I. INTRODUCTION

In this paper we continue a study of a model that one of us studied previously\(^1\). The model was introduced to describe the possible ordering of metal ions that can occur in aluminum substituted nickel layered double hydroxides \(\text{Ni}_{1-x}\text{Al}_x\text{(OH)}_2\text{(CO}_3\text{)}_{x/2} \cdot y\text{H}_2\text{O}\). The ordering is assumed to occur due to long-range Coulomb interactions, and overall charge neutrality is provided by a negative background representing the hydroxide planes and \(\text{CO}_3^{2-}\) anions. The previous study was restricted to the ground state properties. Here we use a Monte Carlo technique to extend the study to finite temperatures. The model predicts that, at some values of the concentration \(x\), the system can exhibit an instability and phase separate. In order to evaluate the precision of these Monte Carlo procedures, we first study a linear chain with finite ranged interactions where exact solutions can be obtained using a transfer matrix method. For a linear chain with infinite-ranged interactions, we use a devil’s staircase formalism to obtain the dependence of the energy of the equilibrium configurations on \(x\). Finally we study the two dimensional triangular lattice using the same Monte Carlo techniques. In spite of its simplicity, the model predicts multiple first order phase transitions. The model can be useful in applications such as the modelling of the ordering of intercalated metal ions in positive electrodes of lithium batteries or in graphite.

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rated by large distances is taken into account because of the relatively short screening length\textsuperscript{16–18} caused by free electrons.

It is generally accepted that in layered hydroxides the Coulomb interaction between positively charged metal planes, negatively charged hydroxide planes and negatively charged anions [CO\textsubscript{3}\textsuperscript{2−}] in the galleries are important. The screening length in layered hydroxides should be significantly larger than in metal alloys, because dielectric screening caused by water and other polar molecules is weaker than screening caused by free electrons. Thus a model that takes into account long range Coulomb interaction and interaction between positive metal ions in the plane with negative hydroxides layers and negative anions in the galleries might be more suitable than a lattice gas model to describe the ordering of metal ions in layered double hydroxides. The role of ordering due to Coulomb interactions has been discussed previously by Thompson\textsuperscript{19}.

We have previously suggested a simple model to describe the ordering of metal ions in layered hydroxides\textsuperscript{4}. In this model two kinds of positively charged metal ions occupy the sites of a triangular lattice. The lattice is immersed in a negatively charged background which represents the hydroxide layers and negative anions in the galleries. It was assumed that the background charge is the same at every site of the triangular lattice. Thus the total charge at every site is formed by the positive charge due to the metal ion and the negative background charge. The interaction potential between sites was assumed to be a long ranged 1/r Coulomb type.

In the previous work\textsuperscript{1} the dependence of the ground state energy of this model system on the concentration of Al was studied assuming a homogeneous concentration of metal ions in the plane. Equilibrium ordering configurations of ions that can occur at each concentration in the range 0 ≤ x ≤ 1 were calculated and compared with corresponding X-ray diffraction patterns.

In this paper we suggest a new interpretation of the previous results. It will be shown that at some concentrations x the system is unstable with respect to phase separation into phases with concentrations x\textsubscript{1} and x\textsubscript{2} such that x\textsubscript{1} < x < x\textsubscript{2}. We calculate the phase diagram of the system in the (T, x) plane using the grand canonical ensemble by introducing a chemical potential \( \mu \). In the case of the layered hydroxides, the chemical potential under consideration is not related to the voltage on the electrodes and represents only a useful way to obtain the phase diagram.

The model is quite general and can be employed to describe ordering and first order phase transitions in ionic systems with long range interactions. It may have some application to the ordering of intercalated Li ions in rechargeable Li-batteries\textsuperscript{19–21}. Predicted phase separations can lead to the staging when homogenous planes with different concentrations of metal ions will form. In plane long range interaction in this case can be similar to that occurring in staged graphite intercalation compounds\textsuperscript{22,23}.

The paper organized as follows. In section II we define our model. Then in section III we discuss the details of the Monte Carlo (MC) method that was used to obtain the phase diagrams. Section IV describes an application of the method to the linear chain. Subsections IV A and IV B are devoted to the case of finite ranges of interaction where an exact solution can be obtained using transfer matrix techniques. The case of a linear chain with infinite range Coulomb interaction in which the energies of equilibrium configurations can be calculated exactly using the devil’s staircase method, is discussed in subsection IV C. Finally in section V we study the case of the two dimensional triangular lattice. Our results are summarized in the conclusion.

II. MODEL

Consider a system composed of two types of positive ions which occupy the sites of some lattice. Every site of the lattice is occupied either by a black ion with charge \( Q_b \) or by a white ion with charge \( Q_w \). The concentration of black ions is x and the concentration of white ions is 1−x. In addition to these two types of positive ions there is also a negative compensating uniform background charge \( q \), at every site of the lattice, that ensures charge neutrality in the system. Hence at any site i we have a total charge equal to either \( \Delta_b = Q_b + q \) or \( \Delta_w = Q_w + q \). The Hamiltonian of the system of charges can be written in terms of the pairwise interactions \( V_{ij} \):

\[
H = \sum_{i<j} V_{ij} \Delta_i \Delta_j .
\]

(1)

For the Coulomb interaction \( V_{ij} = 1/R_{ij} \), where \( R_{ij} \) is the distance between sites i and j. In the following we will also consider the case of truncated Coulomb interaction for which there is interaction only between neighbors that are in some range.

