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Excess Number and Charge Functions in Liquids

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Definitions for the excess number and charge functions are given. They are used to show how the structure of a liquid about a reference particle differs from the average values. Some features of the structure are illustrated more clearly by this representation than by the radial distribution functions.

The mean number of particles contained within a sphere of radius, R , about a reference particle is given by

$$N(R) = 4\pi n \int_0^R r^2 g(r) dr \quad (1)$$

where n is the number density and $g(r)$ is the pair distribution function. The use of $N(R)$ has been commended by Hutchinson *et al.*¹ for discussions which involve short range order in the liquid state and its application to the freezing transition showed it to be a more useful function than $g(r)$ for that purpose. In this letter we suggest that it is also worthwhile to consider the excess number of particles in a sphere of radius, R , about a reference particle defined by

$$\delta N(R) = 1 + 4\pi n \int_0^R r^2 (g(r) - 1) dr \rightarrow S(0) \neq 0 \quad R \rightarrow \infty \quad (2)$$

This measures by how many the number of particles in a sphere of radius, R , exceeds the number corresponding to the number density of the system. In the limit as $R \rightarrow \infty$, $\delta N(R)$ reduces to the zero wavevector limit of the structure factor, $S(0)$. $\delta N(R)$ for a potential of the form of the inverse twelfth power² is shown in Figure 1(a). It is clear that the disturbance of the structure caused by the reference particle at the origin is very long ranged with the

envelope of the curve decaying only slowly to its asymptotic value of $S(0) = 0.018$. $(g(r) - 1)$ for $r/\sigma \simeq 6.0$ is of order 10^{-3} , where σ is the collision diameter of the particle, but there is still present a considerable amount of physically significant information which is more readily seen from $\delta N(R)$. In particular it shows why it is not possible to obtain the structure factor by Fourier transforming a truncated pair distribution function and why it is not a good

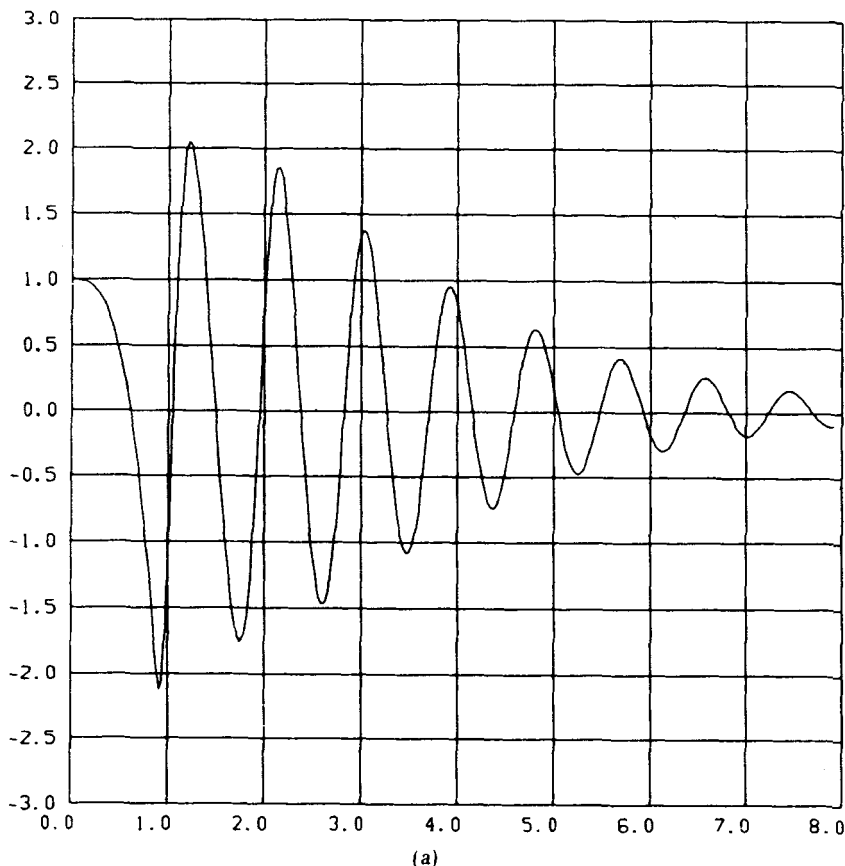


FIGURE 1 $\delta N(R)$ for monatomic systems. Abscissa in units of the collision diameter, (a) Inverse twelfth power; $n = 1.06$.

