The Structure Factor of Expanded Liquid Alkali Metals at the Long-Wavelength Limit

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$S(0)$ values of expanded alkali metals are calculated in random phase approximation. The results reproduce positive values of $S(0)$ at sufficiently high temperatures showing the validity of RPA in one-component plasma systems.

One of the important properties characterizing a liquid is its static structure factor $S(q)$, which is a measure of particle correlations in the reciprocal space. Apart from that, the main features of $S(q)$ are determined by the effective pairwise potential $\Phi(r)$. Evans and Schirmacher [1] showed that the oscillatory part of $\Phi(r)$ has an important effect on the structure factor at the long wavelength limit $S(0)$ and hence the isothermal compressibility. In this paper we attempt to account for the variation of $S(0)$ from metal to metal using a perturbation theory based on the one-component plasma reference system (OCP) with the long-ranged oscillatory interaction treated in a random phase approximation (RPA) [2]. This enables us to examine the validity and usefulness of the pseudopotential approach for states away from the melting point. It is interesting to ask how well such a nearly-free-electron pseudopotential description can account for the observed structure and thermodynamic properties of expanded liquid metals for which the density is substantially reduced below its value at the melting point. At densities ϱ approaching the critical density ϱ_c we can expect the nearly-free-electron approximation to fail since the electron-electron correlation effects will become more important and the electron-ion interaction less amenable to a pseudopotential description. The one-component plasma, a system of point ions of charge Ze in a neutralizing uniform electron background, is characterized by the coupling parameter Γ, where $\Gamma = \beta(Ze)^2/a$, $\beta = (k_B T)^{-1}$, $a = (4\pi\varrho/3)^{-1/3}$ and $\varrho = N/V$ is the number density of the ions. One requires the knowledge of the effective charge Z_{eff} [3] on the ions, which physically corresponds to the effective charge carried along by the ions. The physical meaning of Γ^{eff} is not very clear to date. In view of this, in the present work we have regarded Γ^{eff} as an adjustable parameter obtained by choosing the Γ value so as to fit the experimental value of $S(0)$ at the melting temperature. In the hard sphere reference system, McLaughlin and Young [4] have concluded that the mean density approximation (MDA) provides the best description of low q behaviour of the structure factor. The RPA is obtained by dropping the final term in the expression for the MDA; see Eq. (1) of reference [4]. Thus we compare our results with those obtained from MDA we find RPA provides a useful overall description in the OCP.

The structure factor in the RPA can be readily expressed as [2]

$$S(q) = \frac{1}{1 - \varrho\,[C_{\text{ocp}}(q) - \beta\,\mu_{\text{sc}}(q)]}. \tag{1}$$

Here $C_{\text{ocp}}(q)$ is the Fourier transform of the direct correlation function expressed by Baus and Hansen [5]. The second term in the brackets of (1) is the indirect interaction between the ions, which can be expressed in terms of normalized energy wave number characteristics $F_N(q)$:

$$\mu_{\text{sc}}(q) = -\frac{4\pi Z^2 e^2}{q^2} F_N(q). \tag{2}$$

We arrive at the following analytical expression for the long-wavelength limit of the static structure factor [2], using the Ashcroft model potential [6]:

$$S(0)^{-1} = 1 - \frac{\Gamma X_0^2}{6} + \frac{3\Gamma}{a^2}\left[r_c^2 + \frac{\pi}{4K_F} - \frac{\nu_0}{K_F^2}\right], \tag{3}$$

