



Bicontinuous phases in coulombic systems. The role of specific interactions

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Abstract

The effects of specific interactions in a two dimensional coulombic system are investigated. In the framework of a field theoretical approach, we have shown that the electric properties of the system are strongly modified when two ionic species have a tendency to demix. By means of a Langevin dynamics, we investigate here a model system where, in the absence of electrostatic interaction, the specific interactions are such that the system demixes. This phase separation cannot take place in the presence of the coulombic potential, as a result of the electroneutrality condition in the system. The snapshots of the system obtained in the simulation, show large local concentration inhomogeneities, which are also charge inhomogeneities reminiscent of the tendency of the two species to separate. This is an unusual feature in a charged system, as it corresponds to the gathering of ions of the same sign. These inhomogeneities are constituted by a continuous network of lines of ions of the same species, the adjacent line being of the opposite sign. This structure is similar to a bicontinuous phase. One property of these lines: the average distance between the lines, has been studied by means of a simple field theoretical model. The Hamiltonian includes entropy, electrostatic and specific interactions. In the mean field approximation, we obtain a distance between the lines in agreement with what is found in the simulation. © 2000 Elsevier Science B.V. All rights reserved.

Introduction

In a recent paper [1], we have discussed the effect of specific interactions on the electric properties of ionic systems. Using the fact that concentration and charge fluctuations are related, we showed that any modification of the concentration fluctuations has strong repercussions on the electric properties of the system, for instance the screening length. This effect is all the more dramatic, when the virtual non charged system approaches a demixion transition, the concentration fluctuations are enhanced and screening in the system is also expected to increase.

In this paper, we focus on the competition between the long range coulombic interaction and short range specific interactions. The coulombic interaction tends to associate ions of opposite sign and separate ions of identical sign, leading to the usual screening and in the case of the two dimensional Kosterlitz-Thouless transition [2] to the pairing of ions. To oppose this effect we choose for the specific interactions those of a non charged binary mixture which demixes. The purpose of this work is to study the consequences of this competition. In particular considering the difference in range of the two interactions, can one expect a new length scale, dividing different kinds of behaviour ? Is it then possible to expect some peculiar spatial redistribution of the two species, or even appearance of new phases ?

In this paper, we investigate a two dimensional charged system. We describe it in Section 1 and present our choice for the specific interactions. Using simple arguments, we compare the behaviour of the systems with only specific interactions, with only coulombic interactions and with both interactions. Then we perform Langevin dynamic simulations for these systems in Section 2. A peculiar spatial organization of the particles is found. In Section 3, we present a simple model describing one characteristic feature of the obtained results.

1 The system

We consider a binary system in two dimensions. The two species can interact via two different potentials: the coulombic potential and a short range specific potential. The Coulomb potential energy between two charges e_i and e_j is:

$$\beta V_{ij}^C(r) = \frac{e_i e_j}{\varepsilon k_B T} \ln \frac{r}{r_0}, \quad (1)$$

where r_0 is an arbitrary length defining a reference potential, ε is the dielectric constant accounting for the media and $\beta = (k_B T)^{-1}$ is the inverse temperature. We take $r_0 = 1$ and the species are assumed to carry one unit of charge. The specific interaction potential is:

$$\beta V_{ij}(r) = A_{ij} e^{-r^2/a^2} \quad \text{where } i, j = +, - \quad (2)$$

a is the length scale for the specific interaction which is also taken equal to 1.

To understand the competition between these two interactions, we will first describe qualitatively systems interacting with just specific interactions, then with only electrostatic interaction and finally with both of them.

1.1 Non charged system

We want our system to demix in the absence of electrostatic interaction. In a binary mixture, we can distinguish two types of second order phase transitions, a pure demixion dominated by concentration fluctuations, and liquid-gas type phase transition dominated by density fluctuations [1]. The latter is characterized by a vanishing inverse compressibility. To rule out this possibility we take purely repulsive potentials. The demixion is achieved by choosing a strongly repulsive component A_{+-} , thus we have chosen the coefficients to be $A_{++} = A_{--} = 1.5$, and $A_{+-} = 7.5$.

