Charged-hard-sphere system: A self-consistent-field approximation

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A charged-hard-sphere liquid system was studied using a self-consistent-field approximation which includes short-range correlations through a local-field correction. Static and dynamical properties such as structure factor, pair-correlation function, and dispersion relation are presented as functions of the plasma parameter and the packing fraction. The results are compared to those obtained by other methods.

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I. INTRODUCTION

The research of ionic systems is not recent, and its practical interest in electrochemistry, nuclear materials, molten salts, and fast ionic conductors are enormous. The first model to describe an electrolytic solution in equilibrium is due to Debye and Hückel.

The primitive model of electrolytes consists of charged hard spheres with additive diameters, in a uniform neutralizing background. The study of the thermodynamical and structural properties of this system has been done through the years with different approaches. The exact solution in the mean spherical approximation (MSA) was first reported by Palmer and Weeks [1]. Lado performed a mixed-integral-equation approach as a redefined-hypernetted-chain approximation (RHNC) [2] and a Monte Carlo calculation was done by Hansen and Weis [3]. A thermodynamic approach was reported by Abernethy and Silbert [4] using the MSA model more recently by Badirkhan, Pastore, and Tosi [5] through a modified-hypernetted-chain approximation (MHNC) and interpolation between MSA and HNC. Although many results have appeared in the literature, practically nothing was presented about the dynamics of this system.

In this work we investigate the structural correlations and some dynamical properties of a charged-hard-sphere system using a different approach, the self-consistent-field approximation due to Singwi, Tosi, Land, and Sjölander (STLS) [1–6], which has been successfully applied to different systems [7]. In the STLS model the inclusion of short-range correlation correcting the local field in the radial-pair-correlation-function calculations improves considerably the results obtained from MSA principally in the region of a weak- and intermediate-coupling constant. This paper is organized in four sections. The STLS is discussed in Sec. II, and the results are presented in Sec. III. Concluding remarks are given in Sec. IV.

II. SELF-CONSISTENT-FIELD APPROXIMATION

Consider a system of N charged hard spheres in a neutralizing rigid background. The pair-interaction potential is described by

$$\Phi(r)=\begin{cases}\infty, & r\le d\\ \dfrac{e^2}{r}, & r>d\ ,\end{cases} \tag{1}$$

where d is the diameter of the spheres and e is the electronic charge.

Two parameters, which are external parameters, characterize the model. One specifies the density and is characterized by the packing fraction $\eta=\pi\rho d^3/6$, where ρ is the average number density; and the other, the plasma parameter $\Gamma=\beta e^2/a$, where a is the average ionic radius given by $4\pi a^3\rho/3=1$ and $\beta=1/k_BT$, incorporates both temperature and density specification. Two extreme cases, $\eta=0$, corresponding to the classical one-component plasma, and $\Gamma=0$, the neutral-hard-sphere fluid, are very well known for several values of η and Γ [8–11].

The self-consistent-field approximation relates the effective pair potential $\Psi(\mathbf{q})$ with direct-correlation function $\tilde{c}(q)$ through

$$\tilde{c}(\mathbf{q})=-\beta\Psi(\mathbf{q})\ , \tag{2}$$

where $\Psi(\mathbf{q})$ is the Fourier transform of $\Psi(\mathbf{r})$ which is given by

$$\nabla_r\Psi(\mathbf{r})=g(\mathbf{r})\nabla_r\Phi(\mathbf{r})\ , \tag{3}$$

and $g(\mathbf{r})$ is the pair-correlation function.

The direct-correlation function, together with the pair potential, Eq. (1), can be written as

$$\tilde{c}(q)=-4\pi\frac{\beta e^2}{q}\cos(qd)-4\pi\frac{\beta e^2}{q}\int_d^\infty r\sin(qr)dr\int_r^\infty\frac{h(x)}{x^2}dx\ , \tag{4}$$

where $h(\mathbf{r})$ is the total-correlation function defined as $h(\mathbf{r})=g(\mathbf{r})-1$.

By taking the function

$$y(\mathbf{r})=g(\mathbf{r})-1-c(\mathbf{r}) \tag{5}$$

and making use of the Orstein-Zernike equation, we can write

$$\tilde{y}(\mathbf{q})=\frac{\rho\tilde{c}(\mathbf{q})^2}{1-\rho\tilde{c}(\mathbf{q})}\ , \tag{6}$$

where $\tilde{y}(\mathbf{q})$ is the Fourier transform of $y(\mathbf{r})$.

Equations (4)–(6) constitute a set of equations to be solved self-consistently. It is important to note that the definition of $y(\mathbf{r})$ assumes faster convergence in the numerical procedure.

