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Order–disorder transitions in the intercalation compounds with repulsive interactions: application to Li_xTiS_2 battery

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Abstract. We have studied the triangular lattice gas model subject to nearest-neighbour repulsive interactions in the mean-field approach, leading to a clear understanding of the order–disorder transition and its effect on the intercalation process in transitional compounds such as Li_xTiS_2 . The triangular lattice division into three sublattices enables us to emphasize the appearance and the growth of the ordered phase. The computation of the incremental capacity defined as the response function of the TiS_2 cell to the Li^+ intercalation allows us to obtain information about the global behaviour of the system with regard to the intercalation process.

1. Introduction

The two-dimensional lattice gas model with nearest-neighbour repulsive interactions is of great interest since it provides a reasonable model for studying the transport properties of superionic conductors [1], intercalation processes in rigid host structures [2] or surface diffusion with the formation of ordered states [3].

Lithium intercalation batteries based on layered materials such as the transition-metal dichalcogenides seem capable of providing an efficient new method of electrical energy storage [4–6]. Thompson [7] has recently proposed that anomalies in the voltage–discharge curve of a system such as Li_xTiS_2 result from the ordering of the two-dimensional lattice gas of Li^+ ions due to the long-range Coulomb repulsion. In particular, he claims that peaks in the negative inverse slope $-\Delta x/\Delta V$ of the voltage versus composition curve appear at compositions for which there exist ordered arrangements of Li^+ ions. Thompson [7] obtained this result by adopting the electrochemical technique which involves applying a series of constant potential steps to an electrochemical cell. At each potential step the cell is permitted to attain quasi-open-circuit conditions by letting the current decay to a small but finite value. When small voltage steps are applied, the voltage–charge relation is highly precise and accurate in relation to the thermodynamic properties of the cell. Application to the Li_xTiS_2 couple show that the accumulated charge on each voltage step resembles an electrochemical potential spectrogram that provides evidence for the structural ordering of lithium in Li_xTiS_2 .

The data are collected in a derivative format that produces peaks in ‘intensity’ (incremental capacity) at the phase transition in cell components and when two-phase products are formed. The incremental capacity is then a response function to the

electrochemical cell analogous to the isothermal compressibility where the pressure is replaced by the cell potential at open circuit and the volume is substituted by the charge.

Therefore, this paper is specifically concerned with a general mean-field approach of the triangular lattice gas model for the problem of ordering of Li^+ ions in the system Li_xTiS_2 . This problem was studied by Berlinsky *et al* [2], through a renormalization group calculation. These systems favour the appearance of the order–disorder transition [8, 9] in which the lattice symmetry is broken. The order discriminates different sublattices which can be referred to by an index; for instance, in the case of the triangular lattice with $z = 6$ nearest neighbours the order discriminates three sublattices denoted A, B and C. In this paper we are concerned with the overall variation on the order parameter (regarded as the difference between the occupations of the three sublattices) with the average concentration \bar{p} , and the variation in the incremental capacity $d\bar{p}/d\mu$ which characterizes the response to the intercalation process.

2. Lattice gas model

The hopping approach to the many-particle problems is based on the lattice gas model in which each possible configuration is specified by a set of occupation numbers referring to the different lattice sites available for the mobile particles:

$$\{n\} = \{n_1, n_2, \dots, n_N\}.$$

The total Hamiltonian for the static properties of the system is written in terms of these occupation numbers as

$$H = -\frac{1}{2} \sum_{ij} \varepsilon_{ij} n_i n_j - \mu \sum_i n_i \quad (1)$$

where ε_{ij} denotes the pair interaction energy and is taken to be negative to represent repulsive interactions [10], μ is the chemical potential determining the average occupation number [11] and n_i represents the state of the i th site; n_i is equal to unity if the site i is occupied and is equal to zero if it is empty.

