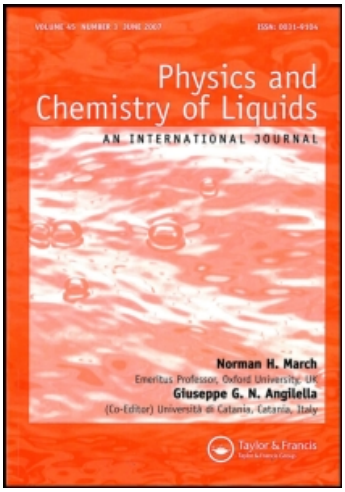

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Structure of Classical Fluid of Charged Hard Spheres and Point Ions in the Perturbation of a Small Non-Responsive, Uniform Background Density

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In liquid Te, the model of Cabane and Friedel is based on the coexistence of a network of strong covalent bonds with a metallic-like electron gas. We have attempted to simulate the gross features of this situation by studying a classical fluid of charged hard spheres, plus point charges (classical electrons!), all moving in a small neutralizing negative background density.

An exact solution of even this model will require computer simulation. We have therefore worked in the approximation of the mean spherical model. Also, we treat the neutralizing background only to first order in the background density.

The main effect of the background is to increase the height of the contact value of $g(r)$ for the hard sphere pair correlations. This appears to correspond qualitatively with the high temperature behaviour of liquid Te.

1 INTRODUCTION

Gillan *et al.*[1] have recently studied a model of charged hard spheres and point ions, in order to simulate an ionic fluid where there is a major difference between the diameters of the ions. One conclusion which was drawn from Monte Carlo calculations on this model was that at strong coupling the system polymerized. The linear chains thus formed, arising, of course, from a purely classical description, prompted us to enquire whether the model might have further utility in a different area of fluid structure, namely to simulate chemical bonds in a monatomic fluid.

There are then only very few such fluids to which such a model would have relevance, one of which is liquid Te. Here Cabane and Friedel[2] describe the

short range order at high temperatures (900°C) by a structure where most atoms have 3 first neighbours, joined by strong bonds similar to the covalent bonds of the chains in solid Te. Such a network of covalent bonds coexists with delocalized electrons forming a metallic-like electron gas.

We have gone into the case of liquid Te, not because the model set out in section 2 can hope to quantitatively simulate such a situation, but in order to motivate the study of the influence on structure of delocalizing some fraction of electrons, initially in covalent bonds. The remainder of the paper focusses therefore on this point; it would be premature with such a crude model to attempt any detailed comparison with experiment.

Even the simple model studied here appears to be soluble exactly only by computer simulation. Therefore we shall work here in the approximation of the mean spherical model (MSM) discussed in section 2 below. We know from the work of Gillan *et al.*[1] that this approximation becomes less accurate as the coupling strength increases. Therefore, it may subsequently be necessary to supplement the present treatment by computer simulation.

2 MEAN SPHERICAL APPROXIMATION TO MODEL

For a classical fluid of charged hard spheres, the mean spherical model is defined as

$$\begin{aligned} g_{ij}(r) &= 0 \qquad & r < \sigma_{ij} \\ c_{ij}(r) &= -\frac{\beta e_i e_j}{\varepsilon r} \qquad & r > \sigma_{ij} \end{aligned} \tag{2.1}$$

where $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$; σ_i, σ_j being ionic diameters of type i and j: $g_{ij}(r)$ are the partial radial distribution functions, $c_{ij}(r)$ are partial direct correlation functions, ε is the dielectric constant (if appropriate) $\beta = 1/k_b T$ and e_i is the charge of the ith ion.

The system we treat below consists of positively charged hard spheres, plus point classical electrons, but now all moving in a background of non-responsive negative neutralizing charge to simulate some "delocalized" electrons. The electrical neutrality condition may be expressed as

$$\rho_1 e_1 + \rho_2 e_2 + \rho_3 e_3 = 0 \tag{2.2}$$

where ρ_1 is the number density of the point electrons, ρ_2 that of the charged hard spheres while ρ_3 is the background density. The background, we emphasize again, is taken as not allowed to respond to ionic motions.