function to attempt to extrapolate. The long range disturbance must arise primarily from packing effects since the potential has effectively decayed to zero at $r/\sigma = 2$, and the direct correlation function is of similar range to the potential. The maxima in $\delta N(R)$ occur when $(g(r) - 1)$ changes from positive to negative and the minima occur when it changes from negative to positive. The presence of a particle at the origin excludes other particles from

approaching much closer than σ , leading to a rapid decrease in $\delta N(R)$ from $+1$ for $R = 0$ to -2.2 for $R = 0.9\sigma$. Once R is near σ it is possible for other particles to cluster round the reference particle and so $\delta N(R)$ increases sharply to 2.1. Each of these particles has its own exclusion sphere which forces $\delta N(R)$ to go negative and each has its own co-ordination sphere which

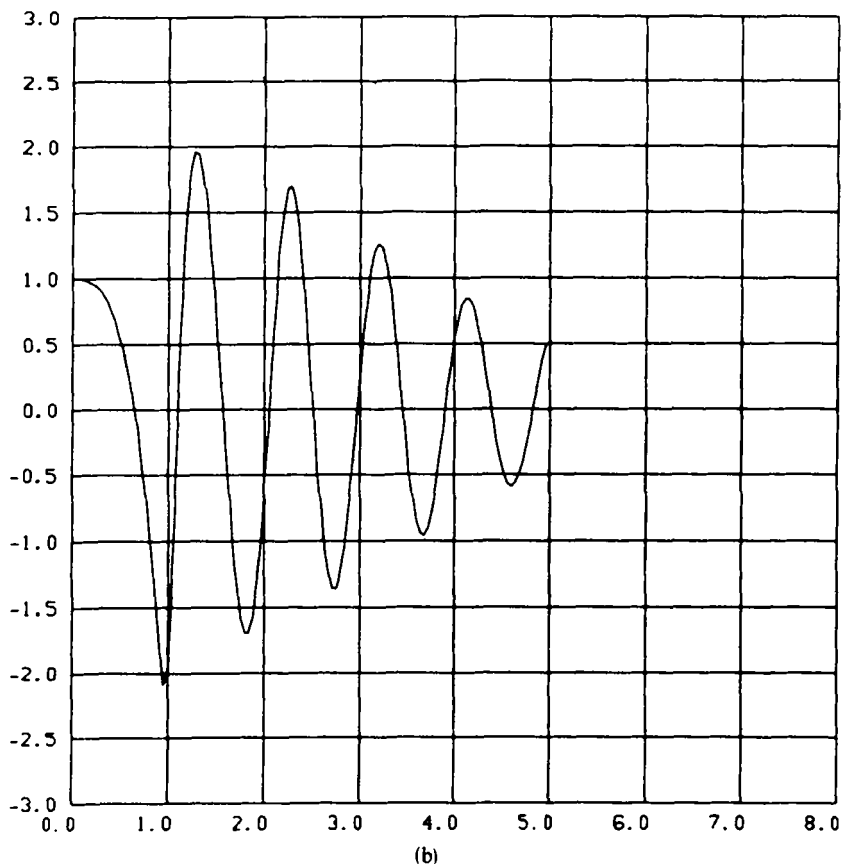


FIGURE 1 $\delta N(R)$ for monatomic systems. Abscissa in units of the collision diameter. (b) Lennard Jones; $n = 0.88$.

leads to another positive value of $\delta N(R)$. In this manner the disturbance is propagated over very long ranges.

Features similar to those discussed above are exhibited by a wide range of monatomic liquids. Liquid argon, liquid rubidium, and a classical one component plasma fall into very different categories of monatomic liquid and yet the molecular dynamics simulations of Verlet³, Rahman,⁴ and

Hansen⁵ all yield $\delta N(R)$ which have similar features to those noted for the inverse twelfth power potential; see Figure 1(a-d). It is clear that the disturbance measured by $\delta N(R)$ is very considerable at distances comparable to those used in simulations. Using a procedure devised by Dixon and Hutchinson⁶ it is possible to obtain the structure factor for short ranged potentials

