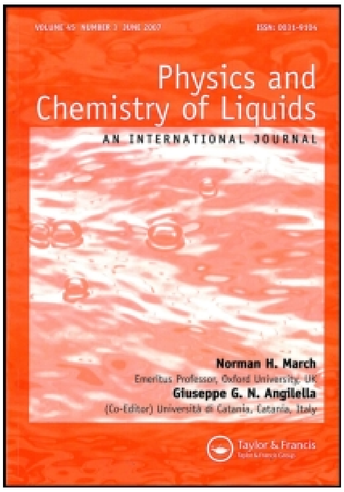

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On the Mean Density Approximation

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LETTER

On the Mean Density Approximation

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The mean density approximation for the structure factor in the long wavelength limit for a hard sphere potential with an attractive Yukawa tail is evaluated for simple liquid metals from a simple expression. The contibution is found to be significant.

KEY WORDS: Direct correlation function, Hard sphere diameters.

The structure factors $S(q)$ of liquid metals have been evaluated by dividing the potential into a reference system such as a hard sphere system and a perturbing tail. To describe the long wavelength portion (i.e. low q) of the structure factor where the tail of the potential is important, Henderson and Ashcroft[1] introduced the Mean Density Approximation (MDA). McLaughlin and Young[2] used the MDA to describe the structure factors of simple liquid metals in the low q region using interatomic potentials with the standard pseudopotential formalism and applying the WCA theory[3]. These calculations were complex especially when compared with the simpler Random Phase Approximation[4,5] (RPA). However considerable improvement was obtained over the hard sphere results by using the MDA in this low q region of the structure factor and reasonable agreement was found with experiment.

The MDA has been employed to describe liquid metals using model potentials other than the hard sphere system. Ono and Yokoyama[6] calculated the MDA for the one-component plasma reference system and found the contribution to be small. Victor and Hansen[7] have used the MDA for the DLVO potential in order to describe charged colloidal dispersions and found that the contribution from this approximation was important in the long wavelength limit especially when compared with the RPA predictions.

In this letter we describe a simple method of calculating the MDA for liquid metals using a hard sphere reference system and an attractive Yukawa tail. The pair potential $\phi(r)$ is divided into the hard sphere reference $\phi_0(r)$ and the attractive Yukawa tail $\phi_1(r)$, i.e.

$$\phi(r) = \phi_0(r) + \phi_1(r) \tag{1}$$

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where[7]

$$\phi_0(r) = \infty \quad r < \sigma$$
$$= 0 \quad r \geqslant 0$$

and

$$\beta\phi_1(r) = 0 \quad r < \sigma$$
$$= -\frac{K}{r}\exp[-z(r-\sigma)] \quad r \geqslant \sigma. \tag{2}$$

The direct correlation function (dcf) $c(r)$ of the system is expressed in terms of the MDA[1,4] as

$$c(r) - c_0(r) = -\tfrac{1}{2}\beta\phi_1(r)\frac{\partial^2}{\partial\eta^2}[\eta^2 g_0(r)] \tag{3}$$

where $c_0(r)$ is the dcf of the hard sphere reference system at packing fraction $\eta(\equiv \pi\rho\sigma^3/6)$, $g_0(r)$ is the hard sphere pair distribution function and $\beta = (kT)^{-1}$. The RPA is obtained from Eq. (3) taking $g_0(r) \equiv 1$ to obtain

$$c(r) - c_0(r) = -\beta\phi_1(r) \tag{4}$$

Taking the Fourier Transform of Eq. (3)

$$c(q) - c_0(q) = -2\pi\int_0^\infty \beta\phi_1(r)\frac{\partial^2}{\partial\eta^2}\left(\eta^2 g_0(r)\right)\frac{\sin qr}{qr}r^2\,dr \tag{5}$$

Of interest here is the long wavelength limit i.e. $q \to 0$ and then Eq. (5) becomes

$$c(o) - c_0(o) = -2\pi\beta\int_0^\infty \phi_1(r)\frac{\partial^2}{\partial\eta^2}(\eta^2 g_0(r))r^2\,dr. \tag{6}$$

It is always assumed in the MDA that the pair potential is density independent[8]. So that

$$c(o) - c_0(o) = -2\pi\beta\frac{\partial^2}{\partial\eta^2}\left[\eta^2\int_0^\infty \phi_1(r)g_0(r)r^2\,dr\right]. \tag{7}$$

From Eq. (2) this becomes

$$c(o) - c_0(o) = 2\pi k\frac{\partial^2}{\partial\eta^2}\left[\eta^2\int_\sigma^\infty \exp[Z(r-\sigma)]g_0(r)r\,dr\right].$$

This integral is evaluated[7] to give

$$c(o)-c_0(o)=2\pi\sigma\frac{K}{Z}\frac{\partial^2}{\partial\eta^2}\{\eta^2 g_0(\sigma)\} \tag{8}$$

where $g_0(\sigma)$ is the value of the hard sphere pair distribution function at the hard sphere diameter. As we are using the Percus Yevick solution for $c_0(o)$ namely

$$1-\rho c_0(o)=-\frac{(1+2\eta)^2}{(1-\eta)^4}, \tag{9}$$

the value of $g_0(\sigma)$ is taken to be [9]

$$g_0(\sigma)=\frac{1+\eta/2}{(1-\eta)^2}. \tag{10}$$

This gives

$$c_0(o)-c_0(o)=\frac{\sigma K}{Z}2\pi\left[\frac{2+7\eta}{(1-\eta)^4}\right]. \tag{11}$$

This compares with the RPA result from Eq. (4)

$$c(o)-c_0(o)=-\beta\phi_1(o)=4\pi K\left(\frac{\sigma}{Z}+\frac{1}{Z^2}\right). \tag{12}$$

The structure factor $S(q)$ in the long wavelength limit is then given by

$$S_{MDA}(o)=\frac{1}{1-\rho c(o)}=\frac{1}{1-\left[\rho c_0(o)+2\pi\frac{K}{Z}\sigma\rho(2+7\eta)/(1-\eta)^4\right]} \tag{13}$$

for the MDA and a similar expression for $S_{RPA}(o)$ from Eq. (12).

Numerical comparisons are made in Table 1 for a number of simple liquid metals. The parameter values of K and Z and also η could have been adjusted to fit the experimental values. However as we are essentially only interested in the overall effect of the MDA on the results of the hard sphere calculation the parameter values of

Table 1 Comparison of the long wavelength limit of $S(q)$ for the RPA and MDA.

Metal	η	$S_{HS}(o)$	$S_{RPA}(o)$	$S_{MDA}(o)$
Na	0.464	0.0222	0.0224	0.0292
K	0.460	0.0230	0.0233	0.03010
Rb	0.468	0.02137	0.0215	0.0284
Al	0.480	0.01903	0.0192	0.0260
Mg	0.453	0.02475	0.0250	0.0319

previous calculations with the Hard Sphere Yukawa system[10] are used. The hard sphere diameters are very similar to those of McLaughlin and Young[2]. In all cases the MDA result is significant and improves the hard sphere result which is always too low at low q[2]. The MDA is also a significant correction to the RPA at $q = o$. Similar results were found by the more complex calculations of McLaughlin and Young[2].

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