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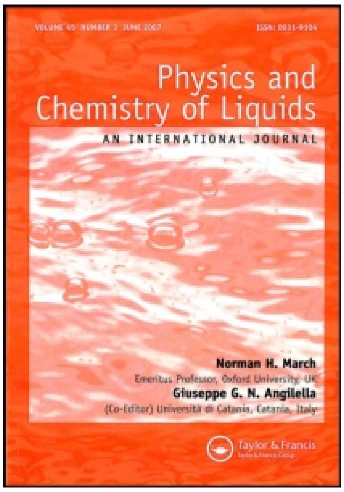

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On the Gaskell Approximation for Structure Factors of Liquid Metals

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The Gaskell approximation for Structure Factors is calculated in the low wave vector region for liquid Aluminium, Lead and Rubidium using the standard pseudopotential formalism of Ashcroft together with Vashishta–Singwi screening. The Gaskell approximation is found to produce only a small change to the random phase approximation in all cases studied.

1 INTRODUCTION

The liquid-state structure factors $S(k)$ of simple metals have created interest recently in the long wavelength (i.e. small k) regime. The structure factor measures the density response of the system to an external potential which may be identified with a potential caused by a test particle at the origin.[1] So the long range part of the potential gives rise to the small k density response and perturbation theories which include the effect of this long range part of the potential on the structure factor have been used by a number of authors to study the small k region. Evans and Schirmacher[2] have used the RPA (and an extension ERPA) and the mean density approximation (MDA) has produced results by McLaughlin and Young[3] which compare moderately well with experiment for a number of simple liquid metals in some cases for a range of temperatures[4] although the MDA is more difficult to compute than the RPA. The procedure was to compute acceptable pair potentials using a standard pseudopotential formalism and then obtain the structure factor, in particular for low k using the RPA or MDA. The results could be adjusted by varying the pseudopotential parameter—in the case of the Ashcroft empty-core form the core radius, r_c, was adjusted. The best values for the core radius were found to be in accord with those obtained by other means.[5]

An alternative approach used by McLaughlin and Young[6] was to use the RPA together with the experimental results at low k to evaluate an effective pair potential. Using relatively simple pair potentials with adjustable parameters Olsson and Dahlborg[7] and Bretonnet[8] also fitted experiments at low k to find effective pair potentials. Similar results were obtained by all authors. Olsson and Dahlborg used the improved random phase approximation of Gaskell[9] although their potential with 6 adjustable parameters was restricted to vary from one period oscillatory function to a simple exponential and so some features of the pair potential such as Friedel oscillations were omitted. In this paper we present a more systematic method of obtaining Gaskell's results and extensions to higher orders and compute the Gaskell approximation for a number of liquid metals using the pair potentials from the pseudopotential formalism. Comparisons are made with RPA results.

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2 BASIC FORMULAE AND METHOD

2.1 Gaskell's approximation

The effective pair potential $\phi(r)$ is separated in the usual manner into a repulsive reference, short-ranged part $\phi_0(r)$ and the long range "tail" $\phi_1(r)$ which is predominantly attractive. The structure factor $S_\mu(k)$ is written[9] as an ensemble average of the Fourier components of the density ($\rho\mathbf{k} = \sum_{j=1}^{N} \exp[-i\mathbf{k}\cdot\mathbf{r}]$) in the following way

$$S_\mu(k) = \frac{N^{-1}\int\cdots\int \rho_{\mathbf{k}}\rho_{-\mathbf{k}} \exp\{-\beta H_0 - (\mu\beta/2N)\sum_{\mathbf{q}}\phi_1(q)\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\}\, \mathrm{d}\mathbf{r}_1\cdots \mathrm{d}\mathbf{r}_N}{\int\cdots\int \exp\{-\beta H_0 - (\mu\beta/2N)\sum_{\mathbf{q}}\phi_1(q)\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\}\, \mathrm{d}\mathbf{r}_1\cdots \mathrm{d}\mathbf{r}_N} \tag{1}$$

the parameter μ is used to switch on/off the long range effects.

$S_{\mu=1}(k)$ can be found to different orders by using the Maclaurin expansion including the remainder term, namely,

$$f(\mu = 1) = \sum_{s=0}^{n-1} \frac{1}{s!}\frac{\partial^s f(\mu)}{\partial\mu^s}\bigg|_{\mu=0} + \int_0^1 \frac{\partial^n f(\mu)}{\partial\mu^n}\frac{(1-\mu)^{n-1}}{(n-1)!}\,\mathrm{d}\mu \tag{2}$$

With $f(\mu) = S_\mu^{-1}(k)$ and $n = 1$

$$S^{-1}(k) = S_0^{-1}(k) + \int_0^1 \mathrm{d}\mu \frac{\partial}{\partial\mu} S_\mu^{-1}(k) \tag{3}$$

where the suffixes have been slightly changed for convenience.