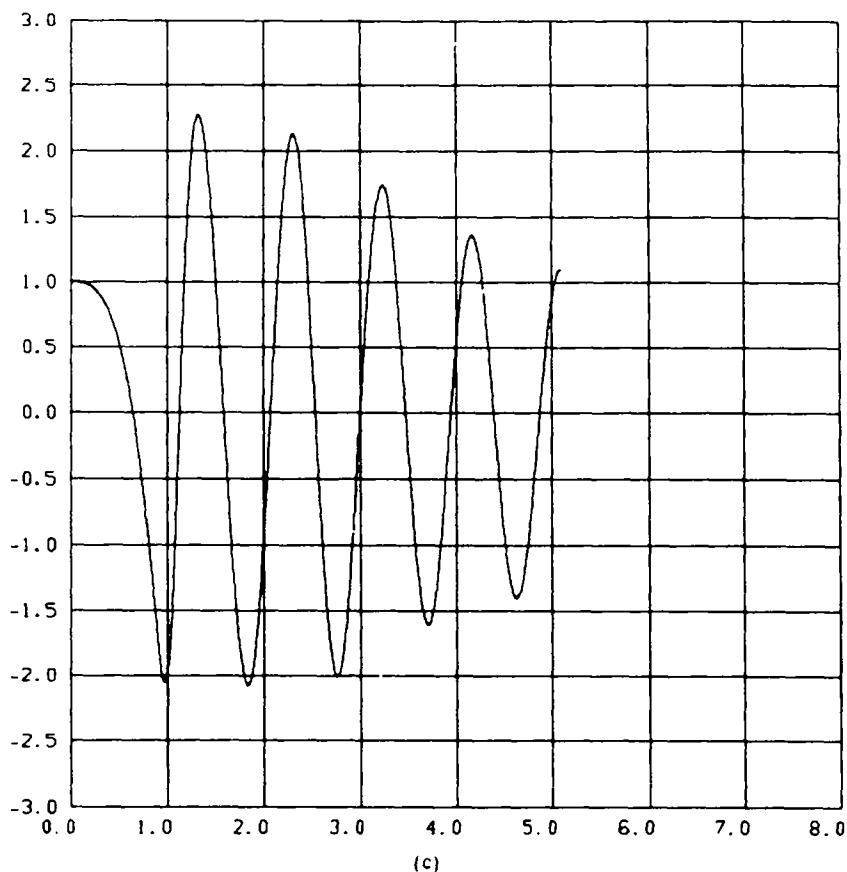


FIGURE 1 $\delta N(R)$ for monatomic systems. Abscissa in units of the collision diameter. (c) liquid rubidium; $n = 0.90$.

from molecular dynamics simulations by transforming from the pair distribution function to the direct correlation function and extrapolating that.

For binary ionic melts, charge ordering as well as packing effects contribute to determining the excess number of particles. We can generalise

Eq. (2) to obtain

$$\delta N_{\alpha\beta}(R) = \delta_{\alpha\beta} + 4\pi n_{\beta} \int_0^R r^2 (g(r) - 1) dr \quad \alpha, \beta = +, - \quad (3)$$

where $\delta N_{\alpha\beta}(R)$ is the partial excess number of particles of type β in a sphere of radius, R , if a particle of type α is the reference particle. For the binary liquid