The value of the background charge depends on the values of \( Q_b, Q_w \) and on the concentrations of those ions. The average charge per site due to the positive ions is

\[
\bar{q} = xQ_b + (1-x)Q_w .
\]

(2)

The value of the charge that provides the uniform background with overall charge neutrality is then given by \( q = -\bar{q} \). Thus \( \Delta_b = Q_b + q = (Q_b - Q_w)(1-x) \) and \( \Delta_w = Q_w + q = (Q_b - Q_w)(-x) \). Introducing \( J_{ij} = V_{ij}(Q_b - Q_w)^2 \) we rewrite Eq. (1) as:

\[
H = \sum_{i<j} J_{ij} (n_i - x)(n_j - x) .
\]

(3)

where \( n_i = 1 \) if site i is occupied by a black ion and \( n_i = 0 \) if site i is occupied by white ion. Thus the precise values of the positive charges do not change the general
properties of the model. From Eq. (3) follows that at a fixed concentration \( x \)

\[
H = \sum_{i<j} J_{ij} n_i n_j - x^2 \sum_{i<j} J_{ij} .
\]  

Thus at fixed concentration the model is essentially a lattice gas model because in this case the second term in Eq. (4) is the same for all configurations of ions. This term is due to the neutralizing background and cancels the divergence of the energy associated with the Coulomb repulsion when the interactions are of infinite range.

It is easy to estimate the values of the constants \( J_{ij} \) if the lattice constant and charges \( Q_b \) and \( Q_w \) are known. For the aluminium substituted nickel layered double hydroxide \( a = 3.032 \text{ Å}^2, Q_b = 3e \) and \( Q_w = 2e \). For the nearest neighbors we have:

\[
J_{nn} = V_{nn}(Q_b - Q_w)^2 = \frac{e^2}{\epsilon a} .
\]

Thus if we use a dielectric constant appropriate for water \( \epsilon = 80 \), then \( J_{nn} \approx 60 \text{ meV} \) or about 500 K. Short range screening, due to the presence of water and other ions, can effectively decrease the values of the \( J_{ij} \).

In order to use the grand canonical ensemble to study the equilibrium properties of this system of charges we add a chemical potential term \( -\mu \sum_i n_i \) to the Hamiltonian. Now the concentration \( x \) can fluctuate and hence the background charge will also fluctuate. We write the grand canonical Hamiltonian as:

\[
H = \sum_{<ij>} J_{ij} (n_i + q)(n_j + q) - \mu \sum_i n_i ,
\]

where \( q \) describes the uniform background charge which is adjusted to be equal to \( q = -<n_i> = -x \).

Our primary goal is to study the two-dimensional triangular lattice with infinite range Coulomb interactions. However, we will consider the linear chain as an example to gain a better understanding of the model since there are exact analytical methods that can be used in two limiting cases: finite range interactions can be studied exactly using transfer matrix methods and infinite range Coulomb interactions can be described in terms of a Devil’s staircase formalism. The study of the linear chain will give us insight into the precision of the numerical techniques that will be used for the triangular lattice with Coulomb interactions.

In the following sections we address the following questions. What is the equilibrium structure of the charges for a given concentration of the ions? How does the equilibrium energy of the system depend on the concentration of the ions? How does the chemical potential depend on the average concentrations of the ions at different temperatures. Do phase transitions occur in the system and what is the phase diagram of the system at finite temperatures?

III. MONTE CARLO METHOD FOR SIMULATIONS OF THE SYSTEM

We use a Metropolis algorithm to accept or reject elementary moves that we perform on the charges to bring them into an equilibrium configuration. We use two different types of moves: A interchange the positions of black and white ions in the lattice. B change the color of the ion at a particular site.

The simulations can be carried out with either constant values of the concentration or with constant values of the chemical potential. In case of simulations at a constant value of concentration only moves of type A were used. In case of simulations at a constant value of the chemical potential both types of moves A and B were used. The A-move does not change the value of the background charge since it does not change the concentration. The B-move changes the concentration and thus the background charge has to be changed at every site in the lattice. In order to decide whether to accept or reject the move it is necessary to calculate the energy of the system before and after the move. We consider a lattice of size \( N \) in case of the linear chain and \( N \times M \) for the triangular lattice. We apply periodic boundary conditions with respect to this central zone. Periodic boundary conditions mean that the central zone is repeated in each of the \( d = 1 \) or 2 directions. The central zone occurs in the center of bigger lattice surrounded by surrounding zones. In order to calculate the energy of the system we calculate the energy of interaction between all sites inside the central zone and the energy of interaction between the sites in the central zone with sites in all surrounding zones. Since the system is charge neutral, the contribution to the energy from surrounding zones that are far away from the central zone are much smaller than the contribution from surrounding zones that are close to the central zone. In fact, we found that if \( N \) and \( M \) are of the order of 10, then it is enough to consider the lattice of size \( 5N \times 5M \) in order to calculate the energy with sufficient precision for almost all concentrations. In other parts of this paper we refer to the size of the central zone as to the sample size, with the periodic boundary conditions described above.

