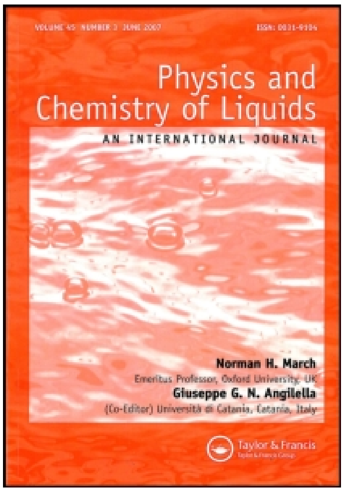

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STATIC DIELECTRIC FUNCTION OF A MODEL CLASSICAL IONIC FLUID

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The behaviour of the static dielectric function $\varepsilon(k)$ of a system of charged hard spheres has been studied, within the Mean spherical Approximation, for a wide range of values of the ionic size ratio α, packing fraction η, and plasma parameter Γ. The results presented are limited to the charge symmetric case.

We find that $\varepsilon(k)$ already takes on negative values for $\Gamma = 1$ when the size of anions and cations are the same and $\eta = 0.30$. Packing and size difference become less significant as the value of the plasma parameter increases. As Γ increases in value $\varepsilon(k)$ becomes negative over an increasing range of values of the wavenumber k. For given vaules of Γ and η, $\varepsilon(k)$ is nearest to zero for a non-zero value of k when $\alpha = 1.0$.

KEY WORDS: Static dielectric function, charged hard spheres.

1. INTRODUCTION

The inverse of the longitudinal dielectric function, $\varepsilon^{-1}(\mathbf{k}, \omega)$, of a system containing charged particles may be viewed as the response function of the system to either an external charge density creating a total charge density, which is the sum of the external and induced charge densities, or a displacement field creating an electric field[1,2].

Using casuality arguments, or stability conditions, it has been shown that in a stable system $\mathrm{Im}\,\varepsilon^{-1}(\mathbf{k}, \omega) \leqslant 0$[1]. Setting $\omega = 0$ result in the following inequalities for the static dielectric function $\varepsilon(\mathbf{k}, \omega) \equiv \varepsilon(k)$

$$\varepsilon(k) \geqslant 1 \quad \text{and} \quad \varepsilon(k) < 0. \tag{1}$$

A violation of Eqn. (1) leads to the appearance of a pole in the response function implying an instability in the system which may be related to symmetry breaking transitions.

The second of the conditions in Eqn. (1) was originally obtained by Martin[3] for jellium. Since this seminal work it has been shown that the dielectric function of both classicals and quantum systems become negative for non-zero values of k.

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This work is concerned with classical ionic fluids. For such systems Fassolino *et al.*[4] have shown that $\varepsilon(k)$ becomes negative in a classical one component plasma (OCP) for sufficiently large values of the plasma parameter Γ. Moreover, the dielectric function of molten salts, ranging from "simple"–NaCl like – salts[4] to those which melt from a superionic phase[5,6,7] shows a behaviour which mimics that of the OCP, more closely in the latter than in the simple salts.

The structure of simple salts has been shown to be qualitatively accounted for by a model ionic fluid consisting of charged hard spheres within the Mean Spherical Approximation[8]. It has also been suggested that the structure of superionic melts can be described by using a similar model with large size difference between ions and partial charges[9]. In this work we explore these suggestions further to examine the effects of ionic size difference, packing and plasma parameter on the behaviour of the static dielectric function. The layout of the paper is as follows. In the following section we describe, very briefly, the formalism used in our calculation. In section 3 we present the results of our calculations. The final section contains a few concluding remarks.

2. FORMALISM

We consider a system of oppositely charged spheres interacting via the potential

$$\frac{\phi_{ij}(r)}{k_B T} = \begin{cases} \infty & r < d_{ij} \\ \dfrac{Z_i Z_j \Gamma a}{Z^2 r} & r > d_{ij} \end{cases}. \tag{2}$$

We assume the hard sphere diameters to be additive, namely $d \equiv d_{+-} = \frac{1}{2}(d_{++} + d_{--})$. In Eqn. (2) $|Z_i|$ denotes the magnitude of the charge of ion i, $Z^2 = \Sigma_i x_i Z_i^2$, where x_i is the number concentration of ion i such that $\Sigma_i x_i = 1$, and e is the elementary charge. The plasma parameter is defined as

$$\Gamma = \frac{Z^2 e^2}{k_B T a} \tag{3}$$

where k_B denotes Boltzmann's constant, T the temperature, and the ion sphere radius a is given by

$$\frac{a}{d} = \left(\frac{3}{4\pi n}\right)^{1/3} d^{-1} = \left[\frac{1+\alpha^3}{2\eta(1+\alpha)^3}\right]^{1/3}. \tag{4}$$