The Fourier transforms are calculated numerically, and the numerical infinity is, of course, a finite number. It is then very important that the functions we are transforming vanish in the numerical infinity. But, for the direct-correlation function it is known that $c(\mathbf{r})\rightarrow-\beta\Phi(\mathbf{r})$ as $r\rightarrow\infty$. Following the procedure proposed by Springer, Pokrant, and Stevens [12], we can subtract the long-range Coulomb tail by defining the short-range functions

$$c_S(\mathbf{r})=c(\mathbf{r})+u(\mathbf{r})\ , \tag{7}$$

$$y_S(\mathbf{r})=y(\mathbf{r})-u(\mathbf{r})\ , \tag{8}$$

where

$$u(r)=\frac{\beta e^2}{r}\left\{1-e^{-\alpha r}\left[1-\frac{-\alpha r}{2}\right]\right\}, \tag{9}$$

which have the same asymptotic behavior as $c(\mathbf{r})$ and $y(\mathbf{r})$, but are finite at the origin. The Fourier transform of $u(\mathbf{r})$ is given by

$$\tilde{u}(q)=\frac{4\pi\alpha^4}{\alpha^2(\alpha^2+q^2)^2}\ , \tag{10}$$

where α is an arbitrary number chosen such that the functions become extremely small at the numerical infinity. The set of equations to be solved self-consistently can now be written in terms of the functions of short range, i.e.,

$$h(\mathbf{r})=g(\mathbf{r})-1=c_S(\mathbf{r})+y_S(\mathbf{r})\ , \tag{11}$$

$$\tilde{y}_S(\mathbf{q})=\frac{\rho[\tilde{c}_S(\mathbf{q})-\tilde{u}(\mathbf{q})]^2}{1-\rho\tilde{c}_S(\mathbf{q})+\rho\tilde{u}(\mathbf{q})}-\tilde{u}(\mathbf{q})\ , \tag{12}$$

$$\tilde{c}_S(\mathbf{q})=\frac{4\pi}{q}\int_0^d r\sin(qr)c_S(r)dr+\frac{4\pi\beta e^2}{q}\int_d^\infty h(r)\left\{\frac{d^2}{r^2}j_1(qd)-j_1(qr)\right\}dr-\frac{4\pi\beta e^2}{q}F(q)\ , \tag{13}$$

where $j_1(x)$ is the spherical Bessel function and

$$F(q)=\frac{e^{-\alpha d}}{(\alpha^2+q^2)}\left\{[\alpha\sin(qd)+q\cos(qd)]\times\left[\alpha^2+(\alpha^2+q^2)\left[\frac{\alpha d}{2}+1\right]\right]-\frac{\alpha}{2}(\alpha^2+q^2)\sin(qd)\right\}. \tag{14}$$

Note that for $d=0$ and $\alpha=0$ we recover the results for a one-component plasma (OCP) system previously obtained in the same approximation (STLS) by Berggren [13]. The MSA is also obtained when we neglect the short-range correlations and set $\alpha=0$.

III. RESULTS

A. Structure and thermodynamics

The iterative solution of Eqs. (11)–(13) was performed starting from a given $\tilde{c}_S(\mathbf{q})$ [for instance, $\tilde{c}_S(q)=0$], obtaining $\tilde{y}_S(\mathbf{q})$ from Eq. (12), and after Fourier transformation obtaining $h(\mathbf{r})$. This allows us to calculate a new $\tilde{c}_S(\mathbf{q})$, completing the self-consistent approach. The numerical Fourier transformation was done using the method proposed by Lado [14], which ensures the orthogonal nature of the Fourier expansion. This iterative scheme continued until the self-consistent $\tilde{c}_S(\mathbf{q})$ is achieved. The convergence occurs whenever the largest difference between two consecutive results is smaller than some preassigned value. In our case this value was 5×10^{-4}.

In Fig. 1(a) we compare our results with those reported by Lado, using the RHNC approach, for $\Gamma=2.5$ and a very small packing fraction $\eta=1.57\times10^{-5}$. This is practically a pure OCP system. As we can see the overall agreement is very good.

Figures 1(b) and 1(c) display the pair-correlation function for two different pairs of η and Γ, which are $\Gamma=5$ and $\eta=1.0\times10^{-4}$, $\Gamma=10$ and $\eta=1.0\times10^{-3}$, respectively. We can observe that all results from RHNC are out of phase. This also occurs even compared with Monte Carlo data for larger values of η and Γ. Figure 2 shows two different results for two values of the plasma constant, $\Gamma=0.5$ and 5.0, for the same packing fraction $\eta=0.125$. In this figure we can observe competition behavior between the one, coming from the hard sphere, and the OCP system. This results are also in agreement with those obtained from RHNC and MSA. This competition will be discussed in detail below.