The total energy of the system given by Eq. (3) can be separated into three parts which represent interaction between black-black, white-white and black-white sites

\[
E = E_{bb} + E_{ww} + E_{bw} .
\]

It follows from Eq. (3) that \( E_{bb} \) can be written as

\[
E_{bb} = (1 - x)^2 \sum_{i<j} J_{ij} n_i^b n_j^b .
\]

In the sum above, the index \( i \) runs over all sites in the central zone and the index \( j \) over all sites in the central and surrounding zones \( i \neq j \). The quantity \( n_i^b \) is unity if a black ion occupies site \( i \) and zero otherwise. Using the notation \( \sigma_{bb}(j) = \sum_j J_{ij} n_j^b \) Eq. (8) can be rewritten
that the energy remains the same. In order to accept or reject the move we calculate the change in $\Delta E = \mu \Delta \sigma$: 

$$E_{bb} = (1 - x)^2 \sum_i n_i^b \sigma_{bb}(i) = (1 - x)^2 \sigma_{bb}.$$  

(9)

In the same manner we can write $E_{ww} = x^2 \sigma_{ww}$ and $E_{bw} = 2x(1 - x)\sigma_{bw}$. Then the energy of the system per site can be written as:

$$E = \frac{1}{2(N \times M)} [(1 - x)^2 \sigma_{bb} + 2x(1 - x)\sigma_{bw} + x^2 \sigma_{ww}],$$  

(10)

where the first term in square brackets comes from the interaction between black-black sites, the second from black-white sites and the third from white-white sites. It is easy to see from Eq. (10) that the equilibrium energy of the system is a symmetric function, $E(x) = E(1 - x)$, with respect to $x = 1/2$. The ground states corresponding to concentrations $x$ and $1 - x$ can be obtained from each other by changing all white sites into black sites and all black sites into white sites. In this case $x \leftrightarrow 1 - x$, $\sigma_{bb} \leftrightarrow \sigma_{ww}$, $\sigma_{bw} \leftrightarrow \sigma_{bw}$ and it follows from Eq. (10) that the energy remains the same. In order to accept or reject the move we calculate the change in $\Delta E = \mu \Delta \sigma$. For calculation of $\Delta E$ it is necessary to take into account that if we turn a white site $i$ into a black site then charges at the sites corresponding to the site $i$ but situated in the surrounding zones should be changed also. When an elementary move is performed, then values of $\sigma_{bb}$, $\sigma_{bw}$, $\sigma_{ww}$ can be updated by calculating the sums $\sigma_{bb}(i)$, $\sigma_{bw}(i)$, $\sigma_{ww}(i)$ for the particular site $i$ that participate in the move. This significantly reduces the calculation time since it is not necessary to recalculate the energy of the whole lattice again after every move.

We say that one MC step was performed if one attempt to perform operation $A$ or $B$ was made. We say that one MC sweep was made if as many MC steps were made as there are sites in the sample. In simulations at a constant $\mu$ we initially tried to vary the frequency with which operations $A$ and $B$ were performed, but we found that $1 : 1$ ratio was close to the optimum value. For every value of the concentration or the chemical potential, simulations start at a relatively high temperature $T \approx J$. If simulations are to be performed at constant $x$ then in the initial configuration black and white ions in amounts corresponding to $x$ are randomly distributed over the lattice sites. If simulations are to be performed at a constant value of $\mu$, the initial configuration is less important.

We used the following criteria to check the equilibration of the system at a given temperature. Let $E_2$ will be the average value of the energy in the last 10 MC sweeps and $E_1$ will be the average value of the energy in the previous 10 MC sweeps. Let $\sigma_{E_2}$ and $\sigma_{E_1}$ be the average fluctuations of energy in those two cycles. If $|E_2 - E_1| \leq \frac{1}{10} \min(\sigma_{E_1}, \sigma_{E_2})$ then we say that the system is sufficiently equilibrated in order to collect the data. If this condition is not fulfilled another 10 MC sweeps are made until this condition is met and so on.

After the equilibration, in order to obtain statistics, we calculated and stored the values of parameters of interest after every MC sweep. The number of MC sweeps varied depending on the size of the system, type of interaction and temperature. When the necessary data at a temperature $T$ were collected, the temperature was decreased by a small amount $\delta T$. For smaller values of the temperature $T$, a smaller value of $\delta T$ was used.

It will be shown below that first order phase transitions occur in these systems. In other words ions on the lattice should separate into two parts with different concentrations of the black ions in each part. Parts with different concentrations of the black ions should also have differ-
ent values of the background charge. But it is assumed in our model that the value of the background charge is the same everywhere. Thus the background in our simulations does not allow the systems to split into parts with different concentrations and thus does not allow the phase separation to be observed directly.

When we perform simulations at a constant value of average concentration \( x \), it is possible that we may choose some particular average value \( \bar{x} \) that can not occur in a homogeneous system. The energy curve \( E(\bar{x}) \) obtained in this case does not really give the dependence of energy on concentration, but rather shows when phase separation should occur. This will be demonstrated explicitly in the next section using the linear chain as an example.

In simulations with a fixed value of the chemical potential the phase transitions are more pronounced. At high temperatures \( (T/J) \geq 1 \) changes in the chemical potential lead to the smooth changes in average concentration \( \bar{x} \). However, at low temperatures \( (T/J) \ll 1 \) there are discontinuities in the \( \bar{x}(\mu) \) curve. We assume that the borders of the discontinuity region are the borders of the phase separation region.