In Eqn. (4) n is the number density, α denotes the hard diameters ratio

$$\alpha = \frac{d_{11}}{d_{22}}; \quad d_{11} \leqslant d_{22} \quad (1,2 = +,-), \tag{5}$$

and the packing fraction η is given by

$$\eta = \frac{2}{3}\pi n \left[\frac{1+\alpha^3}{1+\alpha^3}\right] d^3. \tag{6}$$

The calculations are carried out within the Mean Spherical Approximation (MSA) for which analytic solutions are available[10,11]. We have used Γ, η and α as input parameters, and we have assumed d, the distance of closest approach between unlike ions, to be the unit of distance.

Within this model we have calculated the charge-charge partial structure factor $S_{QQ}(k)$[12]. An approximate relation, valid for rigid ions obeying classical statistical mechanics, between $\varepsilon(k)$ and $S_{QQ}(k)$ is given by[12]

$$\varepsilon^{-1}(k) = 1 - \frac{4\pi n e^2}{k_B T k^2} S_{QQ}(k). \tag{7}$$

We have used Eqn. (7) in our calculations; the results are presented in the next section.

3. RESULTS

The range of input parameters explored in our calculations are as follows:

$$0 \leqslant \Gamma \leqslant 160; \quad 0.30 \leqslant \eta \leqslant 0.40; \quad 0.1 \leqslant \alpha \leqslant 1.0.$$

The figures below are, in our view, a representative sample of our calculations. Other results, either in graphical and/or tabular form, are available on request.

We have compared our results with those deduced from the OCP structure factors, $S(k, \Gamma)$, obtained by Rogers *et al.*[13] by using the Modified Hypernetted Chain (MHNC) theory with hard spheres bridge functions. These calculations span the range of plasma parameter $0.1 \leqslant \Gamma \leqslant 180$ and reduced wave number $0.1 \leqslant ka \leqslant 25$. These calculations are in very good agreement with OCP results obtained from computer simulations.

The results presented below are restricted to the charge symmetric case, namely $|Z_+| = |Z_-| = |Z|$. In all the figures $\varepsilon(k)$ is plotted as a function of ka. The OCP results are shown in Figure 1.

Figures 2,3 and 4 illustrate the size effect on $\varepsilon(k)$ at $\eta = 0.30$ and $\Gamma = 1$,40 and 160. It is interesting to note that, as shown in Figure 2, $\varepsilon(k)$ takes on negative values for Γ as low as one when the charges have the same size and, hence, the hard core repulsion is very important. For other values of α, and $\Gamma = 1$, $\varepsilon(k) > 1$ as the Coulomb and hard core repulsion complete in the interaction between like ions. As Γ increases in value $\varepsilon(k)$ becomes negative over an increasing range of values of k. $\varepsilon(k)$ is nearest to zero at the value of k where $S_{QQ}(k)$ has its principal maximum. This position shifts towards smaller values of k both relative to the OCP and as the size