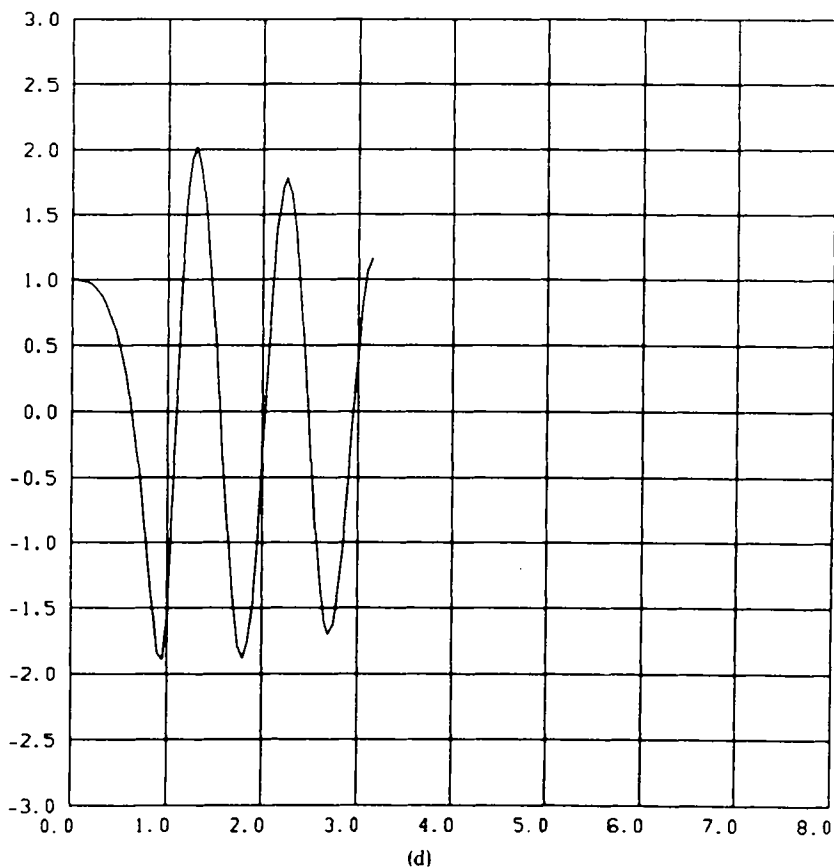


FIGURE 1 $\delta N(R)$ for monatomic systems. Abscissa in units of the collision diameter, (d) Classical one component plasma; $n = 0.24$.

$n_+ + n_-$ corresponds to n for the monatomic liquid and consequently the fluctuating part of Eq. (3) occurs with a reduced scale factor in comparison with Eq. (2). We show in Figure 2(a) the $\delta N_{\alpha\beta}(R)$ obtained by Dixon and Sangster⁷ from a simulation of molten sodium iodide using a polarisable model of the ions. Figure 2(b) gives the corresponding rigid ion model data.

In that work it was apparent that $g_{++}(r)$ was different from $g_{--}(r)$ for both models for small r but at large r the difference was less conspicuous. That separation is much more clearly demonstrated if $\delta N_{++}(R)$ and $\delta N_{--}(R)$ are compared. The long ranged nature of the difference between the distribution of positive ions about positive ions and of negative ions about negative ions is

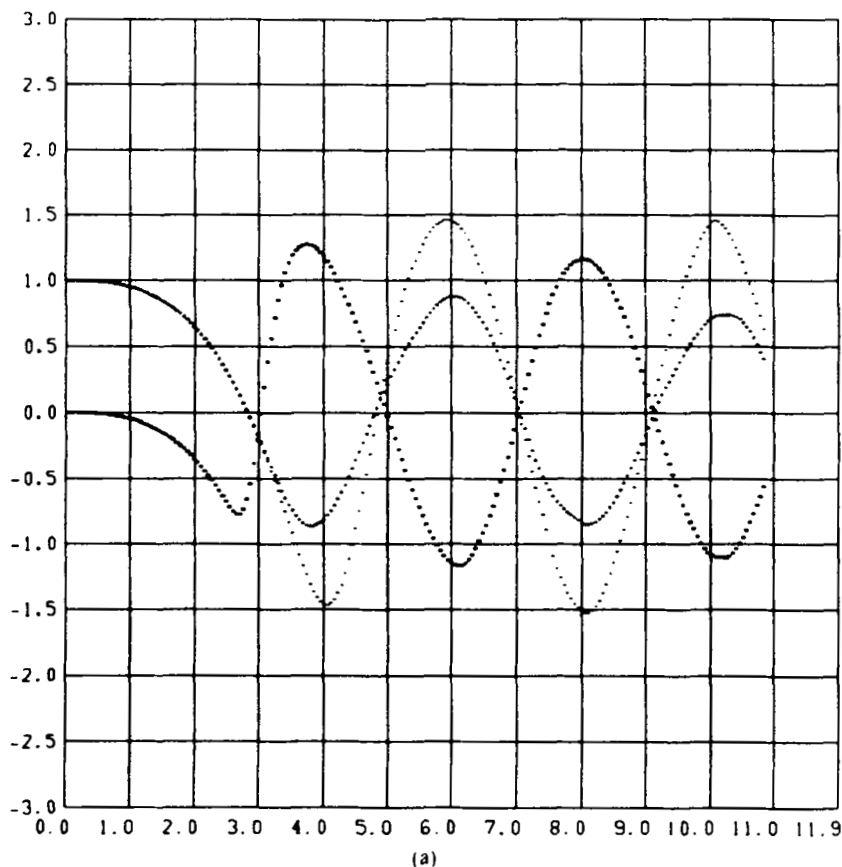


FIGURE 2 $\delta N_{\alpha\beta}(R)$ for molten sodium iodide $n_+ = n_- = 0.34$. Abscissa in Ångstroms; collision diameter = $3.194 \text{ \AA} \equiv \sigma_{+-}$. (a) Polarisable ion model.