The existence of a phase separation can be assessed on the simple level of the second virial coefficient approximation. We consider the system in two different states, the first represents the phase separation: the two species are separate and remain confined to their half-spaces. The second represents the mixed state for the system: the two species are evenly distributed over the entire available space. The corresponding free energies per particle in $k_B T$ units, $F_{sep}^{e=0}$ and $F_{mix}^{e=0}$ respectively, can be expressed in terms of integrals of the Mayer functions, I_s and I_a :

$$I_s = \int [e^{-\beta V_{ii}(r)} - 1] 2\pi r dr \quad \text{where } i = + \text{ or } - \quad (3)$$

$$I_a = \int [e^{-\beta V_{+-}(r)} - 1] 2\pi r dr. \quad (4)$$

We find that

$$F_{sep}^{e=0} - F_{mix}^{e=0} = \frac{1}{2} \ln 2 - \frac{\rho_+ + \rho_-}{4} [I_s - I_a], \quad (5)$$

where ρ_+ and ρ_- are the densities of the species when the whole surface is accessible. The numerical values of the densities are the ones that have been chosen for the simulations in Section 2: $\rho_+ = \rho_- = 0.32$. With the potential we have chosen, we obtain $\rho_+(I_s - I_a)/2 = 0.76$. The entropic contribution is $(\log 2)/2 = 0.35$, which yields $F_{sep}^{e=0} - F_{mix}^{e=0} = -0.41$. The state, corresponding to the demixion, is more stable. The entropic contribution, which is positive favours the mixing of the species, but this is overwhelmed by the specific interactions which finally produce the demixion of the system. The existence of this phase separation has been verified in the framework of the simulation presented in Section 2.

1.2 Charged system, without specific interactions

The properties of the two - dimensional Coulomb gas have been thoroughly studied in the literature [3]. We shall just point out an obvious although essential aspect of charged systems: attraction between opposite sign species and repulsion between ions of the same sign. This results in screening. In the case of two dimensional systems, for temperatures low enough we can also have ion pairing.

1.3 Charged system with specific interactions

If we start from the system with only short range interactions, and switch on the coulombic interactions, we can see from simple scaling arguments that there can no longer be

a phase separation. The electrostatic energy, of the system where we assume we separate the two species, scales as $L^2 \log L$ where L is the typical dimension of the system. This contribution proportional to the square of the electric field is positive. When we assume that the two species mix and we neglect fluctuations, the system is neutral and this contribution vanishes. When we try to separate the two charged species, this large positive contribution to the energy prevents the appearance of macroscopic phases in the thermodynamic limit.

If we start from the pure coulombic system and then introduce the specific interactions, the screening or the ion pairing will now be antagonized by the effect of the short range specific interactions. Although, as we have seen above, a macroscopic phase separation cannot take place, we can expect locally some redistribution of the species.

2 Simulation

2.1 Procedure

We have studied the system using Langevin dynamics [4]. The equations of motion are:

$$\ddot{r}_{ij}(t) = \sum_{i'j'} f_{ij,i'j'}(t) - \eta \dot{r}_{ij}(t) + \hat{f}_{ij}(t), \quad (6)$$

$i = +, -$ labels the type of particle, and j labels the particle within a species, the mass of the particles is taken equal to 1. $\hat{f}_{ij}(t)$ is a stochastic force representing the thermal equilibrium with the heat bath. The viscous force $\eta \dot{r}_i$ is a relaxation contribution. These stochastic forces distributed according to a Gaussian random distribution verify:

$$\langle \hat{f}_{ij}(t) \hat{f}_{i'j'}(t') \rangle = 2\eta T \delta_{ii'} \delta(r_{i'j'} - r_{ij}) \delta(t' - t), \quad (7)$$

where $\langle \dots \rangle$ represents the average over the system, where T is the temperature of the system and η is the friction coefficient which is taken equal to 1. The particles interact with forces derived from the potentials given in equations (1)-(2). The characteristic time scale of equation (6), is given by $\eta^{-1} = 1$. We introduce the Coulomb interaction parameter $\Gamma = \beta e^2 / \epsilon$ where e is the absolute value of the charge. Γ defines the electrostatic interaction with respect to the thermal energy. The temperature scale and Γ are set to 1. In these units, the coulombic interactions and the specific interactions are comparable and of the order of one. The system is simulated in a square box with periodic boundaries, for a total number of particles ranging from 256 particles up to 1024 particles. We have verified that the results presented here do not depend strongly on the geometry and the type of boundary conditions.

