in RPA quite satisfactorily at high temperatures. The same set of parameters produces low and high angle structural properties. The model can work almost near to the critical point if the ion-core radius is allowed to vary systematically in the region $\rho < 2\rho_c$, ρ_c being the critical density. The model can also accommodate the general scaling behaviour observed for the structure factors of liquid alkali metals.

Keywords. Temperature; structure; liquid metals.

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1. Introduction

In recent years there has been considerable development in the structure and thermodynamics of liquid metals through the electron-ion plasma (EIP) model where one takes the EIP to have the same density, temperature and ionic mass as those of the real system [1–5]. There is however, some unsolved problem of consistent description of structure and thermodynamics, long wave and high angle structure factors with single set of parameters for various classical one component plasma (OCP) model available in the literature [6–8]. The clear reason being that all the liquid state theories are approximate in nature and they suffer from thermodynamic inconsistencies. There have been attempts earlier [9] to evolve criterion that could at least partially restore desired consistency.

The aim of the present communication is to present some temperature dependent results based on the analytic solution of EIP in the mean spherical approximation (MSA) [10]. The model enjoys the advantage that it has accommodated within it the analytic and soft sphere nature not found together in hard sphere (HS) and pure OCP models. The two characterizing parameters, packing density, η and plasma parameter, Γ are related via some suitable criterion [11]. The electronic screening necessary to describe low angle structure and thermodynamics, can be included through random phase approximation (RPA), optimized random phase approximation (ORPA) [5, 12] or the mean density approximation (MDA) [13]. The ORPA calculation [12] has shown that the long wave behaviour is not significantly different from RPA results provided considerable reductions in the effective charge (i.e. Γ values) and ion-core radius are allowed. This is also consistent with Gibbs–Bogoliubov (GB) variational calculation [14]. The WCA-ORPA calculation [15] for liquid Rb shows that for moderately high temperature the method works well but for temperatures

beyond 1400 K, the calculated structure factors in general and long wave length values in particular fail to agree with experiment. The failure was attributed to the fact that the density dependence of the interatomic potential was underestimated. The electron mean free path becomes comparable with interatomic separation and the linear screening theory fails. It is now quite well established that in the long wavelength region RPA is a good approximation for quite high temperatures. Henderson and Ashcroft showed that the difference between the long wavelength RPA and experimental structure factors is related to the density derivative of the reference structure factor, the so-called MDA approximation. Young showed that the inconsistencies in Γ values for GB and isothermal compressibility calculations could be reconciled by introducing the idea of MDA term. Ono and Yokoyama [4] however, found that the MDA term is, at least near the melting point not as important as Young's analysis suggested. The recent OCP calculation of Iwamatsu [16] using MDA is relevant. The author uses the GB variational prescription to define the reduced plasma parameter Γ. But since these values were considerably smaller the author used $\Gamma = 155$ [2, 3] and MDA was shown to be consistent with the long wavelength structure factors of Rb at very high temperature and so shown to work better than RPA. But at melting and moderately high temperature MDA and RPA results are comparable. The MDA result at very high temperature too shoots up like RPA though this occurs at a higher temperature.

In view of the calculations mentioned above we find it important to review the RPA calculation for alkali metals at high temperatures. We have also done the MDA calculation to check the relative merits. The present calculation confirms Ono and Yokoyama's and Iwamatsu's observations. In fact, for alkali metals at least, MDA results progressively deviate from experiment as we go to thermodynamic states away from melting pont. RPA presents somewhat better description even at very high temperature provided one considers a systematic change in the ion core radius in the region $\rho < 2\rho_c$, where ρ_c is the critical density. Similar variation of r_c was first proposed by McLaughlin and Young [17]. It is also to be noted that the same set of parameters give in RPA, both the long wave and high angle structure factors quite well.