*** indicates δN_{+-} , +++ indicates δN_{++} , --- indicates δN_{--} .

shown better in this representation. The conclusion of Dixon and Sangster that the introduction of polarisation into the model increased the difference between $g_{++}(r)$ and $g_{--}(r)$ is more clearly visible from $\delta N_{++}(R)$ and $\delta N_{--}(R)$. The amplitudes of oscillation of the $\delta N_{\alpha\beta}(R)$ do not appear to be decaying at all within the distance accessible to a molecular dynamics

simulation indicating that the disturbance introduced by a charged reference particle in an ionic melt is very long ranged indeed. In a low density simulation of molten potassium iodide the envelope of oscillations did show a tendency to decay. Using a straightforward argument based upon the overall electrical neutrality of the molten alkali halide, Abramo *et al.*⁸ have shown

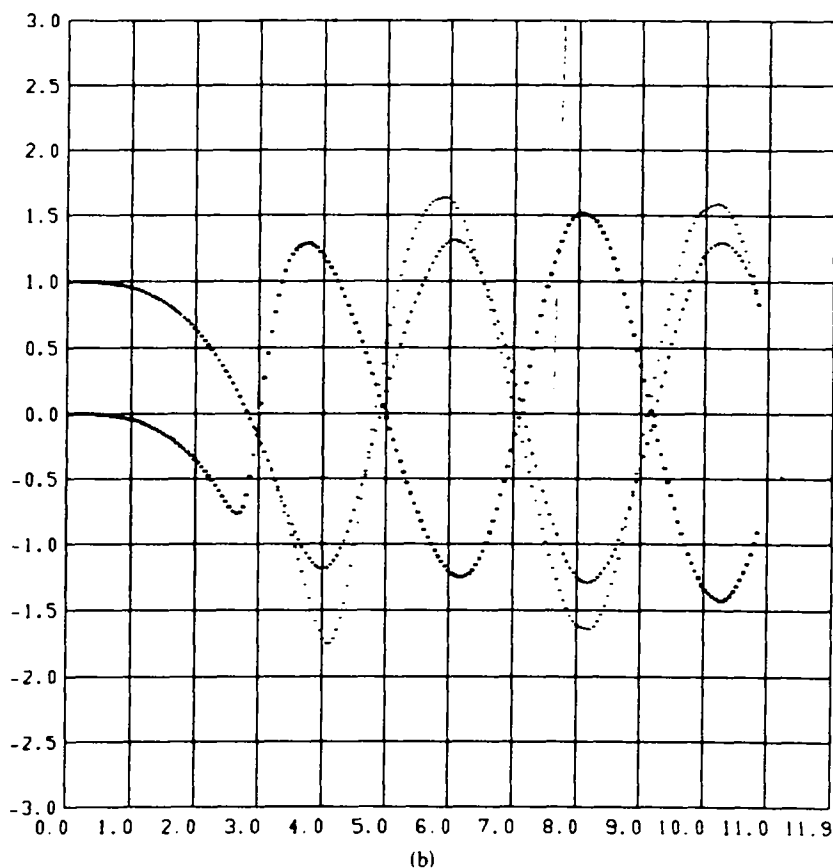


FIGURE 2 $\delta N_{\alpha\beta}(R)$ for molten sodium iodide $n_+ = n_- = 0.34$. Abscissa in Ångstroms; collision diameter = $3.194 \text{ \AA} \equiv \sigma_{+-}$. (b) Rigid ion model.

