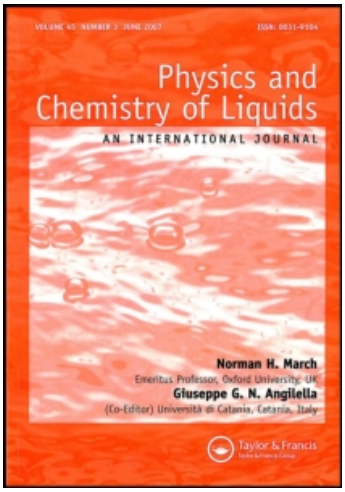

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The Volume-Dependence of Inverse Power Potential Liquid Structure Factors

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The Volume-Dependence of Inverse Power Potential Liquid Structure Factors

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The volume-dependence of the structure factors of the one component plasma (OCP) and of the hard sphere fluid (HSF) are calculated from data derived from computer experiments. In the OCP case the results are in essential agreement with the predictions of a simple formula due to Egelstaff *et al.* which the latter writers have shown to apply to rubidium. This provides further evidence that the OCP is a suitable reference system for the liquid alkalis. The results for the HSF, as expected, do not obey the formula of Egelstaff *et al.* and presumably are more representative of polyvalent liquid metal behaviour.

1 INTRODUCTION

According to Egelstaff and coworkers,[1–3] in suitable cases the isothermal density derivatives of the liquid structure factor may be predicted from a uniform fluid model (UFM). In this model, the electron fluid is assumed to control the position of the ions, so that when compression takes place, all interionic distances, to a good approximation, vary as the inverse third power of the density. This leads directly to the prediction

$$n\frac{\partial g(r)}{\partial n} \simeq \frac{1}{3} r \frac{\partial g(r)}{\partial r} \tag{1}$$

or equivalently

$$n\frac{\partial S(k)}{\partial n} \simeq -\frac{1}{3} k \frac{\partial S(k)}{\partial k} \tag{1}'$$

where $g(r)$ denotes the radial distribution function, $S(k)$ the structure factor, k the momentum transfer and n the number density of the ions. Egelstaff *et al.*[2] have verified experimentally that liquid Rb did indeed satisfy Eq. (1)′ in the region of the first peak of $S(k)$.

On the other hand Price[4] has assumed for liquid Na, in an isothermal compressibility calculation, that

$$n\frac{\partial g(r)}{\partial n} \simeq \frac{1}{3}r\frac{\partial g(r)}{\partial r} + g(r) \tag{2}$$

This implies in inverse space that

$$n\frac{\partial S(k)}{\partial n} \simeq -\frac{1}{3}k\frac{\partial S(k)}{\partial k} + S(k). \tag{2}'$$ (2)′

This assumption was also employed by Kumaravadivel[5] when evaluating the bulk modulus of a metal via the so-called 'long-wavelength method'.

There are two systems, both of the type with potentials $(\sigma/r)^p$, where "exact" results are known and for which all terms of Eq (1) through (2)′ can be calculated. These are the hard-sphere ($p = \infty$) case and the classical one-component plasma ($p = 1$) case.

In this paper we test the assumptions mentioned above using the available "exact" results of inverse power potential liquid structure factors.

2 GENERAL FORMULA

We use as the independent variables $x = r/a$ and $\Gamma = (k_B T)^{-1}(\sigma/a)^p$ where σ and p are the constants characterising the potential (see above) and a is defined as $a = (3/4\pi n)^{1/3}$. Then the radial distribution function g is expressed as $g \equiv g(x, \Gamma)$ and $n(\partial g/\partial n) = -(a/3)(\partial g/\partial a)$. Also,

$$a\frac{\partial g}{\partial a} = a\frac{\partial x}{\partial a}\frac{\partial g}{\partial x} + a\frac{\partial \Gamma}{\partial a}\frac{\partial g}{\partial \Gamma} = -x\frac{\partial g}{\partial x} - p\Gamma\frac{\partial g}{\partial \Gamma}$$

and

$$r\frac{\partial g}{\partial r} = r\frac{\partial x}{\partial r}\frac{\partial g}{\partial x} + r\frac{\partial \Gamma}{\partial r}\frac{\partial g}{\partial \Gamma} = x\frac{\partial g}{\partial x}$$

Therefore we obtain

$$\frac{3n}{g}\left(\frac{\partial g}{\partial n}\right)_r = \frac{r}{g}\left(\frac{\partial g}{\partial r}\right)_n + \frac{p\Gamma}{g}\left(\frac{\partial g}{\partial \Gamma}\right)_x. \tag{3}$$

The final term in this equation is what Egelstaff *et al.* and Price take to be 0 and 3 respectively.