If $P\{n, t\}$ denotes the probability of finding a given configuration $\{n\}$ at time t , the dynamics of the system are governed by the master equation [12, 13]

$$\frac{\partial P(\{n\}, t)}{\partial t} = \sum_{\{n'\}} \omega(\{n'\}, \{n\}) P(\{n'\}, t) - \omega(\{n\}, \{n'\}) P(\{n\}, t). \quad (2)$$

The change from one configuration $\{n\}$ to another $\{n'\}$ occurs through the change in the occupation number in two nearest-neighbour sites. The rate of the configurations exchange is expressed by the transition frequency $\omega(\{n\}, \{n'\})$ which encloses all the physical information of the considered system. Generally, the transition frequency is supposed to satisfy the detailed balance condition

$$\omega(\{n\}, \{n'\}) P_{eq}(\{n\}) = \omega(\{n'\}, \{n\}) P_{eq}(\{n'\}). \quad (3)$$

We should note that different choices of the transition frequency compatible with the detailed balance condition are possible [14]. In our case, we limit the jumps of the mobile particles to between nearest-neighbour sites only. This is represented by the product of the first two Krönecker symbols in the transition frequency given by equation (4). The vectors \mathbf{k} and $\mathbf{k} + \mathbf{a}$ stand for the position of the neighbouring sites.

Exclusion of the hard core ensures that the jump of the particles is possible only if the arrival site is empty. This is taken into account by the factor $n_{\mathbf{k}}(1 - n_{\mathbf{k}+\mathbf{a}})$.

A third Kronecker symbol is added to ensure that the two considered configurations are distinguished by the jump of one and only one particle. Hence, all the occupations other than those referring to the permutation of the neighbouring sites state are conserved.

As the transition frequency contains physical information on the system, it must take into account the particle interactions. We include a transition weight $\omega(\{n\}, \mathbf{k}, \mathbf{a})$ that measures the energy variation caused by the jump of the mobile particles. Furthermore, only nearest-neighbour interactions are considered and are reduced to a site-independent parameter ε . Regarding these conditions, the transition frequency is written as [15]

$$\omega(\{n\}, \{n'\}) = \sum_{\mathbf{k}, \mathbf{a}} \omega(\{n\}, \mathbf{k}, \mathbf{a}) n_{\mathbf{k}} (1 - n_{\mathbf{k}+\mathbf{a}}) \delta_{n_{\mathbf{k}+\mathbf{a}}}^{n'_{\mathbf{k}+\mathbf{a}}} \delta_{n_{\mathbf{k}}}^{n'_k} \delta_{\{n\}, \{n'\}}^{\mathbf{k}, \mathbf{a}} \quad (4)$$

where \mathbf{a} is the jump vector and \mathbf{k} determines the site position.

The evolution is supposed to be a succession of independent jumps and the saddle-point energy is assumed to be insensitive to the environment (the barrier only depends on the depth of the initial site). Then, we assume that the diffusion mechanism is an activated process and the transition weight can be written as

$$\omega(\{n\}, \mathbf{k}, \mathbf{a}) = \omega_0 \exp\left(\gamma \sum_{\substack{i \\ \mathbf{u}_i \neq \mathbf{a}}} n_{\mathbf{k}+\mathbf{u}_i}\right) \quad (5)$$

where $\gamma = -\varepsilon/k_B T$ is the reduced energy, k_B is the Boltzmann constant, ω_0 is the Arrhenius factor and \mathbf{u}_i is the vector associated with the initial and the nearest neighbour sites.

Equation (5) can also be written as

$$\omega(\{n\}, \mathbf{k}, \mathbf{a}) = \omega_0 \prod_i \omega_r(n_{\mathbf{k}+\mathbf{u}_i}) \quad (6)$$

where

$$\omega_r(n_{\mathbf{k}+\mathbf{u}_i}) = \exp(\gamma n_{\mathbf{k}+\mathbf{u}_i}). \quad (6')$$

3. Mean-field approximation

Following the classical phenomenological Cahn–Hilliard [16] approach [17], we can consider averages of the transition weight leading to the thermodynamic analysis [15]. This consideration has the advantage of allowing rigorous and interesting exact mathematical solutions even though it cannot describe properly the physical reality. In fact, the property of symmetry is lost and there is an ambiguity in defining the chemical potential correctly. In this paper, averages are taken in the exponential in order to lead to the usual thermodynamic equilibrium.