*** indicates δN_{+-} , +++ indicates δN_{++} , --- indicates δN_{--} .

that $S_{++}(0) = S_{+-}(0) = S_{--}(0)$ and that each of these is related to the isothermal compressibility. Consequently the oscillations must decay. The simulation results suggest that the disturbance retains its charge ordering over a very long range. It appears that the maxima in the $\delta N_{\alpha\beta}(R)$ occur at a slightly lower value of R than the associated minima. It is useful to consider

four linear combinations of the $\delta N_{\alpha\beta}(R)$

$$\delta N_+(R) = \delta N_{++}(R) + \delta N_{+-}(R) \quad (4)$$

$$\delta N_-(R) = \delta N_{+-}(R) + \delta N_{--}(R) \quad (5)$$

$$\delta Q_+(R) = \delta N_{++}(R) - \delta N_{+-}(R) \quad (6)$$

$$\delta Q_-(R) = \delta N_{+-}(R) - \delta N_{--}(R) \quad (7)$$

$\delta N_{\alpha}(R)$ gives the excess number of particles surrounding a reference ion of type α . The charge ordering ensures that as $\delta N_{\alpha\alpha}(R)$ increases that $\delta N_{\alpha\beta}(R)$ decreases and vice versa. Consequently the fluctuations of the $\delta N_{\alpha}(R)$ have a small amplitude and are considerably less than for the monatomic systems.

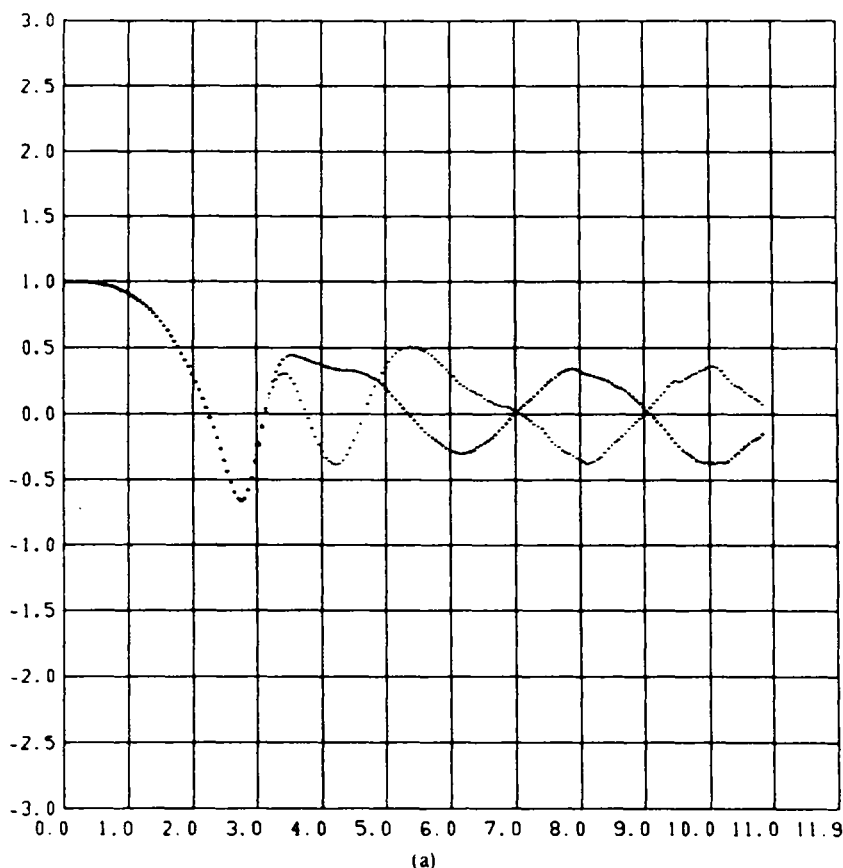


FIGURE 3 Molten sodium iodide (a) δN_{α} for polarisable ion model.

Abscissa in Ångstroms

+++ indicates sodium ion is reference ion

--- indicates iodide ion is reference ion

Figure 3(a and b) show δN_+ and δN_- for the polarisable model and the rigid ion model respectively. For the polarisable model δN_+ and δN_- are identical up to 3.2 Å. The curves then change phase between 3.6 Å and 7.0 Å with the change from regular oscillations occurring first for δN_+ . The curves appear to be attempting to establish oscillations which are out of phase although it would require a simulation with a larger number of particles to confirm this. The curves for the rigid ion model are very different both in terms of the position and the height of the peaks. There appears to be an attempt to form the out of phase oscillation of δN_+ and δN_- but it is nowhere near as well established as for the polarisable case. We show a Figure 3(c and d) the excess charge δQ_α surrounding a reference ion of type α . For