Similar arguments are possible in inverse space where the structure factor S is expressed as $S \equiv S(ka, \Gamma)$ and now Eq. (3) becomes

$$\frac{3n}{S}\left(\frac{\partial S}{\partial n}\right)_k = -\frac{k}{S}\left(\frac{\partial S}{\partial k}\right)_n + \frac{p\Gamma}{S}\left(\frac{\partial S}{\partial \Gamma}\right)_{ka} \tag{4}$$

Once again the estimates of the final term of Egelstaff *et al.* and Price would be 0 and 3 respectively.

3 RESULTS

(i) Analysis in real space

First of all, we begin with the one-component plasma (OCP) ($p = 1$) case. We have used Table III of Slattery *et al.*'s paper[6] and employed chord approximations to estimate the second and third terms in Eq. (3) for the plasma parameter $\Gamma = 150$ which is quite near the melting point.[7,8] For convenience, we use the notation

$$I_1 \equiv \frac{3n}{g}\left(\frac{\partial g}{\partial n}\right)_r \simeq \frac{3n}{g}\left(\frac{\Delta g}{\Delta n}\right)_r,$$

$$I_2 \equiv \frac{r}{g}\left(\frac{\partial g}{\partial r}\right)_n \simeq \frac{x}{g}\left(\frac{\Delta g}{\Delta x}\right)_n,$$

$$I_3 \equiv \frac{\Gamma}{f}\left(\frac{\partial g}{\partial \Gamma}\right)_x \simeq \frac{\Gamma}{g}\left(\frac{\partial g}{\Delta \Gamma}\right)_x.$$

The results of such calculations are shown in Figure 1. Clearly, it is a good approximation to neglect I_3 in comparison with I_2 as one would do in the approximation of Egelstaff *et al.* We also study, in the Appendix, what happens when Γ is much lower than values encountered in metal physics and when the application would be in astrophysics.

Next we proceed to the hard sphere ($p = \infty$) case. When $p = \infty$, I_3 is less obviously defined, although it can be evaluated as $(\sigma/g)(\partial g/\partial \sigma)_{r,a}$. However, since g is usually listed as $g(r/\sigma, n\sigma^3)$ it is easier to calculate I_1 and I_2 direct, and to infer I_3 from $I_1 - I_2$, assuming σ is constant. We have used Table 3 of Watts and Henderson[9] and calculated for $\rho^* \equiv n\sigma^3 = 0.9$ (corresponding to the packing fraction $\eta = 0.47$) using

$$I_1 \equiv \frac{3n}{g}\left(\frac{\partial g}{\partial n}\right)_r \simeq \frac{3\rho^*}{g}\left(\frac{\Delta g}{\Delta \rho^*}\right)_r,$$

$$I_2 \equiv \frac{r}{g}\left(\frac{\partial g}{\partial r}\right)_n \simeq \frac{(r/\sigma)}{g}\left(\frac{\Delta g}{\Delta (r/\sigma)}\right)_n.$$