The static structure factor is shown in Fig. 3 for different values of η and Γ, along with the MSA results. This displays very nicely the competition between hard-core and plasma effects addressed previously. As is well known, for a pure hard-core system the isothermal compressibility is related to $S(0)$ [typically $S(0)\approx0.4$ for $\eta=0.1$], while for a pure Coulombic system $S(q)\approx q^2$ as $q\rightarrow0$ (Debye-Hückel). For small Γ ($\Gamma=0.5$) the shoulder for small-q values is clear. For the remaining curves this is not observed anymore because large values of Γ predominate over the hard core and q^2 behavior is ob-

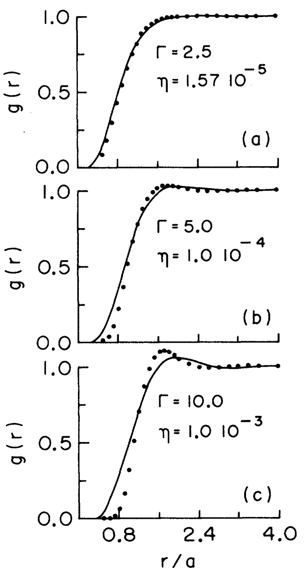

FIG. 1. Pair distribution function $g(r)$ vs r/a for a charged-hard-sphere system at (a) $\Gamma=2.5$ and $\eta=1.57\times10^{-5}$, (b) $\Gamma=5.0$ and $\eta=1.0\times10^{-4}$, and (c) $\Gamma=10.0$ and $\eta=1.0\times10^{-3}$. The circles report the RHNC results of Lado [2].

served for small q.

It is important to note that the Stillinger-Lovett [15] condition

$$\int S(x)dx=0\ , \tag{15}$$

which is the usual electroneutrality condition, is satisfied.

The internal energy and pressure were calculated using the pair-correlation functions from

$$\frac{E_c}{N}=2\pi\rho\beta e^2\int[g(r)-1]r\,dr \tag{16}$$

and

$$\frac{PV}{Nk_BT}-1=\frac{2\pi}{3}\rho d^3 g(d)+\frac{2\pi}{3}\rho\beta e^2\int[g(r)-1]r\,dr\ . \tag{17}$$

The results are shown in Table I together with some RHNC calculations reported in the literature. Recently Badirkhan, Pastore, and Tosi [5] performed some thermodynamic calculations of a one-component classical fluid of charged hard spheres. Although our packing-fraction parameter and plasma parameter are not all the same as the one used by Lado and also Badirkhan, Pastore, and Tosi, the results presented here are consistent as well as with the Monte Carlo results.

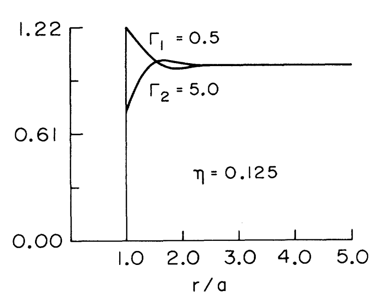

FIG. 2. Pair distribution function $g(r)$ vs r/a for a common parameter $\eta=0.125$ and two values of Γ, 0.5 and 5.0.

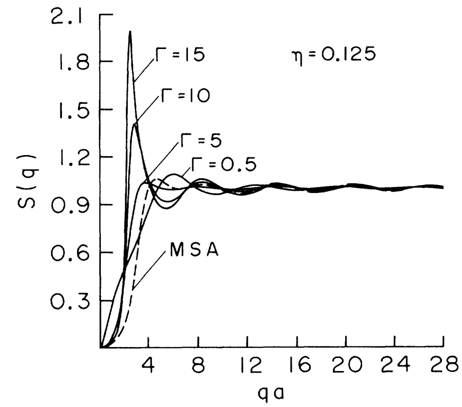

FIG. 3. Static structure factor $S(q)$ vs qa for a common parameter $\eta=0.125$ and several values of Γ. The result from mean spherical model is also displayed for comparison.

Moreover the STLS theory we are working on is not only internally self-consistent, but it is also a complete theory of fluids. In this sense both equilibrium and dynamical properties of this charged classical system are being discussed.

B. Dispersion relation

The dynamical behavior of neutral and charged systems can be drastically different. While the neutral fluid can support only number-density fluctuation, in a charged-fluid system it is possible to have either number-density or charge-density fluctuations. In our case, due to the rigid neutralizing background, these two fluctuations coincide.

In the STLS the density-density response function is given by

$$\chi(\mathbf{q},\omega)=\frac{\chi_0(\mathbf{q},\omega)}{1-\Psi(\mathbf{q})\chi_0(\mathbf{q},\omega)} \tag{18}$$

where χ_0 is the density-density response function of the noninteracting system and $\psi(\mathbf{q})$ is the Fourier transform of the effective pair potential which can be obtained through Eq. (3).