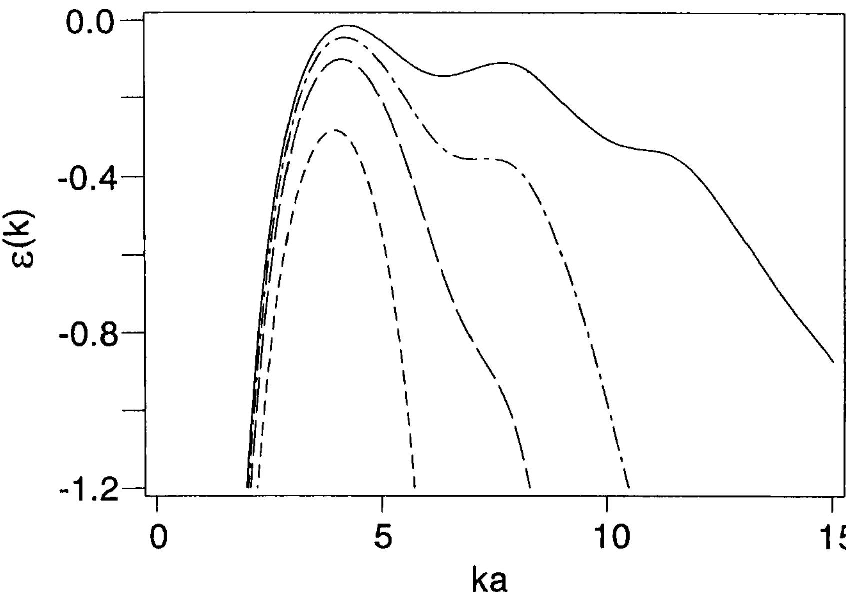

Figure 1 Static dielectric function $\varepsilon(k)$ of the classical one component plasma (OCP) at four values of the plasma parameter, Γ. $\varepsilon(k)$ was deduced from the MHNC calculations by Rogers *et al.*[13]. (i) $\Gamma = 20$, short-dashed line; (ii) $\Gamma = 40$, long-dashed line; (iii) $\Gamma = 70$, short-long-dashed line; (iv) and $\Gamma = 160$, solid line.

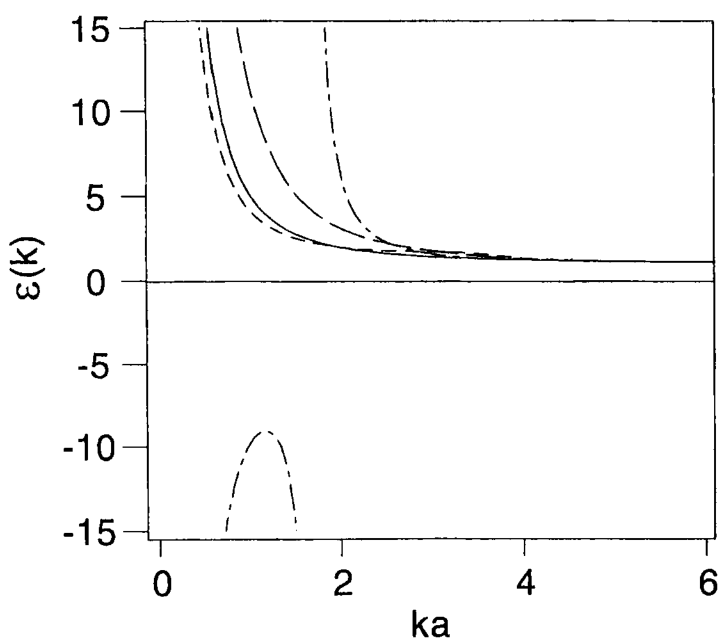

Figure 2 Size effects on the static dielectric function $\varepsilon(k)$ of a system of charged spheres with packing fraction $\eta = 0.30$ and plasma parameter $\Gamma = 1$. The different values of the ions diameter ratio α are: (i) $\alpha = 0.25$, short-dashed line; (ii) $\alpha = 0.50$, long-dashed line; and (iii) $\alpha = 1.0$, long-short-dashed line. The solid line corresponds to the OCP result for $\Gamma = 1$, which is included for comparison.

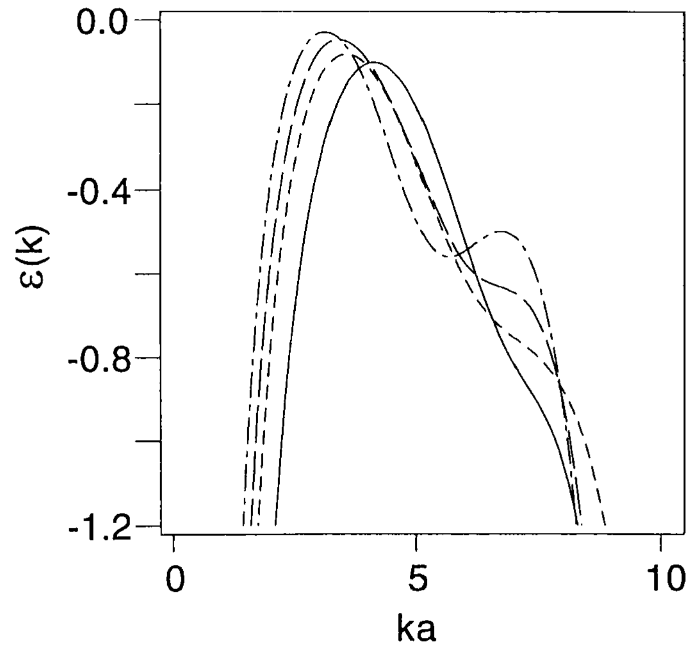

Figure 3 Same caption as in Figure 2, except that value for the plasma parameter is Γ = 40 and the solid line correspond to the OCP result for this value of Γ.