The situation at intermediate temperatures is more complicated. As an example, Fig.1 shows the concentration as a function of the number of MC sweeps for a \( 30 \times 30 \) triangular lattice for three values of \( \mu \) at \( (T/J) = 0.08 \). The sharp jump in concentration from \( \bar{x} \approx 0.88 \) to \( \bar{x} = 1 \) that occurs at \( \mu/J = 0.606 \) shows that both concentrations \( \bar{x} \approx 0.88 \) and \( \bar{x} = 1 \) lead to the same minimum value of Helmholtz free energy and thus are stable. Homogeneous equilibrium configurations in the range of concentrations \( 0.88 < \bar{x} < 1 \) have higher values of the Helmholtz free energy and thus are unstable with respect to phase separation into two parts with concentrations \( \bar{x} = 0.88 \) and \( \bar{x} = 1 \).

Fig.2 shows the histogram of the distribution of concentrations corresponding to those in Fig.1. Peak positions give us the values of average concentrations. For some particular values of \( \mu \) the system migrates between two significantly different concentrations, as for example for \( \mu = 0.606 \). We assume in this case that there is phase separation and relative areas under two peaks give us the relative sizes of the two phases. Thus the appearance or disappearance of a peak tells us about the appearance or disappearance of a phase. We will use the positions of the peaks when they appear or disappear as the borders of the two phase coexistence region.

At low temperatures \( (T/J) \ll 1 \) our MC procedure becomes less effective and the system can become frozen in some configurations. One of the reasons for this is the local character of the moves \( A \) and \( B \) that we use to search for a new configurations e.g. every MC move involves only one or two sites.

IV. LINEAR CHAIN

There are two exact analytical methods to study the model in the one dimensional case of the linear chain. In particular, if the Coulomb interaction is truncated at some distance then a transfer matrix technique can be applied to calculate the free energy as a function of chemical potential and temperature. Then the dependence \( x(\mu, T) \) can be studied and the phase diagram can be obtained.

In case of the infinite range Coulomb interaction at \( T = 0 \), a devil's staircase formalism can be used to predict the equilibrium structure for any concentration and calculate the ground state energy of the system. In both cases exact results will be compared with the results of simulations to establish the precision of the numerical methods.

A. Nearest Neighbors Interaction

If we restrict the range of interaction to nearest neighbors only, the Hamiltonian becomes

\[
H = J \sum_i (n_i + q)(n_{i+1} + q) - \mu \sum_i n_i .
\]

Initially we assume that \( q \) is a constant and is not connected with concentration. Then the grand partition function \( Z_N \) for a cyclic chain of \( N \) sites can be expressed in terms of the largest eigenvalue of the \( 2 \times 2 \) transfer matrix as \( Z_N = \lambda_N^{N} \) with

\[
\lambda_{max} = \frac{e^{-\beta J q^2}}{2} \left[ 1 + \gamma + \sqrt{(\gamma - 1)^2 + 4\gamma e^{\beta J}} \right],
\]

where \( \gamma = e^{\beta(\mu + 2 J q - J)} \) and \( \beta = 1/(k_B T) \). The grand potential per site is given by \( \Omega = -k_B T \ln[\lambda_{max}] \). Using the fact that \( \bar{x} = \langle n_i \rangle = 0 \partial \Omega/\partial \mu \), we can find \( \bar{x} \) as a function of the independent variables \( T \) and \( \mu \). The resulting expression can then be inverted using the charge neutrality requirement, \( q = -\bar{x} \), to obtain \( \mu \) in terms of \( \bar{x} \) and \( T \) with the following result:

\[
\mu = J - 2J \bar{x} + \frac{2}{\beta} \sinh^{-1} \left[ \frac{(\bar{x} - 1/2)e^{\beta J/2}}{\sqrt{2(1-\bar{x})}} \right].
\]

Fig.3 shows the transfer matrix predictions for the \( \mu \) versus \( \bar{x} \) curves for various values of \( T/J \) and also the results of numerical simulations. The upper left frame shows the results of the transfer matrix calculations at various temperatures.

Note that \( \mu = 0 \) corresponds to \( \bar{x} = 1/2 \). At high temperatures, \( \mu \) is a monotonically increasing function of \( \bar{x} \) but at low temperatures, \( \mu \) has regions where the slope is negative. This behavior is thermodynamically unstable and indicates that phase separation occurs. The upper right frame shows transfer matrix predictions and the results of simulations at \( (T/J) = 0.50 \). Simulation points
lie on top of the exact curve. The lower left frame shows the results at temperature \( (T/J) = 0.20 \) which is just above the maximum temperature for which phase separation occurs. The regions with a low density of simulation points indicate the appearance of the regions of phase separation that occur at lower temperatures. The concentration \( \bar{x} \) in this region is the average over the two peaks that occurs at the intermediate temperatures as shown in Fig.1 and in Fig.2. The lower right frame at \( (T/J) = 0.10 \) clearly shows the sharp jumps in concentration that occur at low temperatures.

In the simulations, phase separation manifests itself as a discontinuity in the dependence \( \bar{x}(\mu) \). In contrast, a second order transition would correspond to \( \mu \) increasing monotonically with a discontinuity in slope.