Following the same techniques as Waisman and Lebowitz[3] and Palmer and Weeks,[4] the r-space forms of $c_{ij}(r)$ for $r < \sigma_{ij}$ were obtained (see the Appendix for some further details). It is worthy of note that $c_{22}(r)$ is a 5th order polynomial with the r^4 term absent, while $c_{21}(r)$ is a 2nd order polynomial with the linear term absent. There are four unknown constants a_1, a_2, b_2 and f_2 which appear in the coefficients of these direct correlation functions: the "singularities" method (cf. Gillan *et al.*[1]) of solution for these constants gave four extremely complicated equations. In order to simplify these a process of linearization was carried out, to yield

$$\begin{aligned} a_1 &\simeq a_1^0 + \rho_3 A_1(a_1^0, a_2^0, b_2^0) \\ a_2 &\simeq a_2^0 + \rho_3 A_2(a_1^0, a_2^0, b_2^0) \\ b_2 &\simeq b_2^0 + \rho_3 B_2(a_1^0, a_2^0, b_2^0) \\ f_2 &\simeq \rho_3 F_2(a_1^0, a_2^0, b_2^0) \end{aligned} \tag{2.3}$$

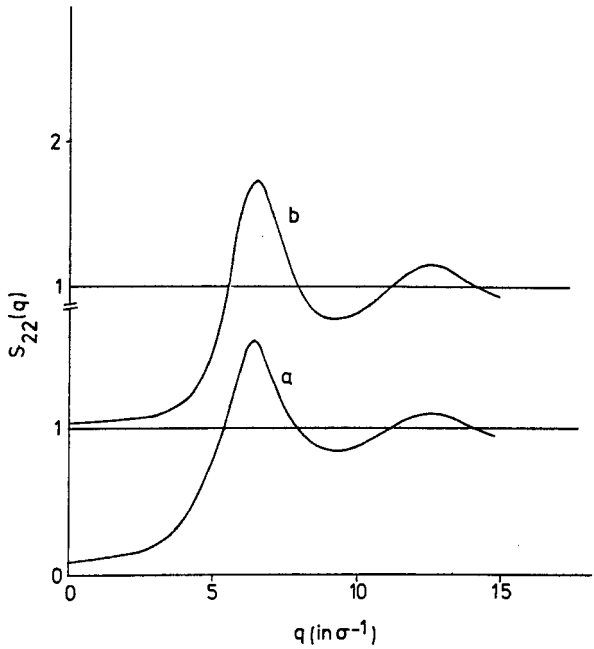

FIGURE 1 Charged hard sphere structure factor $S_{22}(q)$ versus q. Curve a: $\rho_3/\rho_2 = 0$ (limit of Gillan *et al.*[1]). Curve b: with small delocalized background charge given by $\rho_3/\rho_2 = 5.236 \times 10^{-3}$. Note that the height of the first peak is significantly enhanced by even this small background density.

In all four Figures, packing fraction $\xi = 0.3$ while coupling parameter $x = -20.0$.

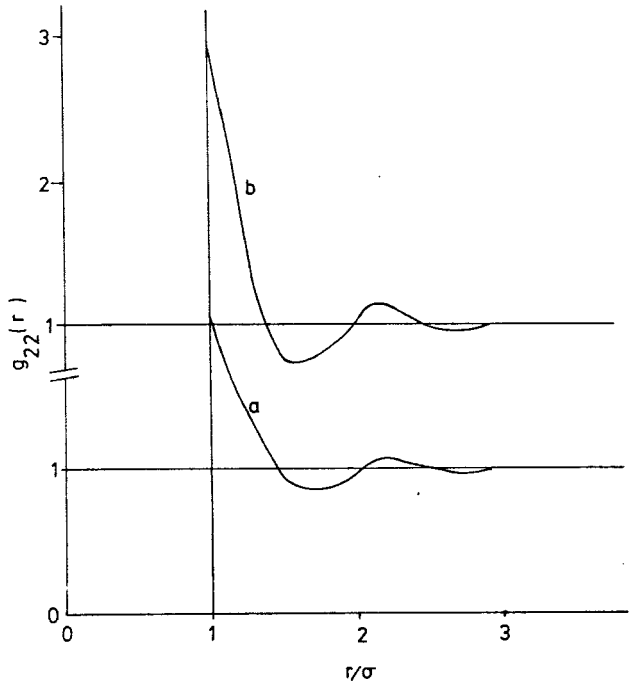

FIGURE 2 Fourier transform $g_{22}(r)$ of structure factor shown in Figure 1 versus r/σ. Curve a: $\rho_3/\rho_2 = 0$ (limit of Gillan *et al.*[1]). Curve b: $\rho_3/\rho_2 = 5.236 \times 10^{-3}$. Note again the substantial increase in contact value $g_{22}(\sigma)$ due to the (small) degree of delocalization.

where a_1^0 etc. are the corresponding constants in the model of Gillan *et al.* with no background charge. f_2 is the new constant appearing in the present case of non-zero background and is also calculated only to first order in ρ_3. The quantities A_1 etc. involve a_1^0 etc. as indicated.

