The final evaluation in (2) is to take place at $\rho(\boldsymbol{r}_1)=\rho(\boldsymbol{r}_2)=\rho$, the homogeneous fluid density. Equation (2) is exact, but it is not possible to evaluate the correlation function since the distribution function for the non-uniform system cannot be evaluated exactly. So various approximations are obtained using different expressions for $\rho^{(2)}$. These include the approximations mentioned above, namely the RPA, ERPA and the MDA (Evans 1979, Evans and Schirmacher 1978). One may, in (3), take only the first term $\rho_0^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ in a MacLaurin series in μ so that (3) becomes

$$K=\int\int \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\rho_0^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)\psi_1(r_{12}). \tag{4}$$

The MDA is obtained from equations (2) and (4) and the expansion of the distribution function $\rho_0^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ about its uniform density value $\rho_0^{(2)}(r_{12})$. This finally results in the expression

$$c(r)-c_0(r)=-\tfrac{1}{2}\beta\psi_1(r)\partial^2\rho_0^{(2)}(r)/\partial\rho^2. \tag{5}$$

In terms of the structure factor $S_0(q)$ we have

$$c(q)-c_0(q)=-\beta\psi_1(q)-\frac{\beta}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\,\psi_1(q)\left(\frac{\partial S_0(|\boldsymbol{k}-\boldsymbol{q}|)}{\partial\rho}\right)+\rho\,\frac{\partial^2 S_0(|\boldsymbol{k}-\boldsymbol{q}|)}{2\partial\rho^2}. \tag{6}$$

If the density dependence of $g_0(r)(\equiv\rho^{-2}\rho_0^{(2)}(r))$ is neglected the ERPA results, then

$$c(q)-c_0(q)=-\beta\psi_1(q)\int \mathrm{d}\boldsymbol{q}\,\psi_1(q)(S_0(|\boldsymbol{k}-\boldsymbol{q}|)-1). \tag{7}$$

However, in all the derivations the density dependence of the potential $\psi_1(r)$ has been ignored by the expansion (5). In order to generalise, it is clear that we must expand the whole integrand in (4), and this leads to

$$c(r)-c_0(r)=-\tfrac{1}{2}\beta(\partial^2/\partial\rho^2)(\psi_1(r)\rho_0^{(2)}(r)). \tag{8}$$

The expression equivalent to the MDA results if the Fourier transform of equation (8) is taken and one writes

$$\rho_0^{(2)}(k)=(2\pi)^3\rho^2\delta(k)+\rho(S_0(k)-1)$$

to give

$$S(k)=S_0(k)\{1+S_0(k)[\beta\rho\psi_1(k)+2\beta\rho^2(\partial/\partial\rho)\psi_1(k) + \tfrac{1}{2}\beta\rho^3(\partial^2/\partial\rho^2)\psi_1(k)+\tfrac{1}{2}A_1(k)+A_2(k)+B_1(k)+B_2(k)]\}^{-1} \tag{9}$$

where

$$A_1(k)=\frac{2\beta\rho}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\left(\frac{\partial}{\partial\rho}\psi_1(q)\right)(S_0(|\boldsymbol{q}-\boldsymbol{k}|)-1) \tag{10a}$$

$$A_2(k)=\frac{\beta\rho^2}{2(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\left(\frac{\partial^2}{\partial\rho^2}\psi_1(q)\right)(S_0(|\boldsymbol{q}-\boldsymbol{k}|)-1) \tag{10b}$$

$$B_1(k)=\frac{\beta\rho}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\,\psi_1(q)\left(\frac{\partial}{\partial\rho}+\frac{1}{2}\rho\frac{\partial^2}{\partial\rho^2}\right)S_0(|\boldsymbol{q}-\boldsymbol{k}|) \tag{10c}$$

$$B_2(k)=\frac{\beta\rho^2}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\left(\frac{\partial}{\partial\rho}\psi_1(q)\right)\left(\frac{\partial}{\partial\rho}S_0(|\boldsymbol{q}-\boldsymbol{k}|)\right). \tag{10d}$$

J. Phys. F: Met. Phys. 15 (1985) L181–L183. Printed in Great Britain

LETTER TO THE EDITOR

On the density dependence of the mean density approximation

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Received 19 April 1985

Abstract. The density dependence of the effective pair potential has been used to obtain generalisations of the mean density approximation for liquid structure factors at long wavelengths.

Recently interest has been shown in the calculation of the structure factors for liquids, in particular, liquid metals from effective pair potentials. This has produced perturbation techniques such as the random phase approximation (RPA), the extended RPA (ERPA), and the mean density approximation (MDA). The MDA was first introduced by Henderson and Ashcroft (1976), rederived by Evans and Schirmacher (1978) using functional analysis and more recently by Itoh (1983) using graphical techniques. The MDA has been used by McLaughlin and Young (1982, 1984) to calculate the long-wavelength limit of the structure factor for a number of liquid metals near their triple points. However, in the derivation of the MDA the effective pair potential has been taken as density independent. Whilst this may be a good approximation in some cases, for example the alkalis, in other cases, for example the polyvalent metals, it will not (Harder *et al* 1979, Hasegawa and Young 1980).

The purpose of this Letter is to derive an expression for the structure factor in which the density dependence of the pair potential is specifically included. The static structure factor $S(q)$ is related to the Fourier transform of the direct correlation function $c(q)$ by

$$S(q) = (1 - \rho c(q))^{-1} \tag{1}$$

where ρ is the number density.

Consider an inhomogeneous fluid in which the interparticle potential is $\psi_0 + \mu\psi_1$. Then, if $\rho^{(2)}(\mu; \boldsymbol{r}_1, \boldsymbol{r}_2)$ is the corresponding configurational two-body distribution function, Evans (1979) has shown that

$$c(\rho, r_{12}) - c_0(\rho, r_{12}) = -\frac{\beta}{2}\left(\frac{\delta^2}{\delta\rho(\boldsymbol{r}_1)\delta\rho(\boldsymbol{r}_2)} K(\rho)\right)_\rho \tag{2}$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$ and

$$K = \int_0^1 \mathrm{d}\mu \int\int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, \rho^{(2)}(\mu; \boldsymbol{r}_1, \boldsymbol{r}_2)\psi_1(r_{12}). \tag{3}$$

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0305-4608/85/070181 + 03 $02.25

The equivalent ERPA is obtained by neglecting the density dependence of the $g_0(r)$ as before. This results in the expression

$$S(k)=S_0(k)\{1+S_0(k)[\beta\rho\psi_1(k)+2\beta\rho^2(\partial/\partial\rho)\psi_1(k) + \tfrac{1}{2}\beta\rho^3(\partial^2/\partial\rho^2)\psi_1(k)+A_1(k)+A_2(k)+A_0(k)]\}^{-1} \quad (11)$$

where

$$A_0(k)=\frac{\beta}{(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\,\psi_1(q)(S_0(|\boldsymbol{q}-\boldsymbol{k}|)-1).$$

The generalisation of the MDA results in terms involving the density derivative of the perturbation part of the potential. The contribution of these terms is difficult to assess as detailed calculations are involved. However, preliminary calculations for rubidium on the first two terms involving the density derivatives in equation (9) indicate only a small contribution.

MM acknowledges discussions and the interest of Dr J Mahanty. IM would like to thank Dr M Itoh for reading the Letter and Professor W H Young for discussions and suggestions in the preparation. IM acknowledges partial support from an SERC Senior Visiting Fellowship grant.

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