The jump probability is then written as

$$\langle \omega_r(n_{\mathbf{k}+\mathbf{u}_i}) \rangle = \omega_0 \prod_i \omega_r(p(\mathbf{k} + \mathbf{u}_i)) = \omega_0 \prod_i \exp(\gamma p(\mathbf{k} + \mathbf{u}_i)) \quad (7)$$

where $p(\mathbf{k} + \mathbf{u}_i)$ is the probability of finding a particle in the site $\mathbf{k} + \mathbf{u}_i$.

Calculation of the time evolution of the concentration is made in the limit of the mean-field approach which states that the probability $P(\{n\}, t)$ can be factorized as

$$P(\{n\}, t) = \prod_{\mathbf{k}} p(n_{\mathbf{k}}, t) = \prod_{\mathbf{k}} p(\mathbf{k}, t). \quad (8)$$

The time evolution of the average concentration $p(\mathbf{k})$ is given by the following equation:

$$\frac{\partial p(\mathbf{k})}{\partial t} = - \sum_{\mathbf{a}} \langle J_{\mathbf{k}, \mathbf{k}+\mathbf{a}}(\{n\}) \rangle \quad (9)$$

where

$$p(\mathbf{k}) = \langle n_{\mathbf{k}} \rangle = \sum_{\{n\}} n_{\mathbf{k}} P(\{n\}, t)$$

and where the density of the current flux is written as

$$\langle J_{\mathbf{k}, \mathbf{k}+\mathbf{a}}(\{n\}) \rangle = \omega(\mathbf{k}, \mathbf{a}) p(\mathbf{k})(1 - p(\mathbf{k} + \mathbf{a})) - \omega(\mathbf{k} + \mathbf{a}, -\mathbf{a}) p(\mathbf{k} + \mathbf{a})(1 - p(\mathbf{k})). \quad (10)$$

4. Lattice division: introduction of the order parameter

The triangular lattice is divided into three interpenetrating sublattices A, B and C, such that any site in one of them, say A, has three nearest neighbours in each of the other two sublattices, B and C (figure 1). This representation can be justified by the work of Kaburagi and Kanamori [18, 19]. The evaluation of the order in the system is then possible through the introduction of three order parameters $\eta^{\alpha\lambda}$ which represent the difference between the occupations of the three sublattices and are defined as follows:

$$\eta^{\alpha\lambda} = |p^\alpha - p^\lambda|$$

with $\alpha, \lambda = A, B$ or C and $\lambda \neq \alpha$.

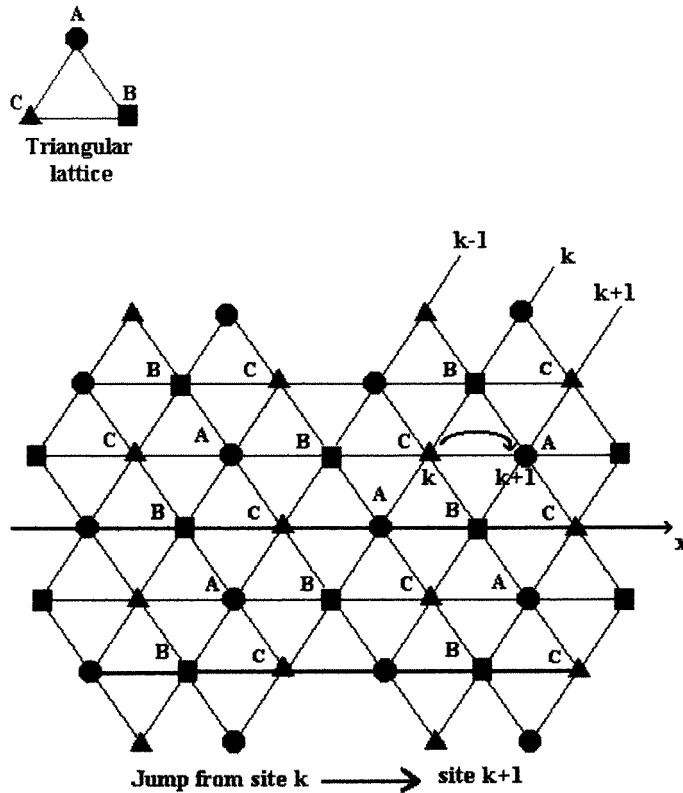


Figure 1. Representation of the triangular lattice with its three interpenetrating sublattices A, B and C, so that any site in one of them, say A, has three nearest neighbours in each of the other two sublattices B and C.