Results for the partial structure factors were obtained for a packing fraction $\xi = (\pi/6)\rho_2\sigma^3 = 0.3$, σ being the hard sphere diameter, and a coupling constant $x = \beta e_1 e_2/\sigma = -20.0$. Even for a very small ratio of delocalized to localized electrons (1/200) a very substantial change in structure was observed. While such a pronounced effect may well be an

TABLE I

ρ_3/ρ_2	$g_{22}(\sigma)$
0.0	2.058
5.236×10^{-3}	2.954
8.727×10^{-3}	3.550

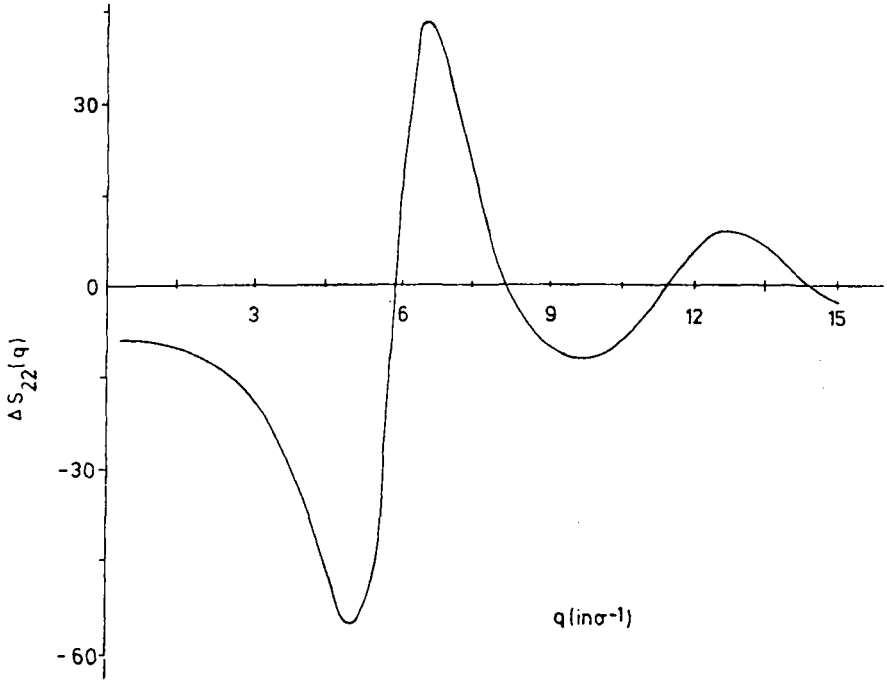

FIGURE 3 Change $\Delta S_{22}(q)$ in structure factor for charged hard spheres as defined in Eq. (2.4).

artefact of the mean spherical model in part, it seems clear that such a delocalization has a quite definite effect on the structure. In particular, as the background is switched on (to $\rho_3/\rho_2 \sim 1/200$) the height of the first peak in the hard sphere structure factor $S_{22}(q)$ changed from 1.5 to 1.7. The second peak height increased from 1.10 to 1.15.

Figure 1 shows $S_{22}(q)$ for the Gillan *et al.* model and for the degree of delocalization as above. Corresponding results for $g_{22}(r)$ are shown in Figure 2 while in Table 1 the contact values of g_{22} are given for different ratios ρ_3/ρ_2. The changes from the Gillan *et al.* structure were calculated numerically from the linearized theory according to

$$S_{ij}(q) \simeq S^0_{ij}(q) + \frac{\rho_3}{\rho_2} \Delta S_{ij}(q) \tag{2.4}$$

and

$$g_{ij}(r) \simeq g^0_{ij}(r) + \frac{\rho_3}{\rho_2} \Delta g_{ij}(r) \tag{2.5}$$