The first order transition can also be seen in plots of the grand potential per site, \( \Omega \), versus chemical potential. Loops corresponding to the unstable branches appear at low temperatures. However, we find it more convenient to plot the Helmholtz free energy per site, \( F = \Omega + \bar{x}\mu \), or the internal energy per site, \( E \), as a function of the concentration \( \bar{x} \).

A finite temperature phase transition is not expected in one dimension for finite range interactions. However, the presence of the background charge effectively makes this an infinite range problem and produces a first order phase transition at a finite temperature. This behavior is similar to that in the Van der Waals theory of liquids where long range attractive interactions lead to condensation phenomena.

Fig.4 shows both energy \( E \) and Helmholtz free energy \( F = E - TS \) as a function of \( \bar{x} \) at \( (T/J) = 0.05 \). The difference between these two curves is due to the entropy of the system. Since the difference between these two curves is significant, the entropy plays an important role even at quite low temperatures.

Since \( \bar{x} \) is the independent coordinate, we apply the double tangent rule to the Helmholtz free energy \( F \) (or to the energy curve at \( T = 0 \)) to determine the equilibrium concentration. The slope of the tangent line gives the value of the chemical potential \( \mu \). This predicts that at \( T = 0 \) the system will separate into two phases with concentrations 0 and 1/2 if \( \bar{x} \) is between those two concentrations.

If in MC simulations we are trying to produce the \( E(\bar{x}) \) curve and we fix the concentration at a particular value that cannot exist homogeneously across the system, then we create an internal stress in the system: the ions tend to separate into two phases but the background charge, through Coulomb interaction, does not allow this phase separation since it is constrained to be uniform. This stress should effectively increase the value of the energy \( E(\bar{x}) \) in the simulations. It is possible sometimes to see in structures obtained from simulations the tendency to phase separation. In Fig.5 one can clearly see this tendency for the phase separation: The average concentration in the top row is 1/2 while the average concentration in the bottom row is 1/3.

Fig.6 shows the phase diagram in the temperature–concentration plane. The solid curve is the transition temperature \( T_c \). This curve was obtained using the equal area rule applied to the \( \mu \) versus \( \bar{x} \) curves (see Fig.3) obtained from Eq. (13). The dashed curve is the spinodal which corresponds to the locus of points for which
The Hamiltonian of the model at fixed concentration $x$ is given by Eq. (3). In the case of nearest neighbor interaction $J_1$ and a second neighbor interaction $J_2$ only, the ground state energy can be obtained directly using the following reasoning: for concentrations in the range $0 < x < 1/3$, the background charges (white charges) contribute an amount $-(J_1 + J_2)x^2$ to the energy per site from the last term in Eq. (4). The black charges can be placed on every third site so as to avoid the repulsion in the first term. However, in the concentration range $1/3 < x < 1/2$ the repulsive interactions contribute an additional amount $(J_1 + J_2)(x - 1/3)$ to the energy. The energy in the range $1/2 < x < 1$ is obtained using the symmetry property $E(x) = E(1 - x)$. Similar reasoning can be used for larger ranges of the interactions but the expressions become more complicated.

Fig.7 shows the ground state energies as a function of concentration $\bar{x}$ at $T = 0$, for finite ranged interactions $J_n = J/n$, where $n = 1, 2, 3, 4, 5$ and 6. The solid curves were obtained using the arguments described above and were verified using the numerical transfer matrix method results at very low temperatures. The MC simulations were performed on lattice samples with 90 and 180 sites and periodic boundary conditions.

The panel 2 in Fig.7 shows the energy curve for the interaction between nearest and second nearest neighbors only. It is easy see that for $\bar{x} = 1/2$ it is energetically favorable for the system to split into two parts with different average concentrations $\bar{x}_1 = 1/3$ and $\bar{x}_2 = 2/3$.

If we apply the double tangent construction to the $E(\bar{x})$ curves in Fig.7, corresponding to the interactions ...
There is a region between $0.25 < x < 0.475$ in which the exact curve has a peak in this region. We believe that the origin for this behavior is the tendency for the configuration of the system to change the phase separation described above. Thus every simulated point in this region is a weighted average of two consecutive phase separation points.

Dotted lines in the figures show limiting case of infinite range Coulomb interaction.

FIG. 7: Dependence of the energy per site on concentration $x$. The solid curve with the devil's staircase formalism on the lattice sample predicted with 1000 sites. Circles give the results of the MC simulations at low temperature for samples with 180 sites.

FIG. 8: Energy per site as a function of concentration $x$ for a linear chain with Coulomb interactions. The solid curve was obtained by knowing equilibrium structures predicted with the devil's staircase formalism on the lattice sample with 1000 sites. Circles give the results of the MC simulations at low temperatures. The Hamiltonian is $H = J \sum_{i,j} S_i S_j$. The transfer matrix formalism can be used again, but the transfer matrix equation is $T_{i,j} = T_{i-1,j} + T_{i,j-1} + T_{i,j}$. The Hamiltonian given by Eq. (6) leads to the transfer matrix equation. The transfer matrix equation is $T_{i,j} = T_{i-1,j} + T_{i,j-1} + T_{i,j}$. The transfer matrix can be solved numerically to obtain the largest eigenvalue of the transfer matrix numerically. If the interactions are then only between nearest neighbors apart and form a pattern such as the one-dimensional analogue of the Wigner lattice, then the black charges are equally spaced along the chain. The weight is proportional to the fraction of the whole sample that is at a given edge concentration. In order to apply the transfer matrix method to the system with range of interaction $n > 1$, we can form group the sites into consecutive blocks of length $n$.
integers, the ground state configuration is periodic with period \( q \) and has \( p \) black charges in each cell. If there is a black charge at site 0 then black charges are at the sites with numbers \( \lfloor nq/p \rfloor = \lfloor n/x \rfloor \) where \( n \) is any integer and \( \lfloor A \rfloor \) denotes the integer part of \( A \). Since the structure is known for any rational value of \( x \) the ground state energy can be calculated using the the same techniques that was used to calculate energies in MC simulations. But since in this case it is not necessary to run a relaxation procedure much bigger samples can be considered.