Hence there are three kinetically coupled master equations referring to the time evolution of each sublattice average concentration. In these equations, the density of current flux describes the diffusion in the Ox direction as the jumps in the Oy direction complement each other:

$$\frac{\partial p^\alpha(\mathbf{k})}{\partial t} = \sum_{\alpha} \sum_{\lambda \neq \alpha} J_a^{\alpha\lambda}(\mathbf{k}) \quad (11)$$

where $J_a^{\alpha\lambda}(\mathbf{k})$ is the density of current from the sublattice α to sublattice λ and $p^\alpha(\mathbf{k})$ is the average concentration of the sublattice α :

$$J_a^{\alpha\lambda}(\mathbf{k}) = \omega^{\alpha\lambda}(\mathbf{k}, \mathbf{a}) p^\alpha(\mathbf{k})(1 - p^\lambda(\mathbf{k} + \mathbf{a})) - \omega^{\lambda\alpha}(\mathbf{k} + \mathbf{a}, -\mathbf{a}) p^\lambda(\mathbf{k} + \mathbf{a})(1 - p^\alpha(\mathbf{k})) \quad (12)$$

where $\alpha, \lambda = A, B$ or C and $\lambda \neq \alpha$.

5. Numerical results

Numerical resolution of equation (11) is carried out, as in the case of the square lattice [20], under the following conditions.

(i) The lattice is semi-infinite in the main diffusion direction Ox and finite and periodically bounded in the Oy direction ($0 < y < L$).

(ii) There is a source at the position $x = 0$ ($p(x = 0, y, t) = 1, \forall t$) which feeds the lattice and a well at a sufficiently large abscissa ($p(x_M, y, t) = 0, \forall t$).

(iii) The calculation was done with box dimensions ($L_y = 101; L_x \gg L_y$).

In figure 2, the dependence of the order parameter on the lattice average concentration is represented for different values of the reduced energy γ . We observe that the order in the lattice is related to a break in the occupation symmetry of the lattice. There exists a minimal concentration which depends on the interaction regime. This critical concentration decreases for increasing pair interaction energy. The transition to an ordered phase is specified by the growth of the ordered structure until the commensurate phases of the lattice. Hence long-range order appears for the concentrations 1/3 and 2/3. Going beyond these values, the intercalation process leads the system progressively into its disordered phase.

The occupation of the sublattices (figure 3) shows that two of them present similar behaviours. Let B and C be the equivalent sublattices. Hence, the kinetic equations (11) are reduced to only two equations which govern the dynamics of the diffusion process. It follows that the order in the triangular lattice can be characterized by only one order parameter that measures the difference between the occupancies of A and the equivalent sublattices.

In figure 3, we have found the ground-state structures for the triangular lattice gas with nearest-neighbour repulsions only; we obtained the following equilibrium configurations.

(1) For $\bar{p} = 1/3$ the A sublattice is more highly occupied than are the B and C sublattices. In the limit of the very strong interactions ($\gamma \gg 1$), we tend to the case where the sublattice A is full and the sublattices B and C are empty.

(2) For $\bar{p} = 2/3$ we have the opposite case.

We define by p^ν ($\nu = A, B, C$) the probability that the site of sublattice ν is occupied by an ion. The resolution affects only half the concentration interval. The second part is attained by means of the usual relation of the symmetry-particle gap with the gap bears on the two equivalent sublattices. The system evolution obtained shows that a long-range order is established for the concentrations 1/3 and 2/3, whereas there is finite-range order on both sides of these concentrations.