2. Calculation procedure

From the RPA expression of free energy the expression for liquid structure factor, $S(q)$ is given by

$$S(q) = \frac{S_0(q)}{1 + \beta\rho V(q) S_0(q)} \tag{1}$$

where, $S_0(q)$ is the reference structure factor, $V(q)$ is the indirect electron mediated ion–ion interaction expressible in terms of suitable pseudopotential and dielectric screening function [4] (in the present case Ashcroft model and Geldart–Vosko (GV) respectively), ρ is the number density and β, the inverse temperature, $(k_B T)^{-1}$. From (1) the long wave expression for structure factor is given by

$$S^{-1}(0) = k_d^2 [k_i^{-2} + k_e^{-2} + r_c^2] \tag{2}$$

where, in au

$$k_d = \frac{\sqrt{3}}{a} \Gamma^{1/2} \tag{3a}$$

$$k_i = k_d/(1-\alpha)^{1/2} \tag{3b}$$

$$k_e = \left[\frac{\pi}{4k_f} - \frac{1}{4\pi k_f^3}\quad (\pi k_f + 0{\cdot}153)\right]^{-1/2} \tag{3c}$$

are respectively the Debye–Hückel, CHS plasma (in the present case) and the electron gas inverse screening lengths, k_f, the Fermi wave vector, a, the interparticle distance and α is a term related to η and Γ of the CHS system and expression for which is available elsewhere [18].

Again note that

$$\underset{q\to 0}{\text{Lt}}\ S_0(q) = \frac{q^2}{k_d^2}\left(1 - \frac{q^2}{k_i^2}\right) \tag{4a}$$

and

$$\underset{q\to 0}{\text{Lt}}\ \varepsilon(q) = 1 + \frac{k_e^2}{q^2}. \tag{4b}$$

So we have the very low q convenient expression for $S(q)$ given by

$$S(q) \cong S(0)\Big/\left[1 + q^2 S(0) k_d^2 \left\{\frac{1}{k_i^2(k_i^2 - q^2)} - \left(\frac{1}{k_e^4} + \frac{r_c^4}{3} + \frac{r_c^2}{k_e^2}\right)\right\} + q^4 S(0) k_d^2 r_c^2 \left\{\frac{1}{k_e^4} + \frac{r_c^2}{3k_e^2} + \frac{r_c^4}{24}\right\}\right]. \tag{5}$$

The MDA expression [13] corresponding to eq. (2) is

$$S^{-1}(0) = S_0^{-1}(0) + \beta\rho V(0) + 2\beta\rho\left(\frac{\partial I}{\partial \rho} + 1/2\,\rho\frac{\partial^2 I}{\partial \rho^2}\right) \tag{6}$$

with

$$I = \frac{1}{4\pi^2}\int_0^\infty \mathrm{d}q q^2 V(q)(S_0(q) - 1). \tag{7}$$

The MDA approximation is thought to be essentially exact for $0 \leqslant q \leqslant 0{\cdot}4k_f$ [13].

For high q calculations via RPA one requires to truncate the screened potential $V(q)$ beyond the first node which occurs near $q \simeq 2k_f$ and the justification is available elsewhere [18, 19] and essentially the ORPA results of [12] could be reproduced for all alkalis at different temperatures.

The CHS plasma is extremely good representation of OCP for $\Gamma \geqslant 10$ if η and Γ satisfy the following criterion [20].

$$C_0(r=0) \simeq -1{\cdot}33\Gamma \tag{8}$$

$C_0(r=0)$ being the CHS direct correlation function at $r=0$. Γ as a function of η is shown in figure 1(b). It is quite well-known that the GB method approximates the true structure factor of the system by reference one with optimum $\Gamma \simeq 155$ [2, 3]. This value of Γ is considerably reduced compared to one from the observed density and temperature using valency, $z=1$ (the bare ionic charge number) for most of the alkalis at melting point ($\Gamma \sim 163 - 210$). Such a reduced Γ represents considerable reduced valency ($z<1$) and this is also qualitatively in accord with entropy analysis