Fig.8 shows the ground state energy as a function of \( x \) for the Coulomb potential obtained using both the exact ground state configurations and our simulation technique. The value of the energy at \( x = 1/2 \) corresponds to alternating black and white charges and is equal to \(-\frac{\ln 2}{4}\). For smaller values of \( x = 1/n \) corresponding to period \( n \) Wigner lattices of equally spaced black charges, the energy per site is given by \( E = x^2 \ln x \). For values of \( x \) between these values the energy is slightly larger than if we use the same formula for all \( x \). The energy curve has a sequence of cusps located at all rational values of \( x \) (devil’s staircase).

Since at \( T = 0 \), the chemical potential is given by \( \mu = \partial E/\partial x \), we predict that at zero temperature \( \mu \) versus \( x \) will display a series of jumps as shown in Fig.9. The double tangent rule applied to the energy curve predicts phase separations for some values of \( x \). For \( 0 < x < 1/3 \), the system should separate into phases with to \( x = 0 \) and \( x = 1/3 \) whereas, for \( 1/3 < x < 1/2 \), it should separate into phases with \( x = 1/3 \) and \( x = 1/2 \).

Phase separation is due to the second term in Eq. (4) which is entirely due to the background. It corresponds to a long range attractive interaction. In the absence of the background, the model would not display phase separation and the chemical potential versus concentration curve would be a devil’s staircase with an infinite number of jumps corresponding to the rational values of \( x \).

The Devil’s staircase formalism can be used to obtain the \( E(\bar{x}) \) curve at zero temperature and thus predict \( \mu(x) \) dependence at zero temperature. In order to obtain the \( \mu(x) \) dependence at non zero temperature we used MC simulations. The \( \mu(x) \) curves at several temperatures obtained from MC simulations are shown in Fig.9. Simulations were performed on samples with 60, 90, 120, 180 and 960 sites. The role of size effects can be seen for the curve \( (T/J) = 0.10 \) for which the results from the samples with 60 and 180 sites are shown. For higher temperatures the differences are less significant. We found that up to very low temperatures there are almost no differences between the results on samples with 120 and 180 sites.

The inset in Fig.9 shows a rather large difference between the predictions for \( \mu(x) \) from the devil’s staircase formalism and from the results of simulations at low temperatures. There can be several reasons for this disagreement. One reason, discussed earlier, is that simulations at low temperatures may not be reliable since the system can become frozen in some local minima that it cannot leave due to the large transition barrier associated with the local character of moves \( A \) and \( B \). On the other hand the entropy contribution can make the “cusps” at \( x = 1/3 \) and \( x = 2/3 \) in the \( E(\bar{x}) \) dependence more “rounded” and this can lead to an extended range of chemical potential near concentrations \( x = 1/3 \) and \( x = 2/3 \) on the \( \mu(x) \) curve.

In order to obtain the phase diagram shown in Fig.10 we used the technique already discussed above. As expected the size of the plateaus corresponding to the regions of phase separation decreases as the temperature increases and the concentrations of both phases becomes
the same at the critical temperature. Only half of the phase diagram is shown since it is symmetric with respect to $x = 1/2$. At temperatures $0.04 \leq (T/J) \leq 0.08$ the data were obtained using a sample with 480 sites. At other temperatures the data were obtained using a sample with 960 sites. There are three distinct regions of phase separation that correspond to the following transitions in concentration at zero temperature: $1/2 \rightarrow 2/3$ with critical temperature $(T/J) \simeq 0.03$, $2/3 \rightarrow 3/4$ with critical temperature $(T/J) \simeq 0.0175$ and $3/4 \rightarrow 1$ with critical temperature $(T/J) \simeq 0.11$.

V. TRIANGULAR LATTICE

The Hamiltonian for triangular lattice with Coulomb interaction is given by Eq. (6):

$$H = J \sum_{<ij>} (n_i + q)(n_j + q) - \mu \sum_i n_i.$$ 

(14)

The details of model and simulation techniques were described in section II and III. In the 2D case with long range interaction we used MC simulations as the main method to study the system. Different sample sizes were used in the previous study\textsuperscript{1} in order to obtain $E(\bar{x})$ dependence shown in Fig.11.

For the triangular lattice there are multiple “cusps” in the $E(\bar{x})$ curve that are similar to the devil’s staircase behavior in case of the one dimensional chain. In the region $1/2 \leq \bar{x} \leq 1$ significant cusps in $E(\bar{x})$ curve occur at concentrations: $1/2, 2/3, 3/5, 3/4, 6/7$.