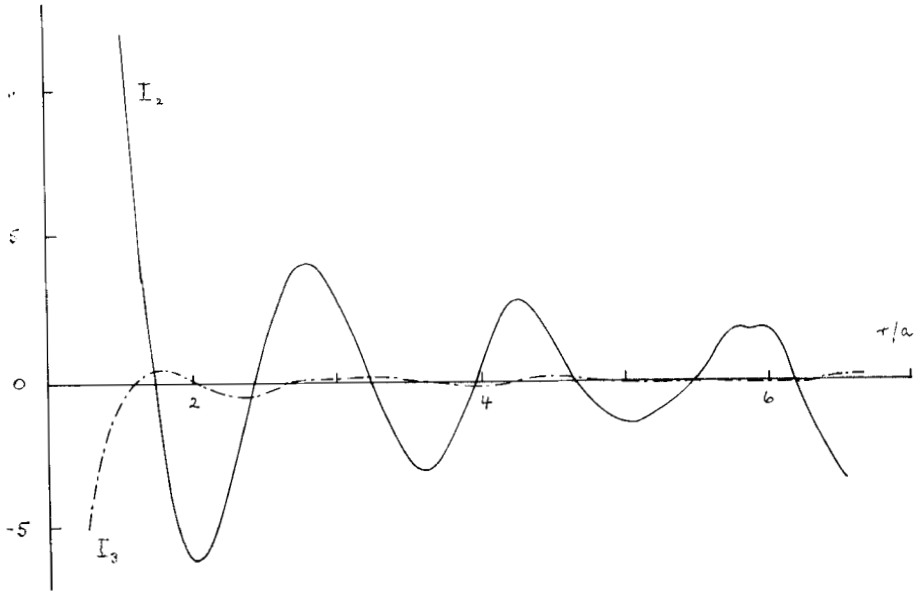

FIGURE 1 I_2, I_3 versus r/a for $\Gamma = 150$ in the case of the OCP radial distribution function. I_3 is negligible compared with I_2, in agreement with what Egelstaff *et al.* would have assumed.

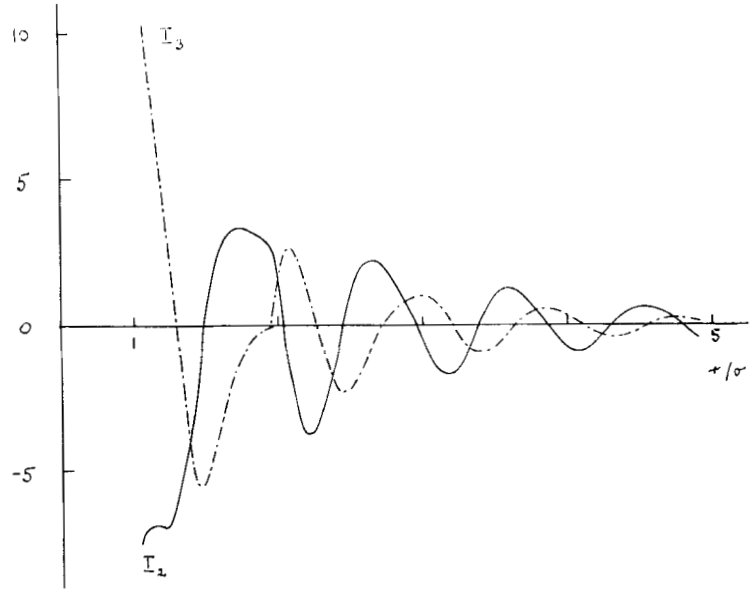

FIGURE 2 I_2, I_3 versus r/σ for $\eta = 0.47$ in the case of the hard-sphere radial distribution function. Neither the Egelstaff *et al.* nor the Price assumption is justified here.

Figure 2 shows the results for this hard-sphere case. As is seen from the graph, neither Egelstaff *et al.*'s nor Price's assumption would be valid here.

(ii) Analysis in inverse space

The same calculations as in (*i*) can be done in inverse space. This time we use the notation

$$\mathscr{I}_1 \equiv \frac{3n}{S}\left(\frac{\partial S}{\partial n}\right)_k \simeq \frac{3n}{S}\left(\frac{\partial S}{\partial n}\right)_k,$$

$$\mathscr{I}_2 \equiv -\frac{k}{S}\left(\frac{\partial S}{\partial k}\right)_n \simeq -\frac{ka}{S}\left(\frac{\Delta S}{\Delta(ka)}\right)_n.$$

$$\mathscr{I}_3 \equiv \frac{p\Gamma}{S}\left(\frac{\partial S}{\partial \Gamma}\right)_{ka} \simeq \frac{p\Gamma}{S}\left(\frac{\Delta S}{\Delta \Gamma}\right)_{ka}.$$

First we start with the OCP ($p = 1$) case and then we examine the hard-sphere ($p = \infty$) case as before. For the OCP we have used the new structure factor data due to Rogers *et al.*[10] which are based on the modified Hypernetted Chain integral equation. Calculations were carried out for $\Gamma = 150$ as in the case of the real-space analysis. Graphs of $\mathscr{I}_2$ and $\mathscr{I}_3$ versus ka are given in Figure 3, and from these we see that $\mathscr{I}_3$ is overall very small compared