2.2 Simulation Results

2.2.1 Non coulombic system

In the absence of electrostatic interaction, the starting configuration is that of the two species separated in two parts of the box. We have observed that the species do not mix

and remain separate for times long enough in comparison with the relaxation time of the system.

2.2.2 Pure coulombic system

We have performed a simulation with just electrostatic interaction, the result is shown in figure 1. With $\Gamma = 1$, we are in the high temperature regime, above the Kosterlitz Thouless transition [2] and we observe both screened ions and pairs of ions of opposite charge.

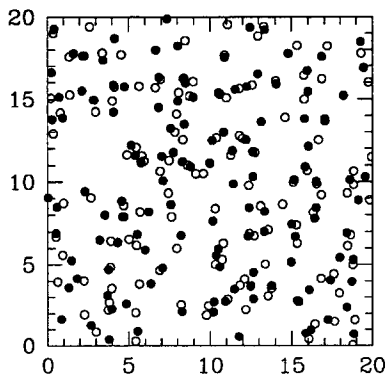


Figure 1: Snapshot of the simulation of the purely coulombic system.

2.2.3 Coulombic system with specific interactions

In the system with both specific and electrostatic interactions, a typical distribution of the ions is shown in figure 2. The spatial distribution of the two species is very different from the previous cases. The two particles no longer separate in distinct phases, and are distributed over the whole surface. Oppositely charged particles do not associate. However, we distinctly see inhomogeneities in the distribution of the ionic species: chains of ions of *identical sign*. This is quite in contrast with the familiar notion of ion pairing. However, a line of a given sign is surrounded by lines of the opposite sign. We can obtain an estimation of the distance between the lines, of the same sign, this is approximately 4.5 ± 0.4 .

Note that this length is not the Debye length $\lambda_D = [2\pi(\rho_+ + \rho_-)e^2/(k_B T \epsilon)]^{-1/2} \approx 0.5$, indicating that the properties are now quite different from those of the purely coulombic system.

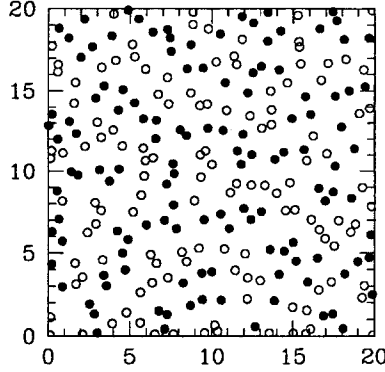


Figure 2: Snapshot of the simulation of the system interacting with both electrostatic and specific interactions

3 Theoretical model

We want to derive a simple theoretical model capable of describing behaviours of the system, in the presence and absence of the electrostatic interaction. We focus on the line structures visible in the snapshots.

3.1 Field theoretical description

3.1.1 The Hamiltonian

We use a field theoretical description [5, 6], the system is described by a Hamiltonian with the following contributions: entropy, electrostatic and specific interactions.

The entropic contribution is:

$$\beta H^{ent} = \int d\mathbf{r} \rho_+(\mathbf{r}) \left[\log \frac{\rho_+(\mathbf{r})}{\rho_0} - 1 \right] + \rho_-(\mathbf{r}) \left[\log \frac{\rho_-(\mathbf{r})}{\rho_0} - 1 \right], \quad (8)$$

where ρ_0 is a reference density for the evaluation of the entropy, $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ represent space dependent density fields for the two species.

The contribution from the electrostatic interaction is:

$$\beta H^{elec} = \frac{e^2}{\epsilon k_B T} \int d\mathbf{r}_i d\mathbf{r}_j q(\mathbf{r}_i) q(\mathbf{r}_j) \log \left(\frac{r_{ij}}{r_0} \right), \quad (9)$$

where $q(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$. Finally the contribution from the specific interactions has the same form as for the particle-particle interaction in the simulation, and is given by:

$$\beta H^{spec} = \int d\mathbf{r}_i d\mathbf{r}_j [\rho_+(\mathbf{r}_i) \rho_+(\mathbf{r}_j) A_{++} + \rho_-(\mathbf{r}_i) \rho_-(\mathbf{r}_j) A_{--} + 2\rho_+(\mathbf{r}_i) \rho_-(\mathbf{r}_j) A_{+-}] \exp \left\{ -\frac{r_{ij}^2}{a^2} \right\}. \quad (10)$$

Numerical values for the parameters are the same as in Section 1.