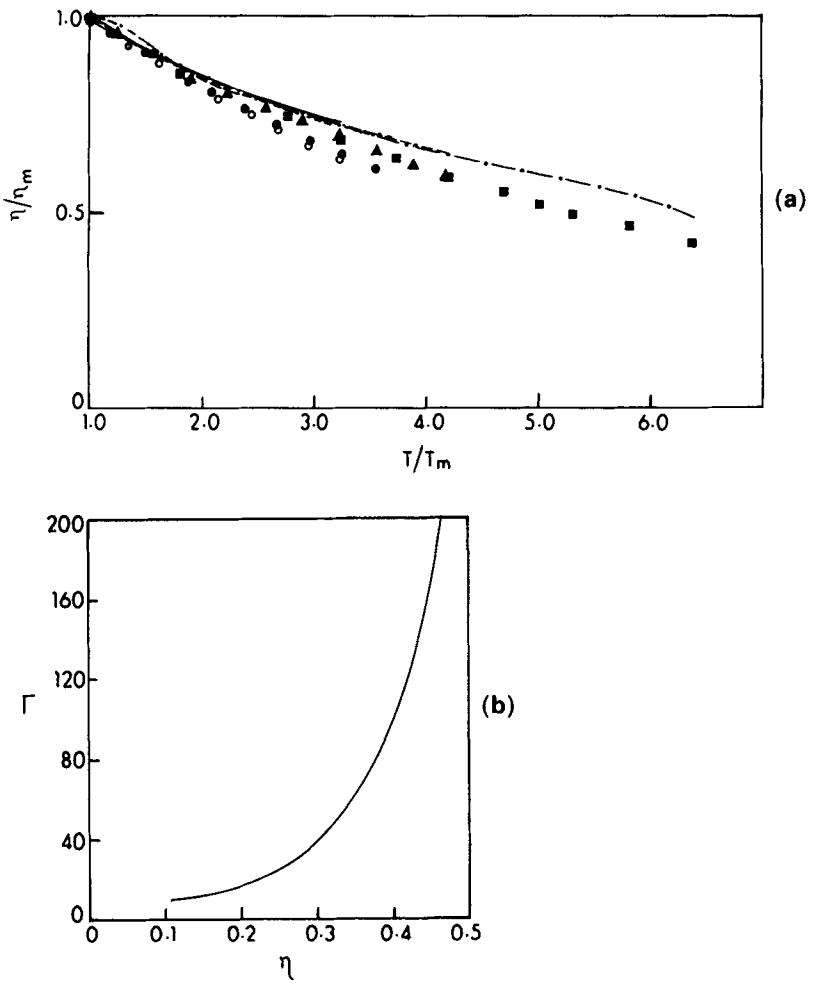

Figure 1(a). η/η_m as a function of T/T_m ——— (Na); – – – (k); –·–·–(Rb); – –·– –·– –·– – (Cs) From eq. (8). ○○○ (Na); ●●● (k); ■■■ (Rb); ▲▲▲ (Cs) with Hs model [23], (b) Γ as a function of η (eq. (8)).

[6]. The isothermal compressibility by the method of long wave, on the other hand, is well described by using $z = 1$ [21]. The OCP is known to freeze at $\Gamma \sim 178$ [22]. We have chosen Γ via (8) by taking η's from the CHS calculation of [18]. These η's are well in accord with the value 0·455 obtained from (8) using $\Gamma = 178$. The Γ's at higher temperature are obtained using the relation

$$\frac{\Gamma}{\Gamma_m} = \frac{T_m}{T}\left(\frac{\rho}{\rho_m}\right)^{1/3} \tag{9}$$

where m refers to melting point and corresponding η's are obtained from (8). η's obtained this way agree well with that for HS model [23] (figure 1(a)) and this is expected. r_c's given in [18] reproduce the isothermal compressibility at melting point quite well and so used in our calculations for $S(0)$ values at melting point (table 1). These r_c's are used for calculations at thermodynamic states away from the m.p. The

Table 1. $S(0)$ values at or near melting points.