Ground state configurations for $x = 1/2, 3/5, 2/3$ and $3/4$ are shown in Fig.12. Ion distributions obtained on the $30 \times 30$ sample with MC simulations at three different values of $\mu$ at $(T/J) = 0.01$ are shown in Fig.13. In the ground state at $x = 6/7$ white sites should form a triangular Wigner lattice with the spacing $a\sqrt{7}$ between ions\textsuperscript{1}.

For values of $x = 1/(m^2 + n^2 + mn) \leq 1/3$ or $1-x \geq 2/3$ where $m$ and $n$ are integers, the ground state configurations are triangular Wigner crystals and the ground state energy can be calculated exactly using the numerical formalism of Bonsall and Maradudin\textsuperscript{27}. For these triangular Wigner crystal structures the energy is given exactly by $E(x) = -2.1067126(x^{1/2} - x^2)$. Between $x = 1/2$ and $x = 2/3$, the ground state configurations have a rectangular rather than triangular geometry. Regular rectangular structures can be formed at concentrations $x = l/(2(l+1))$, where $l$ is any integer\textsuperscript{1}. Thus $l = 4$ corresponds to $x = 2/5$ and is the same structure as for $x = 3/5$ with the interchange of black and white sites. The same numerical method\textsuperscript{27} can be used again to obtain $E(3/5) = -0.1709803$ and $E(1/2) = -0.1755589512$. 
The first row of the table I shows the values of the energies obtained from simulations at \((T/J) = 0.002\) with sample sizes \(\approx 18 \times 18\). For every concentration the sample size was chosen to be commensurate with particular concentration. The second row shows the results of simulations from the lattice samples of size \(\approx 30 \times 30\). The third row of the table shows the exact values of the energies obtained with the method of Bonsall and Maradudin.

The major difference between the simulated and the exact values arises because our simulation method can not relax the system to the exact ground state configurations for concentrations \(1/2, 3/5, 3/4, 6/7\). On the other hand it is easy to obtain the ground state configuration for \(x = 2/3\) and the agreement between the simulated and the exact values of the energy is much better in this case.

<table>
<thead>
<tr>
<th>(\bar{x})</th>
<th>1/2</th>
<th>3/5</th>
<th>2/3</th>
<th>3/4</th>
<th>6/7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{sim}}(18 \times 18))</td>
<td>-0.17056</td>
<td>-0.16534</td>
<td>-0.16953</td>
<td>-0.12450</td>
<td>-0.06794</td>
</tr>
<tr>
<td>(E_{\text{sim}}(30 \times 30))</td>
<td>-0.16964</td>
<td>-0.16456</td>
<td>-0.17070</td>
<td>-0.12671</td>
<td>-0.06807</td>
</tr>
<tr>
<td>(E_{\text{exact}})</td>
<td>-0.17556</td>
<td>-0.17098</td>
<td>-0.17136</td>
<td>-0.13167</td>
<td>-0.07076</td>
</tr>
</tbody>
</table>

TABLE I: Comparison of energies at special concentrations obtained in simulations on lattices with sample sizes \(18 \times 18\), in the first row, \(\approx 30 \times 30\) in the second row and exact values calculated with method of Bonsall and Maradudin in the third row.

Double tangent construction applied to the energy curve Fig.11 shows that only concentrations \(0, 1/4, 1/3, 1/2, 2/3, 3/4, 1\) are stable with respect to the phase separation at zero temperature. Thus at zero temperature the system is always a mixture of parts with these concentrations. For example if \(\bar{x}\) is between 0 and 1/4 then the system should split into two homogeneous parts with \(x = 0\) in one part and \(x = 1/4\) in another.

The slope of the double tangent lines gives the values of chemical potential at which the transition from one concentration to another should occur. In the region \(x > 1/2\) we have: \((\mu/J)_{1/2-2/3} = 0.0003\). \((\mu/J)_{2/3-3/4} = 0.5087\), \((\mu/J)_{3/4-1} = 0.5159\). The corresponding dependence \(\mu(x)\) at zero temperature shown in Fig.14 as the dotted curve.

Direct simulations of the \(\mu(x)\) curve were performed on lattices of different sample sizes: \(9 \times 9, 18 \times 18, 18 \times 20, 24 \times 24\) and \(30 \times 30\). Some results are shown in Fig.14. Crosses for the sample size \(18 \times 18\) show that there is no big difference with the results obtained on the sample of size \(9 \times 9\) at \((T/J) = 0.10\). For higher temperatures the difference is even less significant.

When we consider long range interactions in 2D, the amount of time needed to calculate the energies before and after the MC step increases quickly with the size of the system. In order to save time we tried to perform calculations on smaller samples when possible. Thus at high temperatures, we performed simulations on small \(9 \times 9\) samples. Every point is the result of averaging over 20,000 MC sweeps. Even at \((T/J) = 0.05\) there is almost no difference between the results of simulations on the lattices \(18 \times 18\) and \(30 \times 30\). However, at very low temperatures, there are some structures that can be observed only on large samples. For example at a temperature \((T/J) \leq 0.03\) we can clearly see concentrations \(3/5\) and \(6/7\) on the \(30 \times 30\) sample, but we cannot see these concentrations on the \(18 \times 18\) sample and they are not pronounced in case of the \(24 \times 24\) sample.