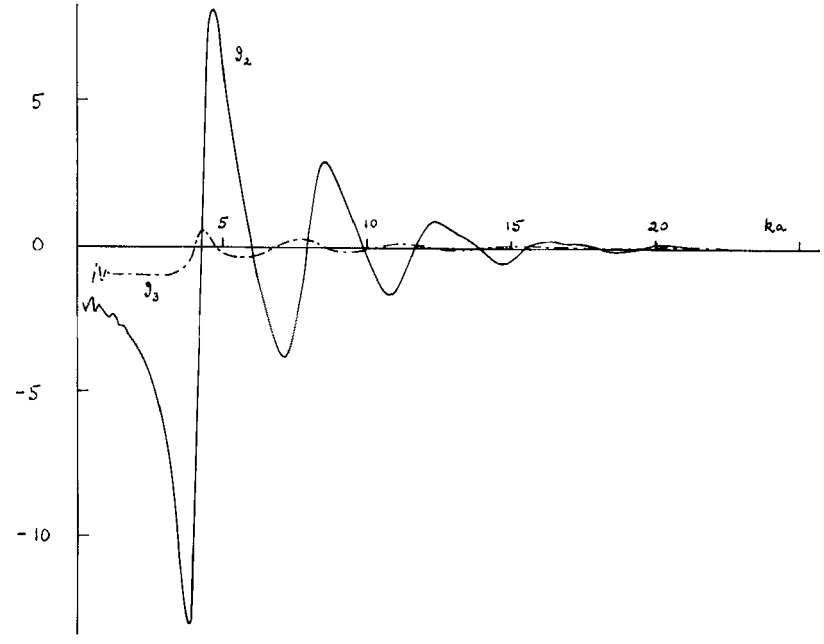

FIGURE 3 $\mathscr{I}_2$, $\mathscr{I}_3$ versus ka for $\Gamma = 150$ in the case of the OCP structure factor. $\mathscr{I}_3$ is negligible compared with $\mathscr{I}_2$, in accordance with the Egelstaff *et al.* assumption.

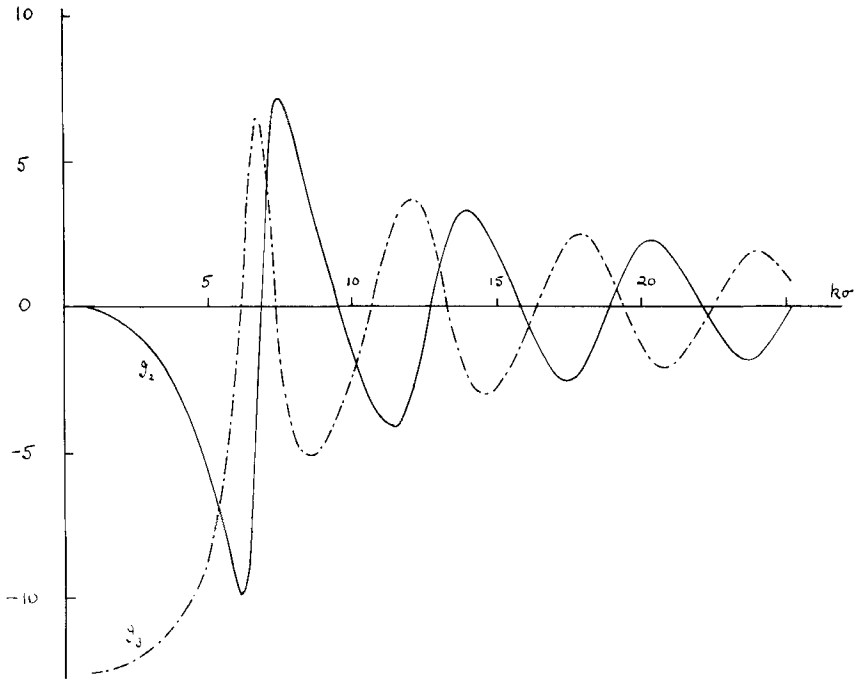

FIGURE 4 $\mathscr{I}_2$, $\mathscr{I}_3$ versus $k\sigma$ for $\eta = 0.45$ in the case of the hard-sphere structure factor. As in Figure 2, neither Egelstaff *et al.*'s or Price's assumption would be valid here.

with $\mathscr{I}_2$, in accord with what Egelstaff *et al.* would assume. For Γ extremely small, an analysis is also given in the Appendix.

As for the hard-sphere case, the Percus–Yevick analytical form used by Ashcroft and Lekner[11] can give direct results for $\mathscr{I}_1$ and $\mathscr{I}_2$, and then $\mathscr{I}_3$ from $\mathscr{I}_1 - \mathscr{I}_2$. Cummings and Egelstaff have already studied this case and decided that it does not describe the experimental situation. However, we performed such a calculation again here for completeness. The result is shown in Figure 4 and is clearly unsatisfactory, as expected.

4 CONCLUSIONS

We have studied the volume dependence of the structure factor for two model liquids. These are the OCP and the hard-sphere systems, the extreme examples of the inverse power potential fluids. Assumptions exist in the literature on how real metallic systems would behave under such circumstances and that of Egelstaff *et al.*, if applied to the above models, would work for the OCP, but not for the hard sphere system.