The partition function of the system is written:

$$Z = \int \prod_{\mathbf{r}_i, \mathbf{r}_j} \mathcal{D}\rho_+(\mathbf{r}_i) \mathcal{D}\rho_-(\mathbf{r}_j) \exp\{-\beta H[\rho_+, \rho_-]\}, \quad (11)$$

where the $\mathcal{D}\rho_+(\mathbf{r}_i)\mathcal{D}\rho_-(\mathbf{r}_j)$ denote functional integration and $H = H^{ent} + H^{elec} + H^{spec}$. The system is defined in a finite surface of dimensions L^2 and there is a given number of particles N_+ and N_- . We define the following reference densities: $\rho_+^0 = N_+/L^2$ and $\rho_-^0 = N_-/L^2$, which take the same values as in the simulation, that is $\rho_+^0 = \rho_-^0 \equiv \rho^0 = 0.32$.

3.1.2 Reduced functional integral: Gaussian line density functions

To calculate Z , we further simplify the problem considering a limited set of functions in the functional integration. Bearing in mind the line structure visible in the snapshot, in figure 2, we assume density distributions which vary along one direction only, for instance the X-axis, that is lines parallel to the Y-axis. Furthermore we assume that the x dependent density profiles can be written as a sum of Gaussian profiles, characterized by only two parameters: l_x which is the distance between two subsequent Gaussian distributions of a given sign and σ_g which represents the relative width of one Gaussian density distribution. The oppositely charged particles are also distributed on a sum of Gaussian distributions with a displacement of $l_x/2$ from the previous set. We shall consider that each Gaussian contribution to the whole density distribution can be considered as a line of a given species. The number of lines is $N_l = L/l_x$, the density profiles are then written:

$$\begin{aligned} \rho_+(\mathbf{r}) &= \frac{\rho_+^0}{\sigma_g \sqrt{2\pi}} \sum_{1 \leq i \leq N_l} \exp\left\{-\frac{(i - \tilde{x})^2}{2\sigma_g^2}\right\}, \\ \rho_-(\mathbf{r}) &= \frac{\rho_-^0}{\sigma_g \sqrt{2\pi}} \sum_{1 \leq i \leq N_l} \exp\left\{-\frac{((i + 1/2) - \tilde{x})^2}{2\sigma_g^2}\right\}, \end{aligned} \quad (12)$$

where \tilde{x} is the coordinate on the X-axis in l_x units.

Although simple, this representation of the densities is sufficient to distinguish between two different situations. In figure 3 we give a section of the profiles for $l_x = 4.0$ and two different values of σ_g : 0.05 and 0.50. A large value of σ_g corresponds to a density profile for the species which strongly overlap describing a mixing of the two species. On the contrary a small value of σ_g corresponds to distinct domains for the two species. Also a large l_x with a finite σ_g corresponds to the existence of a macroscopic phase, with a given ratio of the two species.

The partition function is now written:

$$Z \approx \mathcal{C} \int dl_x d\sigma_g \exp\{-H[l_x, \sigma_g]\}, \quad (13)$$

where \mathcal{C} is a normalization constant. We now give explicitly the different contributions to the Hamiltonian as functions of l_x and σ_g .

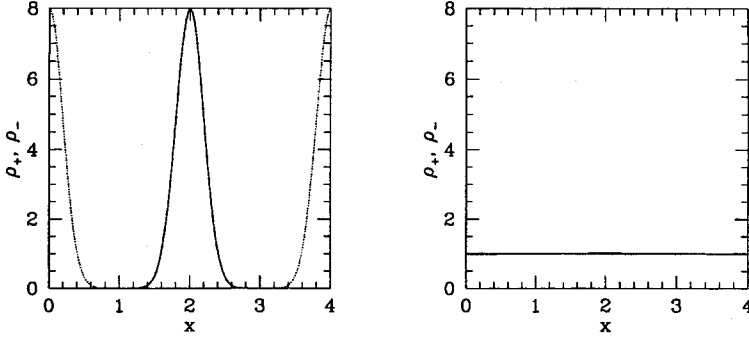


Figure 3: Density profiles for $l_x = 4.0$, for two values of σ_g . The figure on the left is for $\sigma_g = 0.2/l_x = 0.05$, the figure on the right is for $\sigma_g = 2.0/l_x = 0.5$. ρ_+ is plotted in full line, ρ_- in dotted line.