Gaskell uses (3) to obtain his expressions for the direct correlation function. The lowest order expression involves only the structure factor of the reference fluid rather than an integral over the parameter μ. This is obtained using the $n = 2$ term in the expansion (2) and neglecting the remainder term to arrive at

$$S(k) = S_0(k)\left(1 - \frac{1}{S_0(k)}\frac{\partial}{\partial\mu}S_\mu(k)\bigg|_{\mu=0}\right)^{-1} \tag{4}$$

which gives an improved random phase approximation

$$S(k) = S_0(k)\left[1 + S_0(k)\left\{\beta\rho\phi_1(k) + \frac{\beta}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\,\phi_1(q)S_0^2(q)[S_0(|\boldsymbol{k}+\boldsymbol{q}|) - 1]\right\}\right]^{-1} \tag{5}$$

The RPA approximation is just the expression (5) neglecting the last term. Evans and Schirmacher[2] obtained a similar extension of RPA (ERPA which they obtained by a different expansion technique. Their expression did not include the $S_0^2(q)$ term. It should be noted that all these approximations are easier to compute than the MDA. Higher order expressions may be obtained by including more terms of the Maclaurin expansion but these involve higher order density correlation functions. In fact the $n = 3$ case involves terms of the form $\langle N^{-3}|\rho_{\boldsymbol{k}}|^2|\rho_{\boldsymbol{q}}|^2|\rho_{\boldsymbol{w}}|^2\rangle$ which represent sixth order density correlation functions.

2.2 Method of calculation

In all our calculations we used the Ashcroft empty-core form for the pseudopotential

$$v(k) = \frac{-4\pi Z}{k^2}\cos(kr_c) \tag{6}$$

and the Vashishta–Singwi expression

$$G(k) = A\{1 - \exp[-B(k/k_F)^2]\} \tag{7}$$

to describe the electron gas. The potential is separated using the WCA[10] procedure into core and residual parts and the structure factor for the core is calculated via the Jacobs and Andersen[10] version which is important in the low k region. The ancillary hard sphere description is that of Verlet and Weis.[11] McLaughlin and Young[3] used this prescription in their calculations of the structure factor in the MDA and full details are contained therein.

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3 RESULTS

The Gaskell approximation has been calculated for Aluminium, Lead and Rubidium and comparisons made with the RPA and ERPA results. Where possible the experimental results of Waseda[12] are included. The parameter details are presented in Table I.

TABLE I

Data relevant to Figures 1–4 (a_0 = Bohr radius)

Metal	$T(K)$	r_c/a_0	Density/$10^{-3}a_0^{-3}$	Hard core diameter σ/a_0	Packing fraction
Al	943	1.12	7.85	4.94	0.495
Pb	613	1.47	4.59	5.75	0.456
Rb	313	2.45	1.53	8.31	0.459
Rb	1900	2.60	0.668	7.63	0.155

The Aluminium results are presented in Figure 1. The RPA, Gaskell and ERPA results are indistinguishable on the scale shown in Figure 1(a). All these results improve the hard-sphere WCA result but as shown by McLaughlin and Young[3] the MDA is close to the experimental result. In Figure 1(b) on a magnified scale the ERPA and RPA results are still inseparable but the Gaskell result actually worsens the agreement with experiment. The various terms contributing to the structure factor are presented in Figure 1(c) showing the small contribution of the Gaskell term.

It is well known that there is some arbitrariness in the potential $\phi_1(r)$ for separations, r, less than the principal minimum and so calculations were performed varying the value of $\phi_1(r)$ for r less than the principal minimum. This did not alter the overall conclusions of the previous calculations when comparing the various approximations.

Similar results were found for Lead and Rubidium, and these are presented in Figures 2 and 3 respectively.