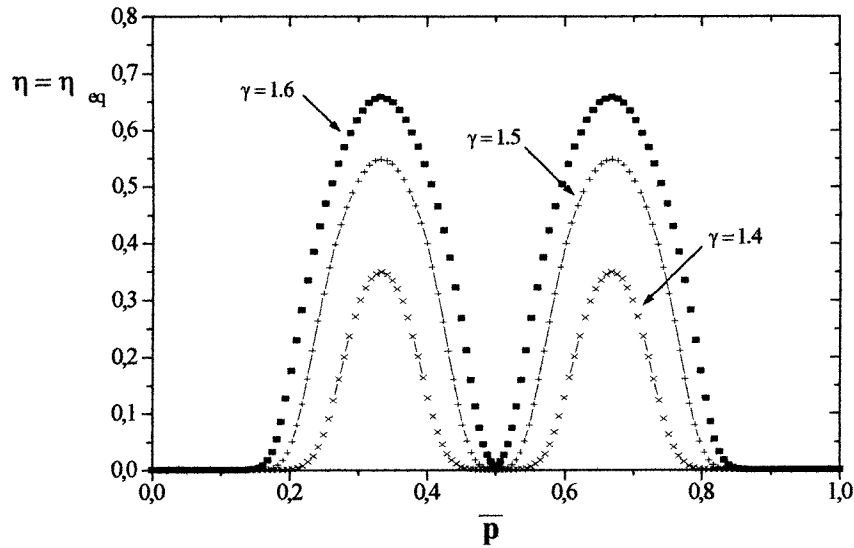


Figure 2. Evolution of the order parameter for different reduced energies. The arrows indicate the different values of the reduced energies.

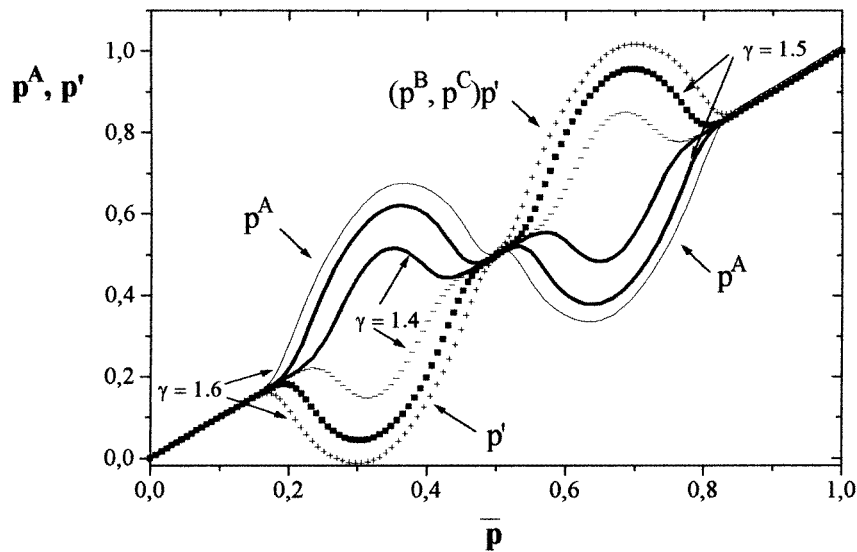


Figure 3. The breakdown of the occupation symmetry of the triangular lattice.

Nevertheless, the dynamics of the triangular lattice are governed by the temporal evolution of the average concentrations p^A and p' where upper index and apostrophe denote the sublattice A and the equivalent sublattices B and C, respectively. The equations can be written in terms of the order parameter η and the lattice average concentration \bar{p} at abscissa k .