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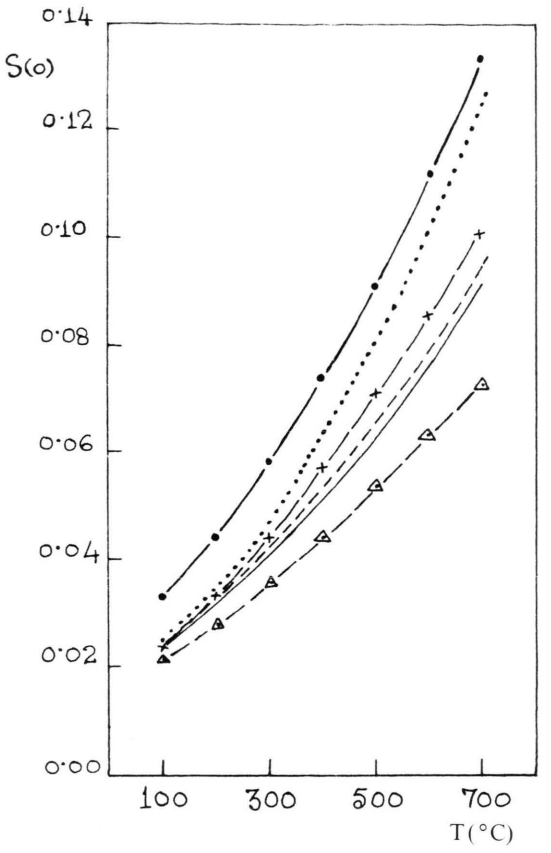

Fig. 1. $S(0)$ against T for liquid Na along the liquid-vapour co-existence curve. Hard sphere results: RPA (–·–·–), MDA (·····), WCA (–△–△–△–); OCP results in RPA: VS screening (– – – – –), GV screening (———); experimental values: (–×–×–×–).

where r_c is Ashcroft's parameter and v_0 is a dimensionless parameter connected to the local-field correction $G(q)$. For the Vashista-Singwi (VS) dielectric function $v_0 = AB$, where A and B are defined by Eq. (41) of [7], whereas for Geldart-Vosko (GV) dielectric screening [8]

$$v_0 = (0.25 + 0.153/4\pi K_F).$$

We calculate $S(0)$ for Li, Na and Cs as a function of density at different temperatures and compare our results for various dielectric screenings. The density measurements for expanded liquids are very meagre. For our purpose we use the data compiled by Lucas [9]. We fit the $S(0)$ value at the melting temperature by treating Γ as a variable parameter. We find that the $S(0)$ value is sensitive to the form assumed for

Table 1. $S(0)$ of expanded Li and Cs along the liquid-vapour coexistence curve for GV and VS dielectric screening functions as calculated from (3), ϱ is the number density, Γ the plasma parameter. The pseudopotential parameter $r_c(\mathrm{Li}) = 1.28$ a.u. and $r_c(\mathrm{Cs}) = 2.67$ a.u.; $x_0^2 = 2.34$.

Metal	T	ϱ^*	GV		VS	
	(°C)	(10^3 kg m^{-3})	$S(0)$	Γ	$S(0)$	Γ
Li	180.5	0.508	0.026	182.45	0.026	204.50
	200.0	0.507	0.027	174.62	0.027	195.60
	400.0	0.490	0.041	121.34	0.042	135.93
	600.0	0.474	0.058	92.51	0.059	103.64
	800.0	0.457	0.077	74.35	0.079	83.30
	1000.0	0.441	0.099	61.94	0.102	69.38
Cs	28.6	1.837	0.023	187.0	0.023	210.0
	100.0	1.796	0.030	150.0	0.030	168.5
	200.0	1.739	0.041	117.0	0.041	131.4
	300.0	1.682	0.054	95.5	0.054	107.3
	400.0	1.625	0.069	80.4	0.071	90.3
	500.0	1.568	0.087	69.2	0.091	77.7
	600.0	1.510	0.110	60.5	0.117	67.9
	700.0	1.453	0.138	53.6	0.149	60.2
	800.0	1.396	0.173	47.9	0.193	53.8

* $\varrho_{\mathrm{Li}} = 0.508 - 0.82 \times 10^{-4}(T - T_f)$; $T_f = 180.5$ from Been (S.A.) – U.S. Dept. Com. Office Techn. Ser. PB Rept. 162 003 1950, p. 26.
$\varrho_{\mathrm{Cs}} = 1.837 - 5.71 \times 10^{-4}(T - T_f)$; $T_f = 28.6$ from SHPIL'RAIN (E.E.) et Coll-Teplofiz Vysshikh Temp. Akad. Nauk SSSR (S.U.) 3 1965, p. 930.