The contribution from the entropy per particle is:

$$\frac{H^{ent}}{N_+ + N_-} = \int_0^{\frac{1}{2}} \tilde{\rho}_+(\tilde{x})[\log \tilde{\rho}_+(\tilde{x}) - 1] + \tilde{\rho}_-(\tilde{x})[\log \tilde{\rho}_-(\tilde{x}) - 1] d\tilde{x}, \quad (14)$$

where \tilde{x} is the abscissa in l_x units and $\tilde{\rho}_i = \rho_i/\rho_i^0$. Because of the scaling properties of $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ this quantity does not depend on l_x .

The assumption that we have only x dependent profiles, allows a simple calculation of the electrostatic energy. The electrostatic energy can be rewritten in terms of the electric field:

$$H^{elec} = \frac{\epsilon}{2k_B T} \int E^2(\mathbf{r}) d\mathbf{r}. \quad (15)$$

We consider the lines to be infinite along the Y-axis, although the system only delimits a finite portion of length L of these lines. The field is orthogonal to the Y-axis, and given the periodicity in the X direction of the system, it is possible to calculate the electrostatic energy of a strip: which is the portion of profiles for x between 0 and $l_x/2$, see for instance figure 3. A simple use of the Gauss theorem gives the electric field in terms of the profile:

$$E(\tilde{x}) = \frac{q(\tilde{x})}{\epsilon}, \quad (16)$$

where $q(\tilde{x}) = e \int_0^{\tilde{x}} [\rho_+(\tilde{x}') - \rho_-(\tilde{x}')] d\tilde{x}'$ is the line density of the charge between the abscissa 0 and \tilde{x} given in l_x units. Because of the electroneutrality of one strip, there is no influence of this strip on the neighbouring ones. Multiplying by $2N_l$, *i.e.* the number of strips, we find that the electrostatic energy per particle is:

$$\frac{H^{elec}}{N_+ + N_-} = \Gamma l_x^2 \rho_+ \pi \int_0^{1/2} d\tilde{x} \left[\int_0^{\tilde{x}} [\tilde{\rho}_+(\tilde{x}') - \tilde{\rho}_-(\tilde{x}')] d\tilde{x}' \right]^2. \quad (17)$$

Finally the specific interaction contribution, per particle is:

$$\frac{H^{spec}}{N_+ + N_-} = \frac{\rho^0 l_x^2}{2} \int_0^{1/2} d\tilde{x}_1 \int d\tilde{x}_2 \exp\{-\tilde{r}_{12}^2 \frac{l_x^2}{a^2}\} [\bar{\rho}_+(x_1)\bar{\rho}_+(x_2)A_{++} + \bar{\rho}_-(x_1)\bar{\rho}_-(x_2)A_{--} - 2\bar{\rho}_+(x_1)\bar{\rho}_-(x_2)A_{+-}] , \quad (18)$$

where the points 1 and 2 are defined by $\mathbf{r}_1 = (x_1, y_1)$ and $\mathbf{r}_2 = (x_2, y_2)$ and \tilde{r}_{12} is the distance between them in l_x units. The integrals are such that point 1, is restrained to the strip and point 2 is in a range from particle 1 corresponding to the interaction potential, not necessarily in the same strip. The integral on y_1 has been performed using the translational invariance of the system along the Y-axis.

3.2 Mean Field approximation

In the mean field approximation, we minimize the Hamiltonian with respect to the density profiles ρ_+ and ρ_- . With the trial functions, it amounts to calculate the two parameters l_x^{MF} and σ_g^{MF} minimizing H :

$$\left. \frac{\delta H}{\delta l_x} \right|_{l_x^{MF}} = 0 , \quad (19)$$

$$\left. \frac{\delta H}{\delta \sigma_g} \right|_{\sigma_g^{MF}} = 0 . \quad (20)$$

The contributions to the Hamiltonian as a function of l_x and σ_g are given in equations (14), (17) and (18).