Liquid metal	T(K)	ρ (a.u.$^{-3}$)	η	Γ	r_c (a.u.)	$S(0)$ present RPA	$S(0)$ present MDA	$S(0)$ Expt.[23]
Na	371·0	0·0035834	0·449	167·0	1·821	0·0240	0·0228	0·0240
K	337·0	0·0018846	0·457	182·0	2·358	0·0228	0·0211	0·0224
Rb	313·0	0·0015368	0·452	172·5	2·526	0·0257	0·0241	0·0220
Cs	301·6	0·0012340	0·457	182·0	2·790	0·0227	0·0203	0·0237

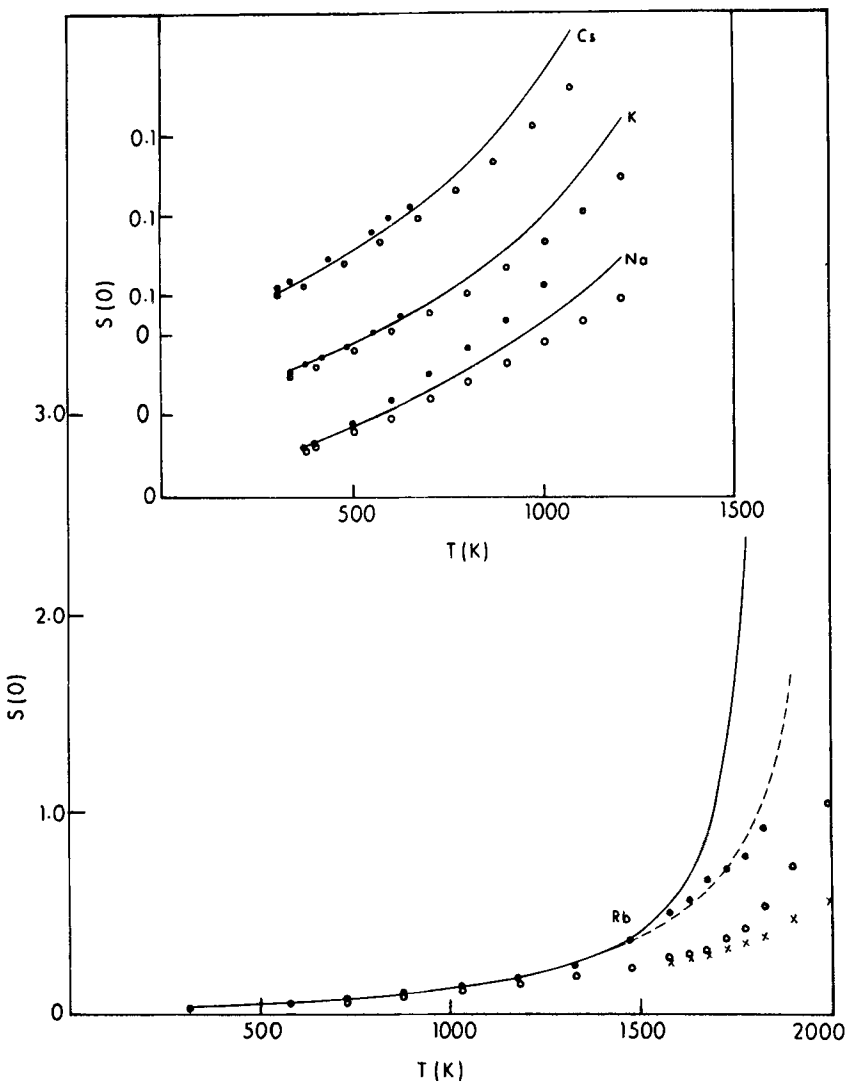

Figure 2. $S(0)$ as a function of temperature ——— RPA calc. (fixed r_c); – – – RPA calc. (variable r_c); ○ ○ ○ MDA calc. (fixed r_c); × × × MDA calc. (variable r_c); ● ● ● experimental [29].

$S(0)$ values are expected to shoot up as the critical point is approached. In RPA however, the result shoots up quite earlier and this behaviour is attributed to possible breakdown of nearly free electron approximation in the region $\rho < 2\rho_c$ since the electron–electron correlation effects would become more important and the electron-ion interaction becomes less amenable to a pseudopotential description [21]. However, a variable r_c, as McLaughlin and Young [17] have observed, could reconcile this discrepancy of the theory and description almost near to the critical point is possible. In the spirit of McLaughlin and Young we have therefore used a variable r_c in the region $\rho < 2\rho_c$, to describe the structural behaviour of liquid Rb for $T > 1500$ K using the relation, $r_c = 1{\cdot}35 + 0{\cdot}19 r_s$ in au with $r_s = az^{-1/3}$, a being the interparticle separation. The argument concerning the volume dependent r_c at low density ($\rho < 2\rho_c$) may be the following. The breakdown of nearly free electron approximation results as the electron mean free path becomes of the order of interatomic distance. It is well-known that the Friedel oscillation arises from the Fourier transform of the logarithmic term in the dielectric function and it is directly related to the assumption that the Fermi surface is sharply defined. At high temperature, the increased blurring of Fermi surface decreases the oscillation and makes the potential more like that of non-metallic liquids. As the volume increases the term due to overlap repulsion should be added, the coulomb repulsion being now relatively small [24]. For metallic potential, the variation of r_c changes the