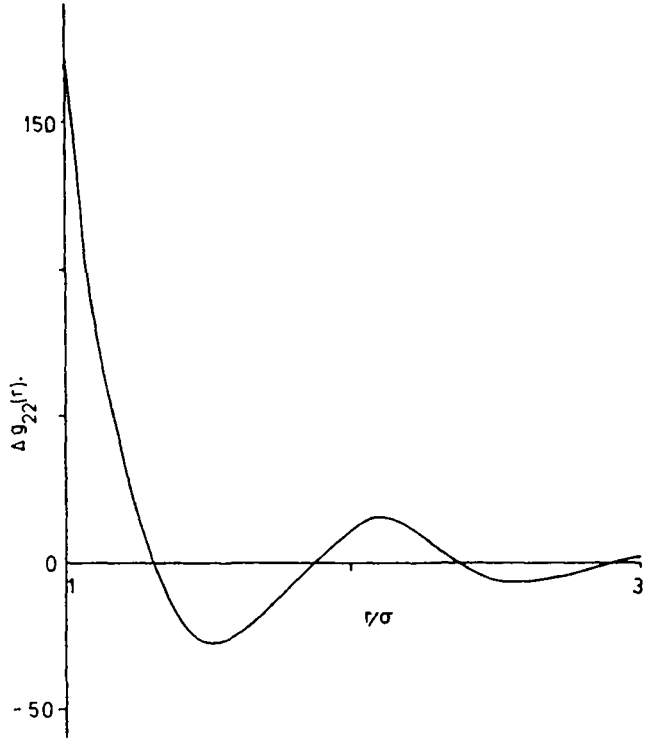

FIGURE 4 Change $\Delta g_{22}(r)$ in pair function for charged hard spheres as defined in Eq. (2.5).

where $\Delta S_{ij}(q)$ and $\Delta g_{ij}(r)$ are quantities involving a_1^0, a_2^0, b_2^0 and system parameters. The quantities $\Delta S_{22}(q)$ and $\Delta g_{22}(r)$ are shown in Figures 3 and 4 respectively.

As mentioned above, the magnitude of the change found may be exaggerated in the mean spherical model; it is certainly very large for such a small ratio of background to localized electron density. Also, it may be that the linearization is exaggerating the effect at the ratio discussed.

It is tempting to enquire, in conclusion, whether such behaviour is qualitatively relevant to liquid Te. When one examines the behaviour of the first peak in $g(r)$ with temperature, one finds that whereas, at first, the height of the principal peak decreases with increasing temperature, this trend reverses as the temperature increases.[5] As there is a trend for the number of conduction electrons to increase with increasing temperature, it seems that this behaviour is consistent with the prediction from the present, admittedly grossly simplified, model.

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Appendix A

A FORM OF DIRECT CORRELATION FUNCTIONS

Following the techniques of Waisman and Lebowitz[3] and Palmer and Weeks[4], the direct correlation functions for this system are found to be, with subscript 1 referring to point electrons, 2 to positively charged hard spheres and 3 to background:

$$-c_{11}(r) = \frac{\beta e_1^2}{r} \qquad \text{all } r \tag{A1}$$

$$-c_{22}(r) = \left[a_2 - \frac{2\beta V_2}{\rho_2}\right] + b_2\left(\frac{r}{\sigma}\right) + c_2'\left(\frac{r}{\sigma}\right)^2 + \mathrm{d}_2\left(\frac{r}{\sigma}\right)^3 + f_2\left(\frac{r}{\sigma}\right)^5 \qquad r < \sigma$$

$$= \frac{\beta e_2^2}{r} \qquad r > \sigma \tag{A2}$$

$$-c_{21}(r) = \left[a_1 + \frac{2\beta V_2}{\rho_1}\left(1 + \frac{\rho_3 e_3}{\rho_2 e_2}\right)\right] + c_2\left(\frac{r}{\sigma}\right)^2 \qquad r < \frac{\sigma}{2}$$

$$= \frac{\beta e_1 e_2}{r} \qquad r > \frac{\sigma}{2} \tag{A.3}$$

where

$$V_2 = \frac{\rho_1}{2\beta\left(1 + \dfrac{\rho_3 e_3}{\rho_2 e_2}\right)} \xi^{-1}\left[a_1(1-\xi) - 1 + 3\xi\left(x - \frac{c_2}{20}\right)\right]$$

$$-c_2' = c_2 = -4x\xi(1-y)$$

and

$$\mathrm{d}_2 = \frac{\xi}{2}\left[a_2 + ya_1 + \frac{\rho_3}{\rho_2}\right] \tag{A4}$$