At low temperatures \((T \approx 0.01)\) there is a significant difference between the direct simulations of \(\mu(x)\) dependence and the predictions from the \(E(x)\) curve. In the simulations, the ranges of stability (with respect to the change in chemical potential) at concentrations \(x = 1/4, 3/4\) and 1/2 are much larger then they should be according to predictions from the energy curve, while at concentrations \(x = 1/3\) and 2/3 the ranges of stability are smaller. In simulations we also see stable concentrations 2/5 and 3/5 that should not appear according to the energy curve. Several effects can lead to this disagreement.

First of all, the difference between the energy and the free energy curves can be significant even at very low temperatures. This difference can lead to higher stabilities of some concentrations. Moreover some concentrations that should not appear, as follows from energy curve, can appear due to entropic contributions to the free energy. For example, configurations at \(x = 1/3\), and \(x = 2/3\) are highly ordered and have relatively small entropy. The concentrations between \(x = 1/3\) and \(x = 2/3\) are highly disordered (large entropy) and have approximately the same energy as energy of the system at concentrations 1/3 and 2/3. Thus one can expect that concentrations 1/3 and 2/3 will have smaller range of stability in \(\mu\), while concentration 1/2 will be more stable than follows from energy curve predictions. This is in agreement with Fig.14. This feature can also lead to the appearance of some configurations with \(1/3 < x < 1/2\) and 1/2 < \(x < 2/3\): for example \(x = 2/5\) and \(x = 3/5\). It also explains why we see this concentrations on larger samples and do not see them on smaller samples.

Another reason can be in the way simulations were performed at a constant value of the concentration. For example, if the system has average concentration \(1/2 < \bar{x} < 2/3\) then it should separate into two parts with concentrations \(x = 1/2\) and \(x = 2/3\). But since at every site the background charge is the same, the system cannot separate. This tendency of the system to phase separation, that cannot occur, creates internal stress and effectively increases the energies of intermediate concentrations. When simulations are performed at a constant value of the chemical potential there is no problem connected with background charge that prohibits the phase separation and there is no stress in the system. Thus energies at intermediate concentrations effectively become smaller.

The last reason that we can mention is the local character of the \(A\) and \(B\) operations that were used to introduce changes in the system. Their local character can also become important at low temperatures.

All the reasons discussed above can lead to the larger
regions of stability for concentrations \( x = 1/4, 1/2, 3/4 \) and to the smaller regions of stability for the concentrations \( x = 1/3 \) and \( x = 2/3 \). They also explain appearance of concentrations \( x = 2/5 \) and \( x = 3/5 \).

One can obtain the phase diagram for the triangular lattice in the same way as for the linear chain. In order to obtain the phase diagram of the system at low temperature we had to perform up to 100,000 MC sweeps on the lattice with the sample size equal to 30 \( \times \) 30. The phase diagram of the triangular lattice is shown in Fig. 15. Only half of the phase diagram is shown since it is symmetric with respect to \( x = 1/2 \). There are five distinct regions of phase separation that correspond to the transitions in concentrations \( 1/2 \rightarrow 3/5, 3/5 \rightarrow 2/3, 2/3 \rightarrow 3/4, 3/4 \rightarrow 6/7, 6/7 \rightarrow 1 \) at zero temperature. Some regions of phase separation exist only at low temperature and it is difficult to obtain an accurate phase boundary for them.

VI. CONCLUSION

We have introduced and studied a model to describe the possible ions ordering in layered double hydroxides. In the model ions situated at the sites of the triangular lattice interact through long range Coulomb interaction. The exactly solvable example of the linear chain was used to get insight into the model properties and to demonstrate the precision of the MC simulation methods employed. The model predicts multiple phase transitions and phase separation regions.

Our results are in agreement with experimental measurements in a sense that concentrations \( x = 1/4 \) and \( x = 1/3 \) are special\(^2\)–\(^6\). However a large number of predicted possible phases with different fractions of metal see in experiments. If we assume that some phase separation really occurs, then we should allow for the fact that there are different amounts of \([\text{CO}_3]^{2-}\) anions in the different regions of the same gallery. Regions with a large number of \([\text{CO}_3]^{2-}\) anions should have a larger interlayer spacing than the regions with a small number of \([\text{CO}_3]^{2-}\) anions. This should lead to mechanical stress in the system and that will also resist the tendency to phase separation. This competition between the Coulomb tendency to phase separation and mechanical stress can lead to the disintegration of the compounds and limit the composition range over which layered hydroxides can be synthesized. However the effect of nonzero temperature can move the system over the phase separation boundary and bring the system to a uniform distribution of charges. In this case there should not be internal stress in the compounds. Thus Al substituted layered Ni hydroxides that are stable at higher temperatures may become unstable and disintegrate at lower temperatures.

It would be interesting to see detailed experimental measurements that can support evidence for the charge ordering and the presence or absence of phase separation in these systems.

VII. ACKNOWLEDGEMENTS

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26 E.P. Wigner, Phys. Rev. 46, 1002 (1934).
28 This exact result only agrees with the approximate expression in equation (11) of reference$^1$ in the limit $x \to 0$. 

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$^*$ This exact result only agrees with the approximate expression in equation (11) of reference$^1$ in the limit $x \to 0$. 

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