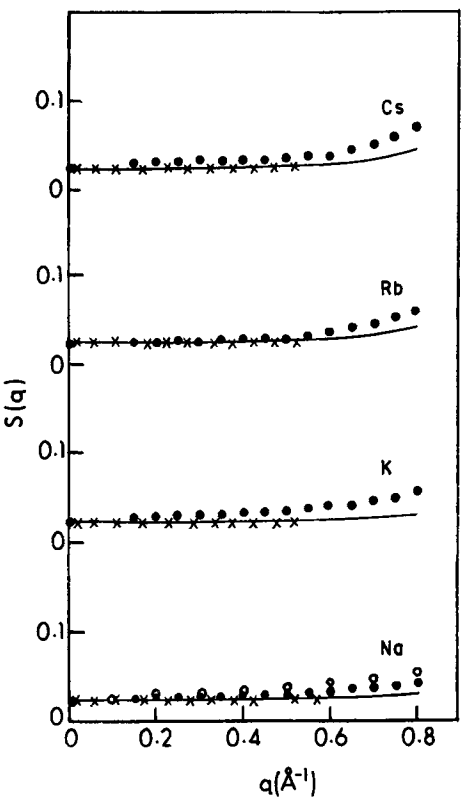

Figure 3. Low angle $S(q)$ as a function of q ——— calc. with eq. (1); × × × calc. with eq. (5); ○○○ MDA calc. by McLaughlin *et al* [13]; ●●● experimental [23].

electron mediated term, the position and depth of the attractive well and also the Friedel oscillation changes significantly. The results of our calculations are shown in fiugures 2–4.

3. Results and discussion

The calculations shown clearly indicate that RPA describes the temperature variation of $S(0)$ over a wide range quite well. For Rb, above 1500 K where $\rho < 2\rho_c$, a variable r_c is used. For thermodynamic states approaching the critical region, RPA result with constant r_c shoots up at a quite lower temperature (figure 2). It is important to note that the addition of MDA term considerably lowers the values at high temperature