Egelstaff *et al.* have observed the variation with volume of the structure factor of liquid rubidium and demonstrated that their theory is applicable to this case. Taken together with the present work we have confirmation of the current belief (e.g. of Chaturvedi *et al.*[7] and of Mon *et al.*[8]) that the OCP is a better reference fluid for the liquid alkalis than a hard sphere one.

Although experimentally difficult on account of the much reduced compressibilities, it would be of great interest to test the hypothesis of Egelstaff *et al.* for polyvalent liquid metals. Here one would expect the hard sphere system to be more relevant and therefore that the Egelstaff *et al.* assumptions would be less successful.

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Appendix

In order to test further the applicability of the UFM to the OCP it is illuminating to see what happens when Γ is extemely small (the particular values chosen for study being largely selected for us by the published print outs). Examples of such cases are shown in Figures 5 and 6. From Figure 5, we see that for $\Gamma = 3$, Eq. (1) continues to hold except at the very lowest values of r/a. This conclusion is borne out by Figure 6 where we see that for $\Gamma = 20$, Eq. (1)′ remains realistic around and beyond the principal peak much as for the $\Gamma = 150$ case considered in the main text (Figure 3).

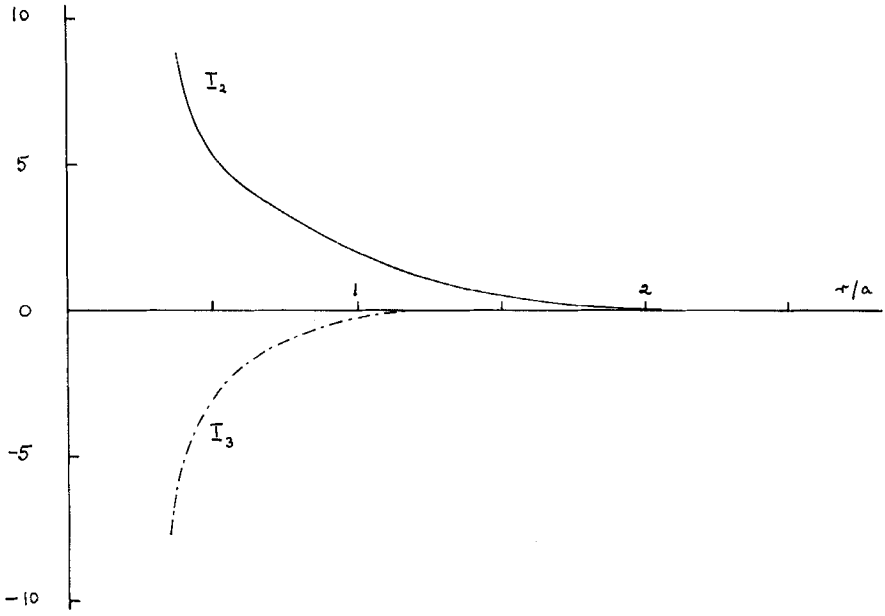

FIGURE 5 As Figure 1, with $\Gamma = 3$.

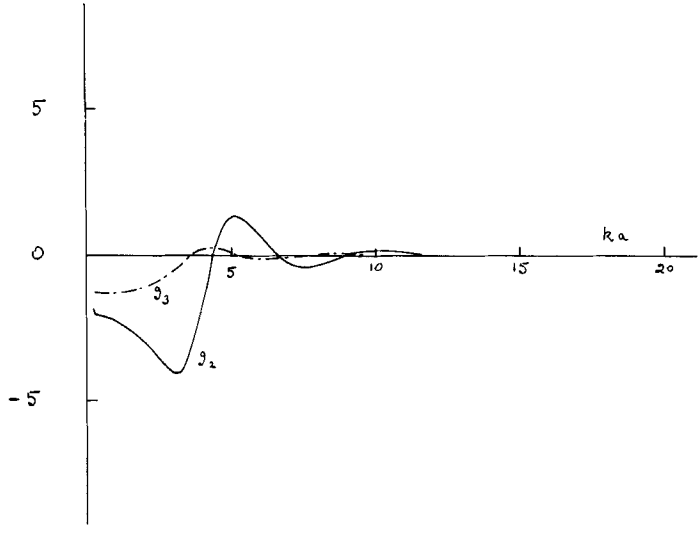

FIGURE 6 As Figure 3, with $\Gamma = 20$.