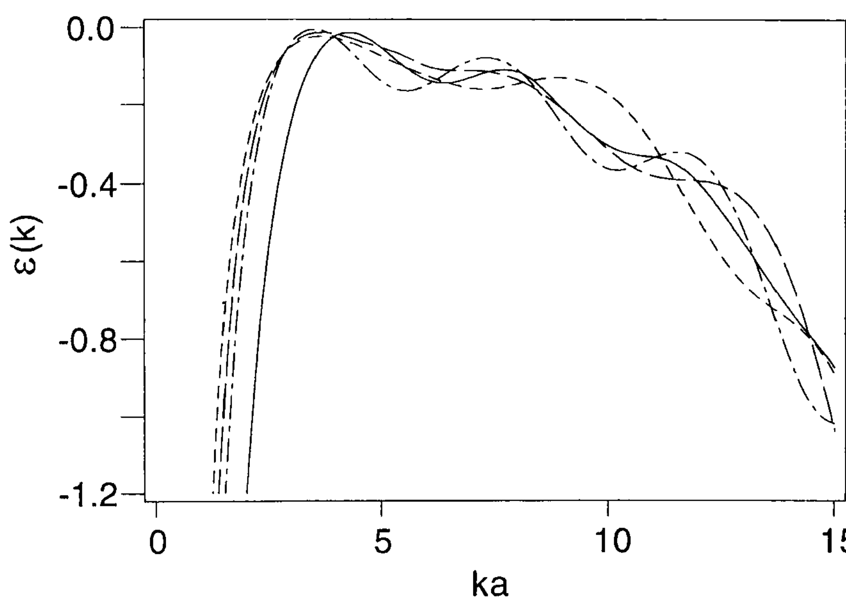

Figure 4 Same caption as in Figure 2, expect that the value of the plasma parameter is Γ = 160 and the solid line correspond to the OCP result for this value of Γ.

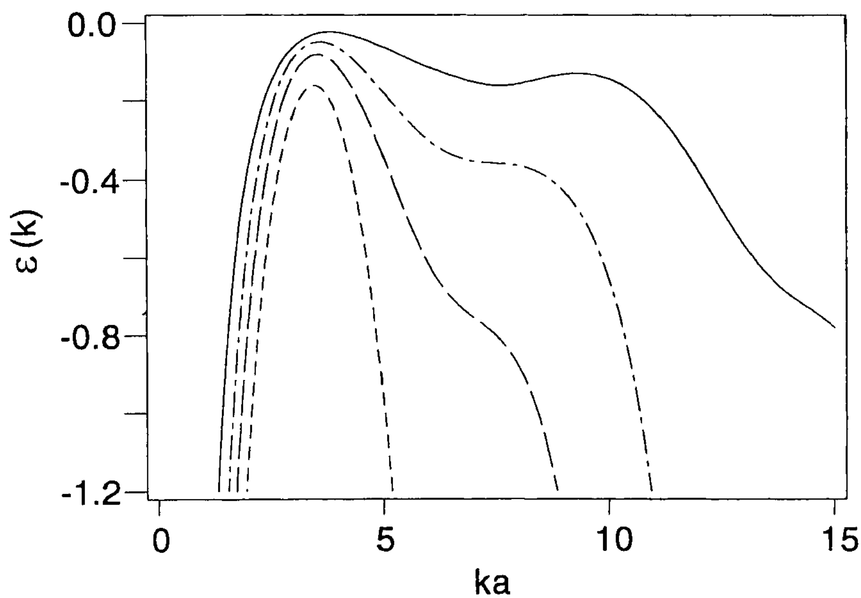

Figure 5 Effect of the plasma parameter Γ on the static dielectric function $\varepsilon(k)$ of a system of charged spheres with packing fraction $\eta = 0.30$ and diameters ratio $\alpha = 0.25$. (i) $\Gamma = 20$, short-dashed line; (ii) $\Gamma = 40$, long-dashed line; (iii) $\Gamma = 70$, short-long-dashed line; and (iv) $\Gamma = 160$, solid line.