In some cases Olsson and Dahlborg found that their hard sphere results were closer to the experimental results than the other approximations. However all their results were presented near the melting point where the hard sphere and RPA, for example, are closer than at higher temperatures nearer the critical point. For this reason results for Rubidium at 1900 K

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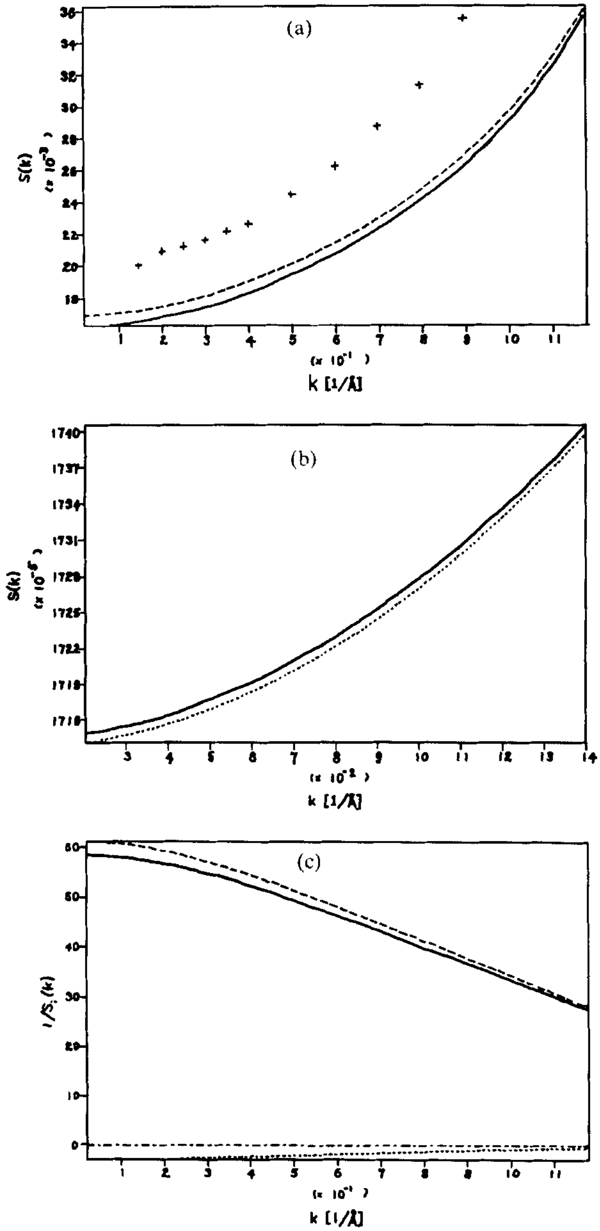

FIGURE 1 (a) The Structure Factor for Liquid Aluminium $T = 943$ K. ——— WCA ——— RPA + experiment. To this scale Gaskell's approximation (and ERPA) is indistinguishable from RPA. (b) The Structure Factor for Liquid Aluminium $T = 943$ K on a magnified scale ——— RPA ——— GASKELL (the ERPA is indistinguishable from RPA). (c) The Various Terms $1/S_i(k)$ contributing to the Structure Factor for Liquid Aluminium. ——— $1/S(k)$, ——— $1/S_{\mathrm{WCA}}$, ——— $1/S_{\mathrm{RPA}}$, ——— $1/S_{\mathrm{GASKELL}}$ such that $1/S(k) = 1/S_{\mathrm{WCA}} + 1/S_{\mathrm{RPA}} + 1/S_{\mathrm{GASKELL}}$.

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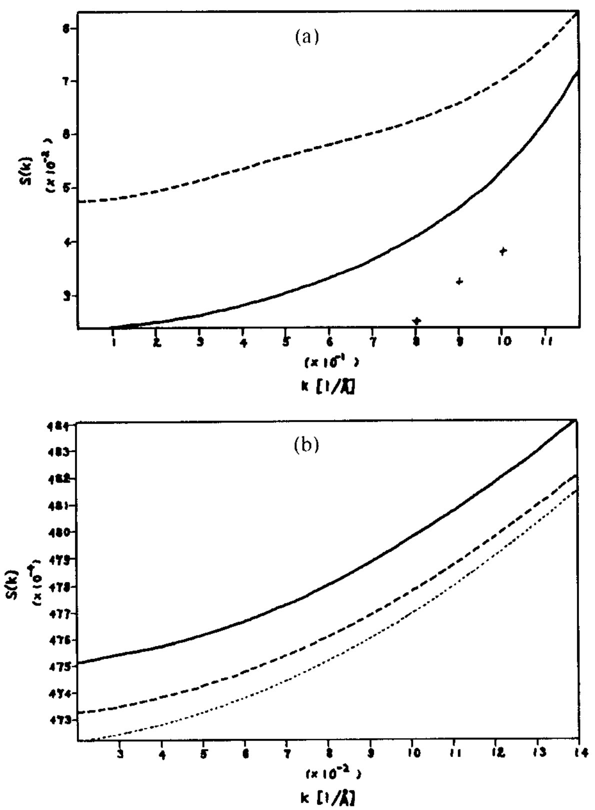

FIGURE 2 (a) The Structure Factor for Liquid Lead $T = 613$ K—notation as in Figure 1a. (b) The Structure Factor for Liquid Lead $T = 613$ K on a magnified scale—notation as in Figure 1b and ——— ERPA.