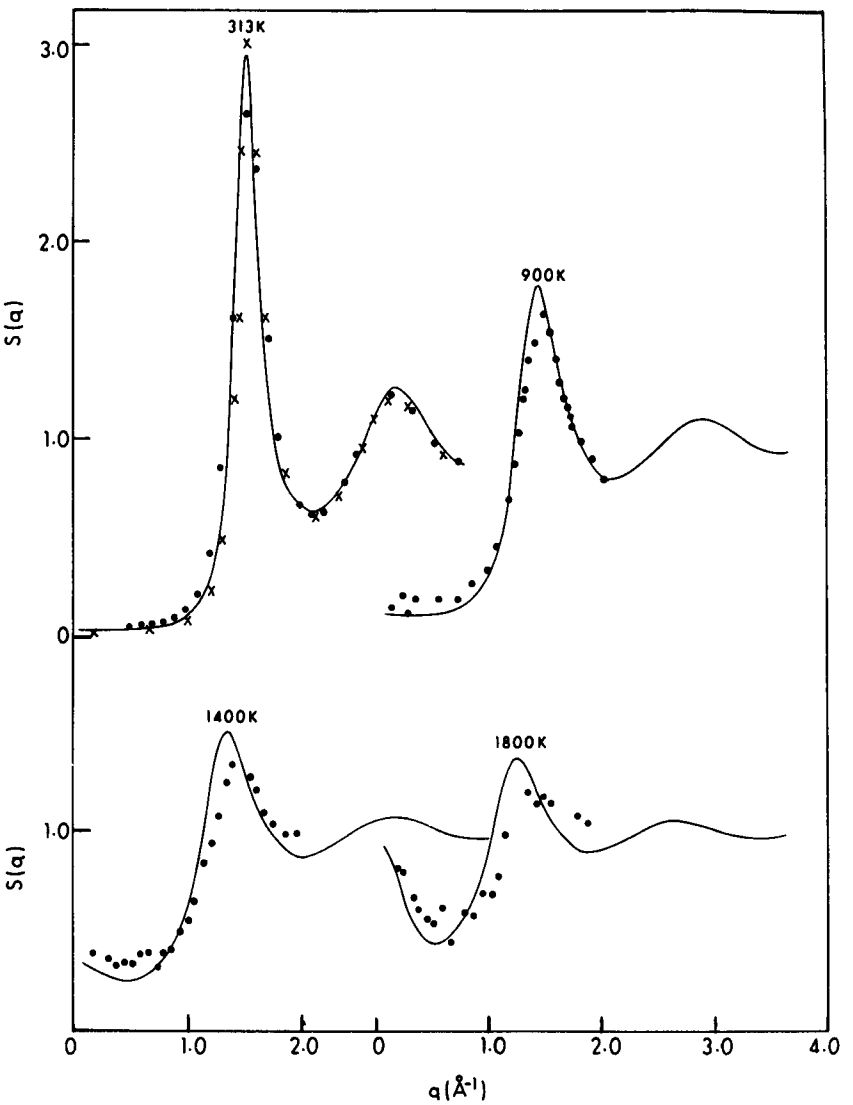

Figure 4. $S(q)$ as a function of q for Rb at different temperatures. ——— Calc.; × × × MD data [30]; ● ● ● experimental [29].

and in fact the result progressively deviates from the experimental result. This is compatible with observations in [4] and [16]. Of course, originally MDA was developed for hard cores [13] and it provided satisfactory description of the region near the critical point with variable r_c [17]. RPA with variable r_c also works reasonably near the critical region probably because the increase in r_c reduces the long range oscillations of the effective interionic potential and makes it more like that of a nonmetallic system, almost L–J type. The CHS plasma model based on the OCP criterion (eq. (8)) also describes well the low and high angle structure factors with same set of parameters (figures 3 and 4). It is to be noted that MDA with hard core is more successful for polyvalent metals than alkali metals so far as the high angle structure factor values are concerned [13]. The RPA low q results are satisfactory (figure 3). The very low q behaviour given by (5) reproduces the $S(q)$ values quite well. The low q expression closely resembles the one of Evans and Sluckin [21] and the results are consistent with the Ornstein–Zernike (OZ) behaviour ([25] i.e. $S(q) = S(0)/(1 + \xi^2 q^2)$, ξ being the long range correlation length. The O–Z behaviour suggests that at high temperature the low $qS(q)$ values will shoot up. Evans and Sluckin estimated this transition temperature to be quite low (~ 500 K) in their OCP model. The present model gives this temperature to be ~ 1000 K, much better in agreement with observation. The very low q expression is similar to one observed in liquid argon [26] and does not contain a linear term as has been suggested [27] empirically by the low q experimental data near the melting point. The very low q expression however yields results in good agreement with values from full expression (1) and experimental data. Remembering that there is large uncertainty in the experimental data in this low q region we believe that the expression (5) would describe the system quite well particularly at high temperature where the nearly free electron model progressively fails. It is now quite well-known [28] that for densities $\rho \sim 2\rho_c$ and conditions near the saturation curve, characteristic changes have been observed for both the electrical and magnetic properties which mark the onset of a transition from metallic to nonmetallic states and the effective interaction potential changes to one very similar to that for Kr described by L–J potential. In order to explore this point we have computed full structure factor curves of liquid Rb at different temperatures for this model through (1). The screened potential $V(q)$ has been truncated beyond its first node. The results at high temperature are reasonable and OZ behaviour is well produced. The high temperature results are compared with the experimental data of Hensel *et al* [29]. The model first peak height decreases less and position shifts to the left more relative to the experimental data as the high temperature is approached. This deviation is attributed to the approximate nature of the OCP criterion (8) which somewhat under reduces the η parameter at high temperature (figure 1(a)). In spite of these discrepancies we feel that the overall behaviour described by the present model at states near the critical point is quite satisfactory. The critical temperature T_c, estimated is ~ 2010 K and this is in excellent agreement with experiment.