Here, the order parameter designates the difference between the occupations the

equivalent sublattices and the third sublattice:

$$\frac{\partial \bar{p}(\mathbf{k})}{\partial t} = \frac{1}{2} \sum_a D_{-a} \bar{J} \mathbf{a}(\mathbf{k}) \quad (13)$$

$$\frac{\partial \eta(\mathbf{k})}{\partial t} = - \sum_a (J_a^{A(BC)}(\mathbf{k}) - J_a^{(BC)A}(\mathbf{k})) \quad (14)$$

where

$$\begin{aligned} \bar{J} \mathbf{a}(\mathbf{k}) &= \frac{1}{2} (J_a^{A(BC)} + J_a^{(BC)A}) \\ p'(\mathbf{k}) &= (p^B(\mathbf{k}) + p^C(\mathbf{k}))/2 \\ \eta(\mathbf{k}) &= (p^A(\mathbf{k}) - p'(\mathbf{k})) \\ \bar{p}(\mathbf{k}) &= (p^A(\mathbf{k}) + 2p'(\mathbf{k}))/3 \end{aligned}$$

and $J_a^{A(BC)}(\mathbf{k})$ is the current from sublattice A to sublattices B and C.

Contrary to equation (13), the temporal evolution of the order parameter cannot be written in the form of a conservative equation as the variable itself is not preserved. Starting from equations (13) and (14), we can recover the exact result concerning the evolution of the order parameter with the average concentration. This result is in good agreement with the result found by the three coupled equations (11). This will be discussed in a future publication [21].

6. Incremental capacity

The basic idea of calculation of the incremental capacity consists in transforming the expression of the currents flux into a contribution S , symmetrical with respect to the initial and final state, and a factor which is the difference between a local function C invariant to the transformations of the local point group of symmetry, taken at the final and initial states [17]:

$$J_a^{A(BC)}(\mathbf{k}) = S(C^A - C') \quad (15)$$

where

$$S = \omega_0(1 - p^A)(1 - p') \quad (16)$$

and

$$C^A = \exp^{(Z\gamma p')} \exp^{(\gamma p^A)} \frac{p^A}{1 - p^A} \quad (17)$$

where Z is the number of nearest-neighbour sites.

At the equilibrium state, the quantities C^A and C' are conserved. C is equivalent to the absolute activity that permits us to define the chemical potential μ :

$$\beta\mu = \ln C.$$

Hence, we derive the following expression for the incremental capacity:

$$\frac{d\bar{p}}{d\mu} = \beta C \left(\frac{\partial C}{\partial \bar{p}} + \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial p} \right)^{-1} \quad (18)$$

and

$$\eta \Big|_{t \rightarrow \infty} = \eta_{eq}.$$

The fine structure which appear in the curve representing the incremental capacity are introduced naturally in this equation as the incremental capacity takes into account the whole variation in the order parameter with average concentration.

The numerical resolution of equation (18) leads to the curve shown in figure 4, where we report the variation in the incremental capacity for different values of the reduced energy, whereas in figure 5 we report its temporal variation for a fixed value of the reduced energy $\gamma = 1.6$. In figure 4, $d\bar{p}/d\mu$ is symmetrical around $\bar{p} = 1/2$. The minimum at $\bar{p} = 1/3$ corresponds to a sharp rise in μ and is produced by the exclusion of nearest-neighbour pairs of occupied sites for $\bar{p} \leq 1/3$, as in other studies [2, 8, 22].