the screening contribution $\Phi_{sc}(r)$ in the pair potential, which reproduces a large difference between the Γ values obtained by different screening functions. The GV dielectric function predicts a value of Γ closer to the fluid-solid phase transition, i.e. $\Gamma = 178$ as proposed by Slattery et al. [10], than those obtained by Vashishta and Singwi dielectric screening [7] at the melting temperature. For liquid alkali metals, the scattering behaviour and the microscopic structure change with changes of the density by varying temperature and pressure [11]. Table 1 reveals that the GV screening function reduces the long-wavelengths limit while the VS screening function increases the long-wavelength limit at high temperatures. We, therefore, conclude that the scattering effects are more significant for low densities. We now analyse our results for a possible demerit of the RPA at higher temperatures. As the temperature increases and the metal expands, the $S(0)$ increases. Evans and Sluckin [12] have shown that a large and negative value of $\varrho\alpha$, the coefficient of q^2 in $\varrho C(q)$, near the critical point is to be attributed to an unphysical behaviour. The thermodynamic instability is not a signature of phase

transition but it is intimately related to the extremely unphysical description of the short range correlation afforded by the RPA. Our results predict a positive value of $S(0)$ at sufficiently high temperatures showing thereby a promissing usefulness of the RPA treatment in the OCP system. Figure 1 reveals that the RPA treatment in the OCP system predicts results closer to the experimental values than those obtained by RPA treatment in the hard sphere system [13] for Na. It may also be noted that the hard sphere results (RPA) deviate more from experiments with increasing temperature than those obtained in the OCP system.

Now we turn to consider the effects of nonlocality. One of the promising papers in this regard was that of Iwamatsu et al. [3]. We recall that the long-wavelength limit of the liquid structure factor, i.e. $S(0)$, is [3]

$$S(0) = [1 - 0.39\,\Gamma' + (K_D^{*}/K_F)^2\,\alpha]^{-1},$$

where $K_D^{*2} = 4\pi\beta\varrho Z^{*2}$. The second term corresponds to a semi-nonlocal treatment, where α includes the nonlocal effects from first-principles. If we set $Z' = Z^* = Z$ (see [3]), we find considerable reduced values of Γ ($\Gamma_{Na} = 147$, $\Gamma_K = 136$ and $\Gamma_{Rb} = 136$). Similar assumptions for a local model potential [6] lead to higher values of Γ ($\Gamma_{Na} = 184.97$, $\Gamma_K = 180.32$ and $\Gamma_{Rb} = 172$) for GV screening.

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[1] R. Evans and W. Schirmacher, J. Phys. **C 11**, 2437 (1978).
[2] J. L. Bretonnet and K. N. Khanna, Phys. Lett. **110 A**, 420 (1985).
[3] M. Iwamatsu, R. A. Moore, and S. Wang, Phys. Lett. **92 A**, 283 (1982).
[4] I. L. McLaughlin and W. H. Young, J. Phys. **F 14**, 1 (1984).
[5] M. Baus and J. P. Hansen, J. Phys. **C 12**, L 55 (1979).
[6] N. W. Ashcroft, Phys. Lett. **23**, 48 (1966).
[7] P. Vashishta and K. S. Singwi, Phys. Rev. **B 6**, 875 (1972).
[8] D. J. W. Geldart and S. H. Vosko, Canad. J. Phys. **44**, 2137 (1966).
[9] L. D. Lucas Densite', Données Physico-Chimique Des Principaux Métaux et Métaloides (France), Techniques de l'Ingénieur (1984).
[10] W. L. Slattery, G. D. Doolen, and H. E. Dewitt, Phys. Rev. **A 26**, 2255 (1982).
[11] G. Franz, W. Freyland, W. Glazer, F. Hansel, and E. Schneider, J. Physique Coll. **41**, C 8, 194 (1980).
[12] R. Evans and T. J. Sluckin, J. Phys. **C 14**, 3137 (1981).
[13] I. L. McLaughlin and W. H. Young, J. Phys. **C 15**, 1121 (1982).