Further, it has been recently found that the structure factors of liquid alkali metals scale if they are plotted against q/q_m where q_m refers to the position of the first peak of structure factor for each system [31]. We have therefore plotted our $S(q)$ against q/q_m to see whether this scaling behaviour follows. The results shown in figure 5 clearly exhibit that the present model can satisfactorily accommodate the scaling behaviour. The scaling property associated with $S(0)$ is also shown to be reasonably justified in this model.

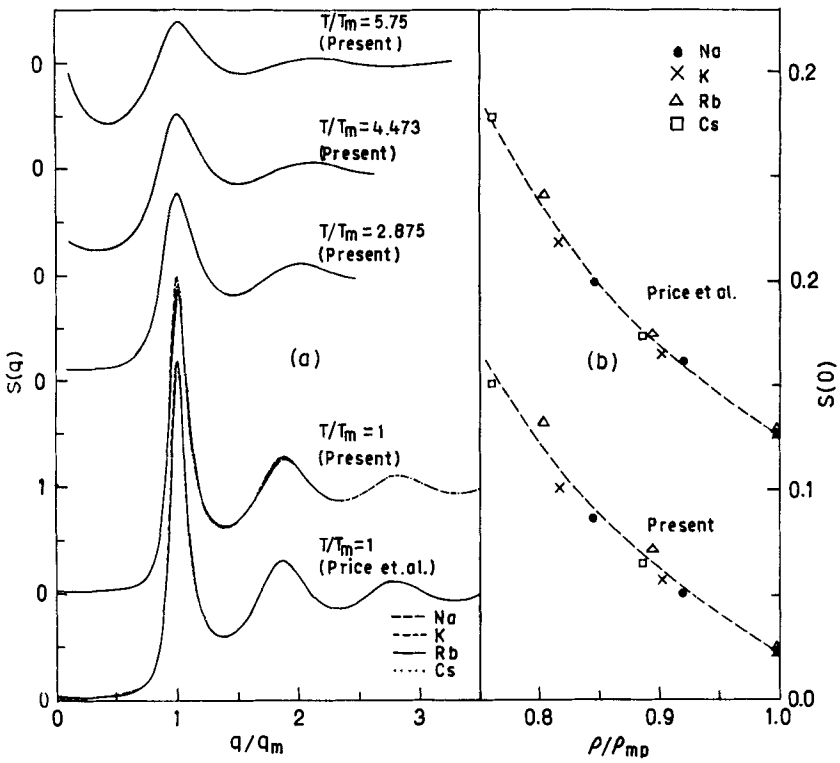

Figure 5. (**a**) $S(q)$ vs q/q_m for Na, K, Rb and Cs. (**b**) $S(0)$ vs $\rho/\rho_{m.p.}$ for Na, K, Rb and Cs.

It is to be noted that we have used GV screening throughout and this screening is known to describe the liquid alkali metals at melting point, quite well. The long wave results depend on screening function to some extent but the use of other screening functions will not change the general behaviour reported here significantly. In fact a slightly different interactomic potential due to Price *et al* [32] (Ashcroft pseudopotential with self consistent screening) is known to yield the Monte Carlo (MC) and molecular dynamics (MD) structure factors [31] in good agreement with experiments. Like Price *et al* potential, the present potential too scales with proper units. To compare the present model results with those due to Price *et al* potential, we have calculated in RPA with length and energy parameters of Price *et al* potential [31] and tested the scaling behaviour. It is clear that the scaling behaviour with Price *et al* potential is only slightly better (figure 5).

Thus in this communication, we have reviewed the RPA calculation for EIP model of liquid alkali metals and shown that with parameters provided by OCP criterion various structural aspects including long wave behaviour are very reasonably described over a wide range of temperature.

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