3.2.1 Non coulombic system

We show in figure 4, the energetic contributions to the Hamiltonian from the entropy and the specific interactions, as a function of σ_g and then as a function of l_x . As an illustration, we have chosen respectively two fixed values of $l_x = 5.0$ and $\sigma_g = 0.13$. The competition between the mixing effect of the entropy and the demixing effect of the specific interactions is visible at constant l_x , as the energy minimum with the parameter σ_g . For a fixed value of $\sigma_g = 0.13$, we see that the specific interactions favour large l_x , as stated in eq. (14) the entropy is independent of l_x and does not contribute. The global minimum corresponds to $l_x^{MF} \rightarrow \infty$ and $\sigma_g^{MF} = 0.13$. The corresponding density profiles are shown in figure 5 for $l_x = 10^4$, the profiles for any larger value of l_x are similar. It is important to note that the value of σ_g is sufficiently small to state that the spatial distribution of two species is well localized. This means that in the limit of infinite l_x we have a phase separation between the two species. If σ_g had a larger value we could not conclude on phase separation because of the overlap of the densities of the two species, as shown in figure 3.

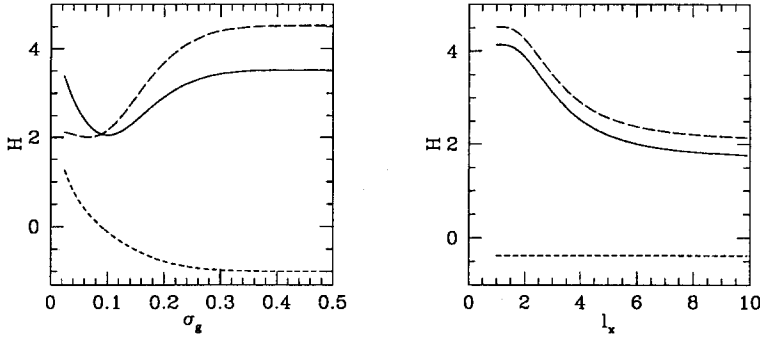


Figure 4: H per particle in $k_B T$ units (full line) as a function of σ_g and l_x , with respectively fixed values of $l_x = 5$ and $\sigma_g = 0.13$. The entropic contribution and the specific interaction contribution are plotted in dashed line and long dashed line respectively.

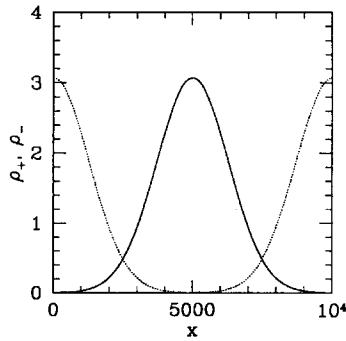


Figure 5: density profiles in the absence of electrostatic interaction, for $l_x = 10000$, for $\sigma_g = 0.13$. ρ_+ is plotted in full line, ρ_- in dotted line.

3.2.2 Pure coulombic system

We show in figure 6, the energetic contributions to the hamiltonian from the entropy and electrostatic interactions, for the same values of the parameters, as in figure 4. At fixed σ_g , the effect of the electroneutrality in the system tends to cancel the inhomogeneities, by a vanishing l_x . And at fixed l_x both the entropy and the electrostatics tend to spread the profiles, which is equivalent to mixing the species. The minimization of the hamiltonian in this case yields $l_x \rightarrow 0$ and $\sigma_g \rightarrow \infty$, which corresponds to a complete mixing. There is no apparent structure in the system, the corresponding density profiles are flat for both species.

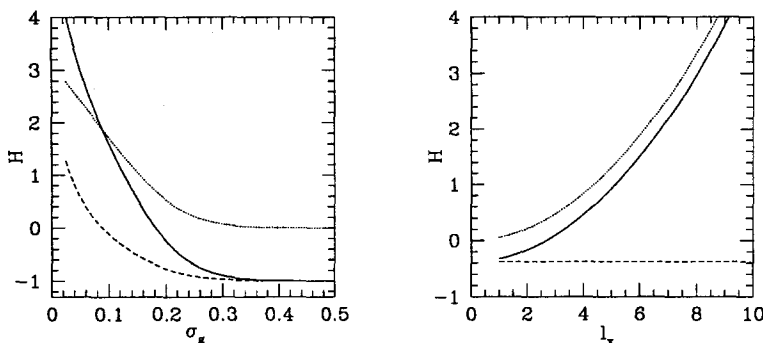


Figure 6: H per particle in $k_B T$ units (full line) as a function of σ_g and l_x , with respectively fixed values of $l_x = 5$ and $\sigma_g = 0.13$. The entropic contribution and the electrostatic interaction contribution are plotted in dashed line and dotted line respectively.