The system parameters ξ, x and y are given by

$$\xi = \frac{\pi}{6}\rho_2\sigma^3 \qquad \text{(packing fraction)}$$

$$x = \frac{\beta e_1 e_2}{\sigma} \qquad \text{(dimensionless coupling parameter)}$$

$$y = \frac{\rho_1}{\rho_2} \tag{A5}$$

In the limit $\rho_3 \to 0$, $y \to 1$ so that c_2, c_2' vanish as also must f_2 in order to reduce to the form given by Gillan *et al.*[1] Thus, putting $f_2 \propto \rho_3$ and taking the limit $\rho_3 \to 0$, the above $c_{ij}(r)$'s reduce exactly to those given by Gillan *et al.*[1] The constants to be determined are now a_1, a_2, b_2 and f_2.

B FOURIER TRANSFORMS OF DIRECT CORRELATION FUNCTIONS

The Fourier transforms $\tilde{c}_{ij}(q)$ of $c_{ij}(r)$ are defined as

$$\tilde{c}_{ij}(q) = 4\pi(\rho_i\rho_j)^{1/2}\int_0^\infty \mathrm{d}r\, r^2 \frac{\sin qr}{qr} c_{ij}(r). \tag{A6}$$

The $\tilde{c}_{ij}(q)$'s for the present case are then found from Eqs. (A1–3) to be

$$\tilde{c}_{11}(q) = -\frac{4\pi\beta\rho_1 e_1^2}{q^2} \tag{A7}$$

$$\tilde{c}_{22}(q) = \frac{4\pi\rho_2\sigma^3}{(q\sigma)^2}\left[L(q)\cos q\sigma - M(q)\frac{\sin q\sigma}{q\sigma} + \frac{N(q)}{(q\sigma)^2}\right] \tag{A8}$$

$$\tilde{c}_{21}(q) = \frac{2\pi(\rho_1\rho_2)^{1/2}\sigma^3}{(q\sigma)^2}\left[P(q)\cos\left(\frac{q\sigma}{2}\right) - Q(q)\frac{\sin(q\sigma/2)}{(q\sigma/2)}\right] \tag{A9}$$

where

$$L(q) = (\alpha + b_2 + c_2' + d_2 + f_2) - \frac{1}{(q\sigma)^2}(2b_2 + 6c_2' + 12d_2 + 30f_2)$$

$$+ \frac{1}{(q\sigma)^4}(24d_2 + 360f_2) - \frac{720f_2}{(q\sigma)^6} - \frac{\beta e_2^2}{\sigma}$$

$$M(q) = (\alpha + 2b_2 + 3c_2' + 4d_2 + 6f_2) - \frac{1}{(q\sigma)^2}(24d_2 + 120f_2 + 6c_2') + \frac{1}{(q\sigma)^4}720f_2$$

$$N(q) = 2b_2 - \frac{24d_2}{(q\sigma)^2} + \frac{720f_2}{(q\sigma)^4}$$

$$P(q) = \left\{a_1 + \frac{2\beta V_2}{\rho_1}\left(1 + \frac{\rho_3 e_3}{\rho_2 e_2}\right)\right\} + \frac{c_2}{4} - \frac{2\beta e_1 e_2}{\sigma} - \frac{6c_2}{(q\sigma)^2}$$

$$Q(q) = \left\{a_1 + \frac{2\beta V_2}{\rho_1}\left(1 + \frac{\rho_3 e_3}{\rho_2 e_2}\right)\right\} + \frac{3}{4}c_2 - \frac{6c_2}{(q\sigma)^2}$$

with

$$\alpha = \left[a_2 - \frac{2\beta V_2}{\rho_2}\right]. \tag{A10}$$

The "singularities" equations are obtained by equating the coefficients of q^{-4}, q^{-6}, q^{-8} and q^{-10} in the large q expansion of $S_{22}(q)$ to zero. These are four pretty complicated equations for the unknowns, which, on linearizing, take the form (2.3).

References

1. M. Gillan, B. Larsen, M. P. Tosi, and N. H. March, *J. Phys.*, **C9**, 889 (1976).
2. B. Cabane and J. Friedel, *J. Physique*, **32**, 73 (1971).
3. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.*, **56**, 3086 (1972).
4. R. G. Palmer and J. D. Weeks, *J. Chem. Phys.*, **58**, 4171 (1973).
5. G. Tourand and M. Breuil, *J. Physique*, **32**, 813 (1971).