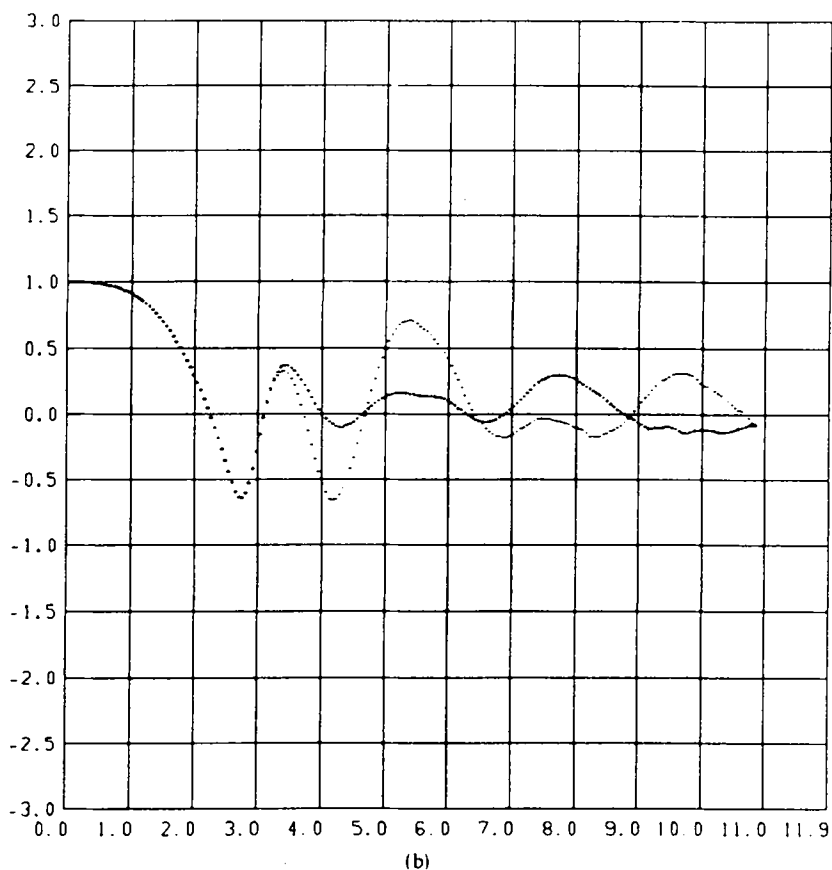


FIGURE 3 Molten sodium iodide (b) δN , for rigid ion model
 Abscissa in Ångstroms
 + + + indicates sodium ion is reference ion
 - - - indicates iodide ion is reference ion

the polarisable model we have taken the ion to be represented by unit charges centred on the core for the construction of δQ . For both models δQ_+ and δQ_- oscillate out of phase: the phase being determined by the sign of the reference ion. The δQ_- have larger amplitudes of oscillation than the δQ_+ . Electrical neutrality requires that $\text{Lt}_{R \rightarrow \infty} Q_\alpha(R) = 0$. The amplitudes of oscillation for the rigid ion model are greater than for the polarisable model for both functions.

Thus by using the functions δN_α , $\delta N_{\alpha\beta}$, and δQ_α we have been able to observe differences in the structure of the ionic melts which were not apparent from consideration of the partial pair radial distribution functions.