3.2.3 Coulombic system with specific interactions

We now consider, both electrostatic and specific interactions. In figure 7 we see that for a fixed value of l_x , the electrostatic contribution and the entropy favour spreading of the profiles which corresponds to large values of σ_g equivalent to the mixing of the species. In contrast, the specific interactions chosen do not favour the mixing of the two species, inducing small values of σ_g . The two competing effects find a compromise in the minimum. For a fixed σ_g , the electrostatics favours small values of l_x , once again trying to reproduce electroneutrality whereas the specific interactions lead to a separation of the two species. Also in this case the two opposing effects generate a minimum. Finally, we can compute the global minimum of H , in the (l_x, σ_g) parameter space and the result is quite different from the previous cases.

The mean field values of the parameters are now: $l_x^{MF} = 4.17$ and $\sigma_g^{MF} = 0.146$. These are in fact the values chosen to plot figure 7. The density profiles for this set of parameters are given in figure 8. Both the distance between the lines and the relatively small finite value of σ_g for well defined lines, seem in agreement with what is visible in the snapshot of the simulation, figure 2.

The change in behaviour of the system is significant. With only specific interactions there is macroscopic demixion into two homogeneous phases. When there is only coulombic interaction the system is homogeneous and electroneutral. In both cases there is no internal structure as for the third case of competing interactions, there are well defined lines and the length l_x different from the Debye length appears. This length defines a scale intermediate between that of the specific interaction and the macroscopic length scales. The existence of series of lines of ions of the same sign in the snapshots, is in agreement with the notion of local demixion introduced in [1].

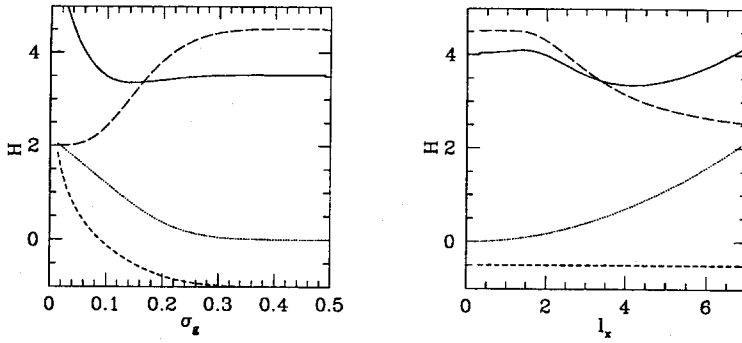


Figure 7: H per particle in $k_B T$ units (full line) as a function of σ_g and l_x , with respectively fixed values of $l_x = 4.17$ and $\sigma_g = 0.146$. The contributions of entropy, specific interactions and electrostatic interaction are plotted in: dashed, long dashed and dotted line, respectively.

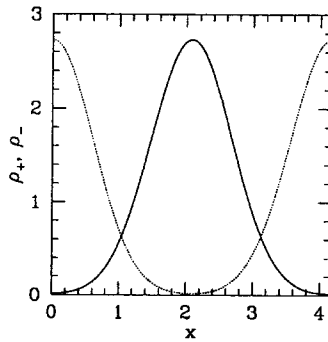


Figure 8: density profiles for $l_x = 4.17$, for $\sigma_g = 0.146$. ρ_+ is plotted in full line, ρ_- in dotted line.

4 Conclusion

In this paper we have seen that specific interactions deeply modify the behavior of a coulombic system. This behaviour results from two antagonistic effects - the mixing effect of electrostatics and the demixion induced by the short range potentials. The two effects coexist in the system with local demixion and induce the phenomenon of clustering of ions of the same sign in contrast with the familiar notions of screening and ion pairing of oppositely charged ions.

An important feature of the competition between coulombic and the specific interactions is the new length. The specific interactions dominate in the length scales shorter than this length where they violate the electroneutrality. In the larger length scales the coulombic interactions no longer admit the charge inhomogeneities created by the specific interactions. The microphase separation is organized into the lines visible in the snapshots suggesting an analogy with bicontinuous phases. There seems to be an interesting parallel between surfactant systems in which the stoichiometric relations can be expressed by long range coulombic like interactions [7] and the coulombic systems which can lead to surfactant like structures reported here.

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