TABLE I. Computed thermodynamic parameters, excess internal energy and pressure, of charged-hard-sphere system in a neutralizing background, using the STLS approximation. The results from the RHNC are from Lado [2].

		$\frac{E}{Nk_BT}-\frac{3}{2}$		$\frac{PV}{Nk_BT}-1$	
Γ	η	STLS	RHNC	STLS	RHNC
2.5	1.57×10^{-5}	-1.666	-1.706	-0.554	-0.568
5.0	1.04×10^{-4}	-3.635	-3.732	-1.200	-1.244
10.0	1.0×10^{-3}	-7.823	-7.936	-2.504	-2.645
10.0	8.0×10^{-3}	-7.321		-2.008	
0.5	0.125	-0.341	-0.341	-0.616	
5.0	0.125	-4.995	-3.870	-0.153	

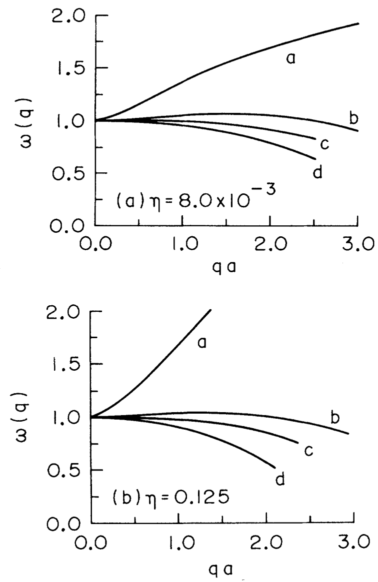

FIG. 4. Dispersion relation $\omega(q)/\omega_p$ vs qa for several values of the plasma parameter (a) $\Gamma=0.5$, (b) $\Gamma=3$, (c) $\Gamma=5$, and (d) $\Gamma=10$ for (a) $\eta=8.0\times10^{-3}$ and (b) $\eta=0.125$.

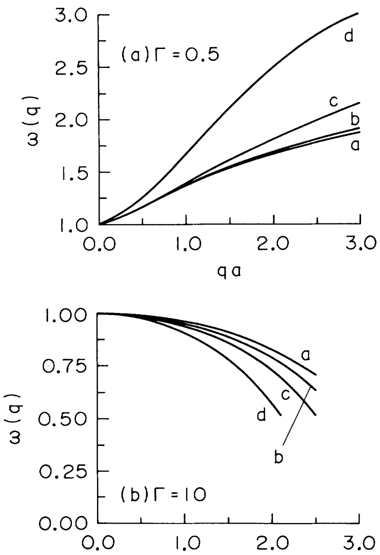

FIG. 5. Dispersion relation $\omega(q)/\omega_p$ vs qa for several values of the packing fraction (a) $\eta=1.57\times10^{-5}$, (b) $\eta=8.0\times10^{-3}$, (c) $\eta=0.027$, and (d) $\eta=0.125$ for (a) $\Gamma=0.5$ and (b) $\Gamma=10$.

From the poles of the density-density response function, and in the long-wavelength limit, the dispersion relation can be written as

$$\omega(q)^2=\omega_p(q)^2\frac{q^2}{3\Gamma}\beta\rho\Psi(q)\left[1+\frac{3}{\beta\rho\Psi(q)}\right], \qquad (19)$$

where $\beta\rho\psi(\mathbf{q})$ is the Fourier transform of the direct correlation function calculated self-consistently and ω_p is the plasma frequency given by

$$\omega_p(q)=\left[\frac{4\pi\rho e^2}{m}\right]^{1/2}. \qquad (20)$$

Equation (20) shows that the frequency of oscillation does not vanish anymore in the limit $q\rightarrow0$, as expected for neutral fluids, but goes to the plasma-frequency value.

From the weak-coupling and intermediate-to-strong-coupling regime, as in the OCP case [10,11], we can observe (Fig. 4) that the dispersion relation changes from positive to negative, i.e., the frequency of the plasmon mode decreases with increasing q. Figure 5 displays the dependence of the dispersion on the packing fraction. When the packing fraction increases, the envelope of the dispersion increases. Thus, for $q\rightarrow0$, the plasma oscillations dominate completely the density fluctuations, and then the change in the curvature of the dispersion relation is just a reflection of the OCP behavior [11].

IV. CONCLUSIONS

We have discussed, using the ansatz proposed by Singwi *et al.*, the structural correlations and some dynamical aspects of a charged hard sphere classical fluid for several values of packing and plasma parameters. The numerical method used to Fourier transform back and forth the self consistent scheme assures the orthogonality between r and q spaces. The dispersion relation was obtained, and it was shown that the density fluctuations are governed by plasma oscillations.

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