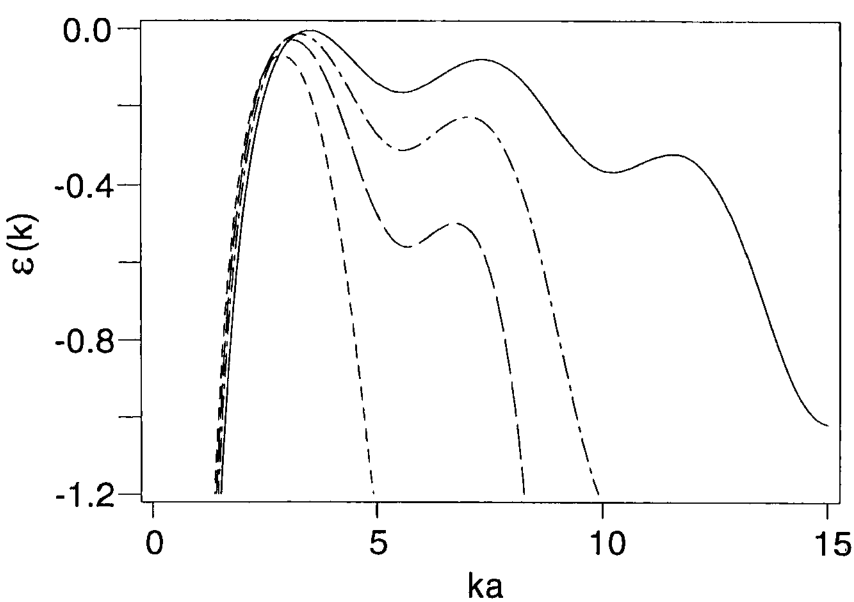

Figure 6 Same caption as in Figure 5 but for $\alpha = 1.0$

difference between the ions decreases. Figures 5 and 6 illustrate the effect of the plasma parameter on $\varepsilon(k)$ for given values of α and η. For $\alpha = 0.25$ and $\eta = 0.30$ the position of the value of $\varepsilon(k)$ nearest to zero hardly changes as Γ changes from 20 to 160 but it approaches zero with increasing Γ. However, when $\alpha = 1$ that position

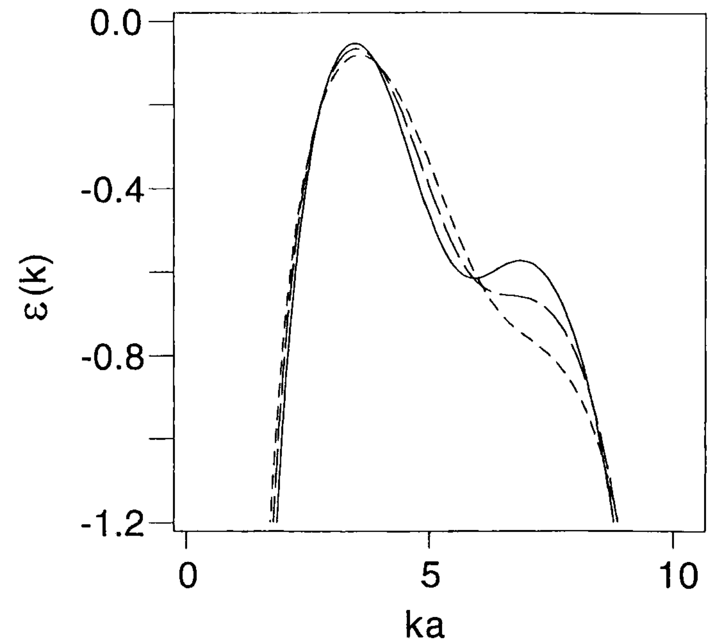

Figure 7 Packing effect on the static dielectric function $\varepsilon(k)$ of a system of charged spheres with plasma parameter $\Gamma = 40$ and diameters ratio $\alpha = 0.25$. (i) $\eta = 0.30$, short-dashed line; (ii) $\eta = 0.35$, long-dashed line; and (iii) $\eta = 0.40$, solid line.

shifts towards larger values of k with increasing values of Γ. We note that, at $\Gamma = 160$ the value of $\varepsilon(k)$ is very small and approaching zero. Finally, the packing effect at $\Gamma = 40$ and $\alpha = 0.25$ is shown in Figure 7. We note that the smaller packing fraction, at this parametrization, mimics better the OCP results. Our calculations also show that packing effects become less important for larger values of Γ.

4. CONCLUSIONS

$\varepsilon(k)$ takes on negative values for a very low value of the plasma parameter if the size of cations and anions are the same. Size difference and packing become less significant in deciding the behaviour of $\varepsilon(k)$ as the value of Γ increases. The behaviour of $\varepsilon(k)$ for the symmetric charge case is mainly determined by the competition between the ion sphere radius a, which characterizes the Coulomb repulsion between like ions, and the hard core repulsion dictated by the size of the ions. There is a richer behaviour of $\varepsilon(k)$ when charge asymmetry is taken into account. Nonetheless, bearing in mind that the number of cations and anions is no longer the same, similar conclusions as those discussed above appear to apply for this case.

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