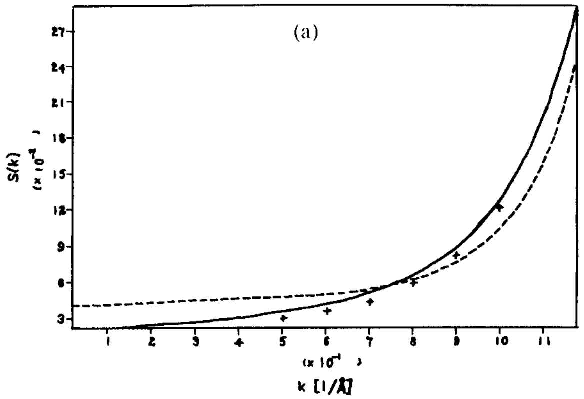

FIGURE 3 (a) The Structure Factor for Liquid Rubidium $T = 313$ K—notation as in Figure 1a.

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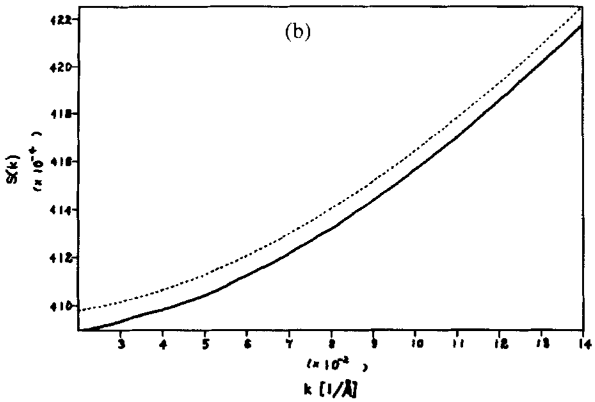

FIGURE 3 (b) The Structure Factor for Liquid Rubidium $T = 313$ K on a magnified scale—notation as in Figure 1b.

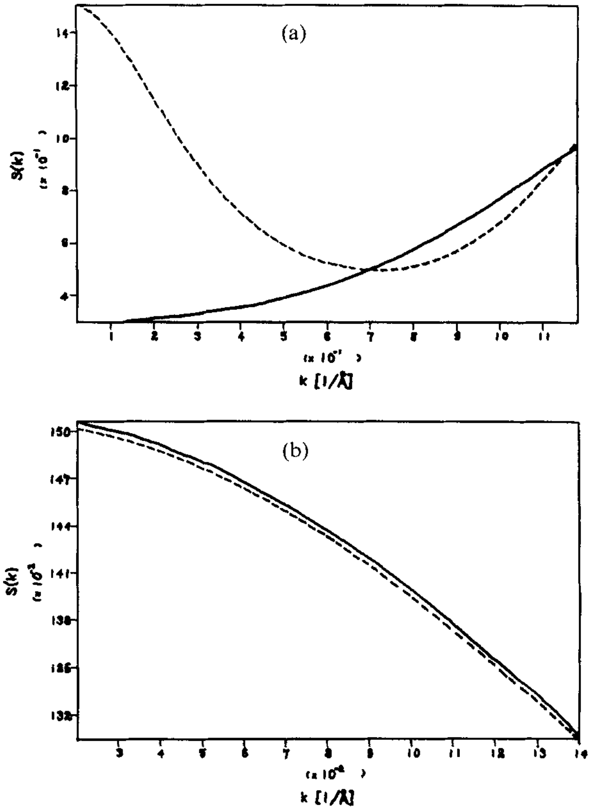

FIGURE 4 (a) The Structure Factor for Liquid Rubidium $T = 1900$ K—notation as in Figure 1a. (b) The Structure Factor for Liquid Rubidium $T = 1900$ K on a magnified scale—notation as in Figure 1b.

are presented in Figure 4. Again the RPA and Gaskell results are indistinguishable and are only a very small improvement on the RPA result. The experimental value for $k = 0$ is estimated[13] to be between 1.78 and 1.95.

4 CONCLUSION

The Gaskell approximation has been tested for a number of liquid metals using the pseudopotential formalism with the accepted parameter input. The Gaskell approximation, although larger than the ERPA in most cases studied, is still found to be only a small change to the RPA results. In fact compared with the MDA results of earlier studies the Gaskell result is negligible.

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