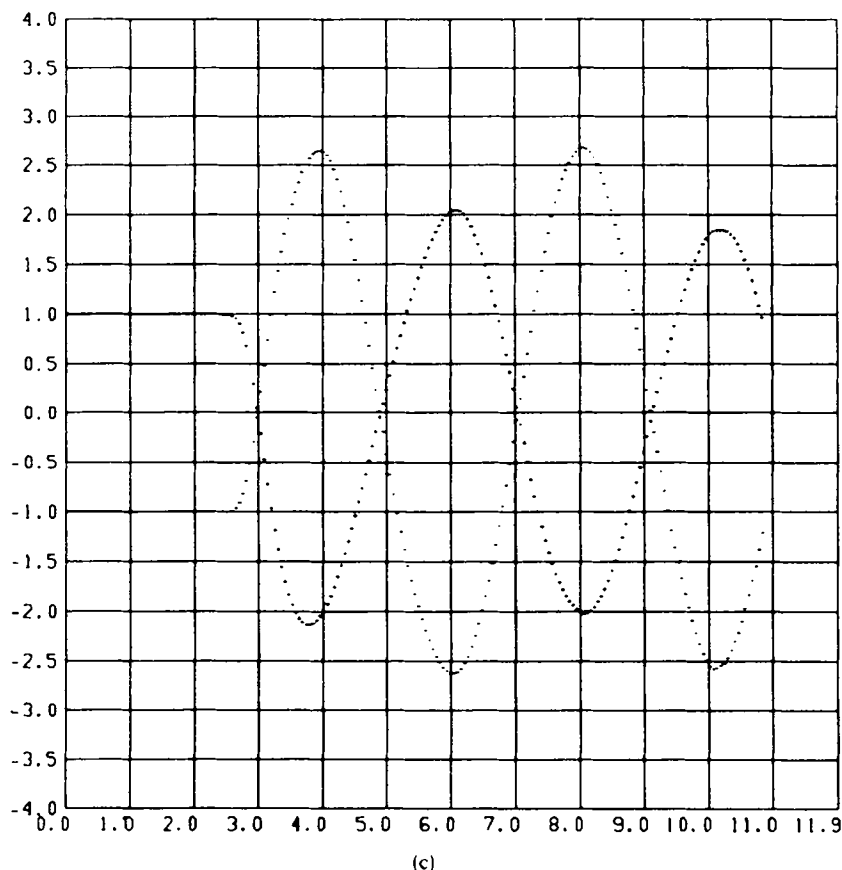


FIGURE 3 Molten sodium iodide (c) δQ_2 for polarisable ion model
Abscissa in Ångstroms

+++ indicates sodium ion is reference ion
--- indicates iodide ion is reference ion

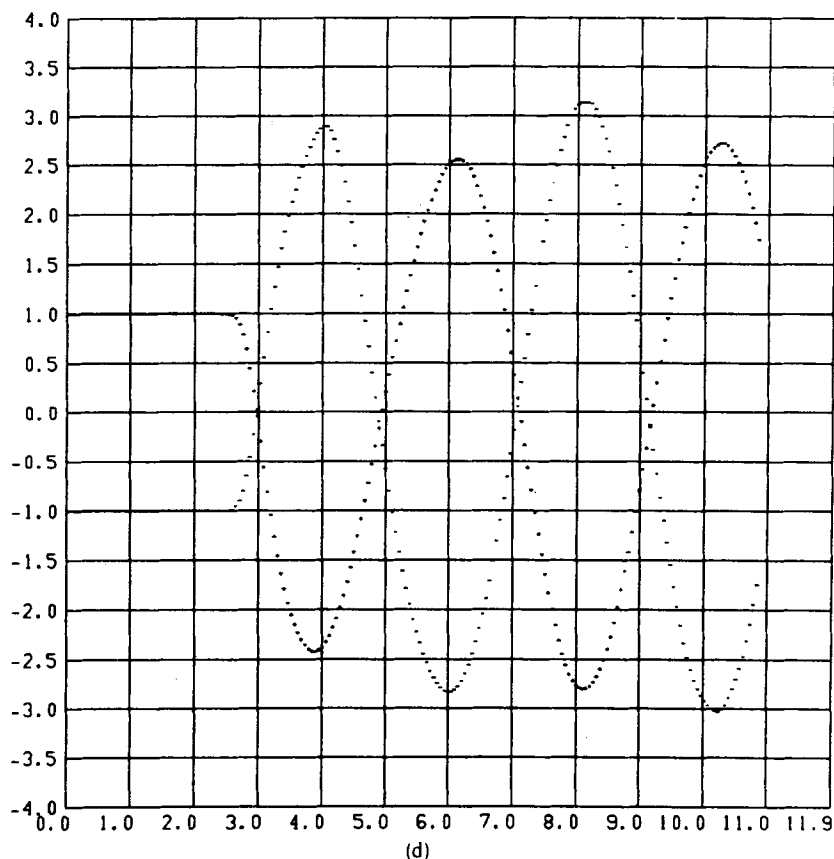


FIGURE 3 Molten sodium iodide (d) δQ_x for rigid ion model
 Abscissa in Ångstroms
 + + + indicates sodium ion is reference ion
 - - - indicates iodide ion is reference ion

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