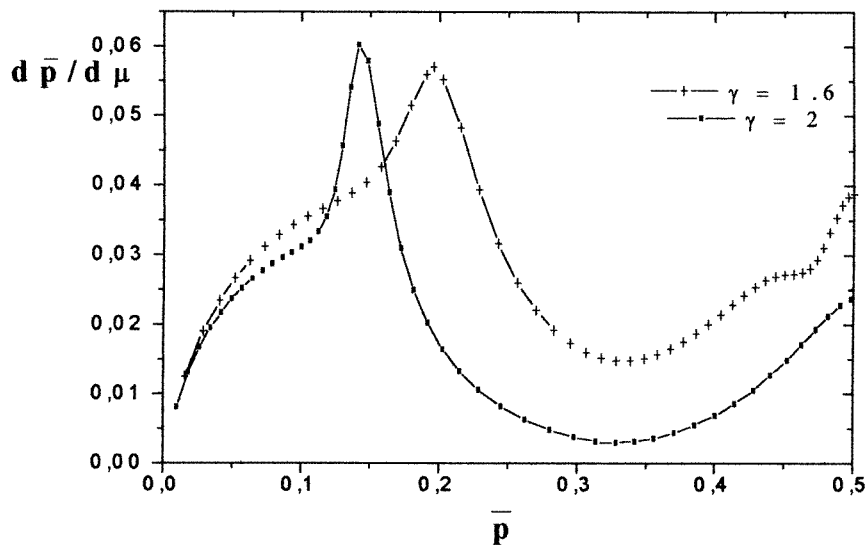


Figure 4. Calculated derivative average concentration $d\bar{p}/d\mu$ with respect to the chemical potential versus average concentration for the triangular lattice gas with different reduced energies.

The peaks near $\bar{p} = 0.15$ for $\gamma = 2$, and $\bar{p} = 0.2$ for $\gamma = 1.6$ correspond to the onset of long-range order as \bar{p} increases, and those near $\bar{p} = 0.4$ correspond to the destruction of this long-range order. In figure 5, we notice that, by increasing the time, only the peaks at $\bar{p} = 0.2$ decrease and that is caused by the increase in the chemical potential μ with time. We thus confirm the conclusions of Berlinsky *et al* [2] and others [22–24] concerning the significance of the minima and maxima of the incremental capacity. The curves obtained are in good agreement with the results obtained by the Monte Carlo and renormalization group [8, 25] methods. The consideration of the mean-field approach permits us to exploit more easily the dynamics of the system. Hence, we shall use the simplicity of the calculations in this approach to compute the diffusion coefficient for both square and triangular geometry and to compare with other studies [26–30].

7. Conclusion

We have presented here the establishment and the evolution of the ordered phase for the triangular lattice gas with only nearest-neighbour repulsive interactions. The main effect

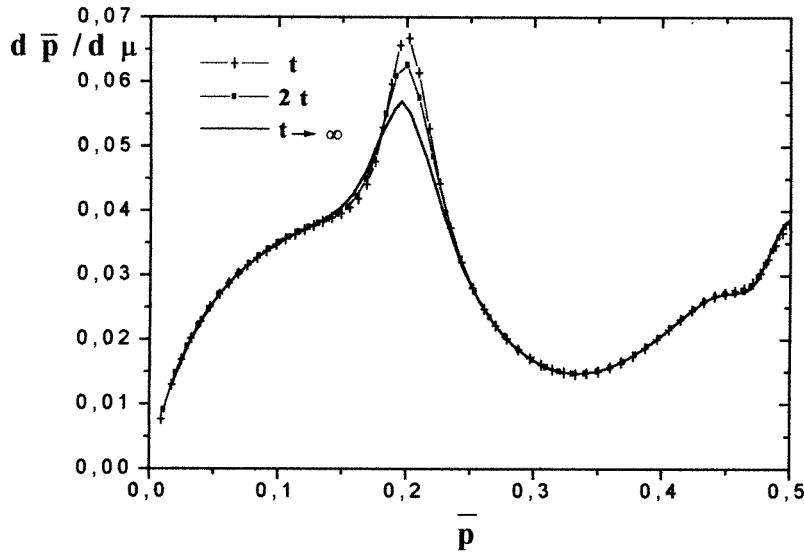


Figure 5. Effects for the order establishment at the equilibrium on the mean-field approach of the incremental capacity. $t \rightarrow \infty$ can be considered as the infinite time ($\gamma = 1.6$).

of this condition is a second-order transition between the ordered and disordered phases at $\bar{p} = 1/3$ and $2/3$. This is reflected in the curves relative to the phase separation and to the response to the intercalation process. We thus confirm the validity of the lattice gas model in the mean-field approach as a first approximation for the problem of ordering Li^+ ions in systems such as Li_xTiS_2 . The advantage of the mean-field approach is to permit us to treat the dynamics of the system more easily; thus we expect to extend this approach to the computation of the diffusion coefficient. More details will be given in a future publication [21].

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