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Molecule Formation and the Farey Tree in the One-Dimensional Falicov–Kimball Model

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The ground-state configurations of the one-dimensional Falicov–Kimball model are studied exactly with numerical calculations revealing unexpected effects for small interaction strength. In neutral systems we observe molecular formation, phase separation, and changes in the conducting properties; while in nonneutral systems the phase diagram exhibits Farey tree order (Aubry sequence) and a devil's staircase structure. Conjectures are presented for the boundary of the segregated domain and the general structure of the ground states.

KEY WORDS: Falicov–Kimball model; ground states; phase diagram; phase separations; molecules.

1. INTRODUCTION

The study of the general properties of fermion systems, such as metal–insulator transitions, crystal formation, and transitions to mixed-valence states, on the basis of microscopic models, is a domain of vigorous research. Among the models being considered, growing attention is being paid to a simple model proposed almost a quarter of a century ago by Falicov and Kimball.$^{(1)}$ This model was put forward to describe metal–insulator transitions in transition-metal and rare-earth materials, where an analysis of the experimental data suggested that these transitions are of purely electronic origin.

Dedicated to Prof. Philippe Choquard, on the occasion of his 65th birthday, and, by anticipation, in honor of his retirement.

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The first investigations of the Falicov–Kimball model, carried out by means of approximate methods, such as mean-field or coherent phase approximations,(2) led to contradictory results and reduced the general interest in the model. However, in 1986 Kennedy and Lieb(3) and independently Brandt and Schmidt(4) obtained rigorous results showing the existence of a phase transition at sufficiently low temperatures. They considered the simplest version of the model with only one band and spinless fermions, later called the spinless Falicov–Kimball model. Even this simplified version has numerous physically sound interpretations.(2, 3) In one of them, related to crystal formation, the system is viewed as consisting of quantum electrons hopping over a lattice and classical ions occupying some of the lattice sites. The interesting case occurs when the lattice consists of two equivalent sublattices and electrons are allowed to hop only from a site belonging to one sublattice to a nearest neighbor that belongs to the other sublattice. The only interaction is the on-site attraction (or repulsion) between electrons and ions and the hard-core repulsion between ions.

If the densities are equal to 1/2, or equivalently, if the chemical potentials correspond to the hole–particle symmetry point (half-filled-band case), then it has been proved that in dimensions two and higher this simple interaction leads to an order–disorder transition as the temperature is varied.(3, 4)

In the low-temperature phase the ions arrange themselves into a periodic structure, where they occupy only one of the sublattices. An important point to achieve this remarkable result is the fact that, in distinction to other lattice fermion models, a study of the Falicov–Kimball model can be reduced to a study of tight-binding Schrödinger equations in a variety of potentials. At each site these potentials assume only two values, say 0 or $-U$, that correspond to the absence or presence of an ion at this site. Let us underline that contrary to band theory, where the potential in the Schrödinger equation is fixed, the potential is here a variable and the problem is to find that potential whose contribution to the partition function is dominant (the so-called annealed problem).

One consequence of this fact is that the model can be studied by comparing the ground-state energies corresponding to certain classes of potentials (ion configurations), i.e., by constructing restricted phase diagrams for a finite or infinite system. Initially the method of restricted phase diagrams was applied to a two-dimensional system in ref. 5 and to a one-dimensional system in ref. 6.

In recent years numerous papers devoted to the spinless Falicov–Kimball model have appeared. They have dealt mainly with the following topics: various generalizations of the first rigorous results (quoted above),(7-10) investigations of the segregation principle (first formulated by Freericks and Falicov(6)),(11-13) investigations of the effective interaction between the ions,(14-17) and attempts to find the general structure of the ground-state phase diagram of the one-dimensional system, in particular new candidates for low-temperature configurations of the ions.(6, 18) We shall refer to the papers cited here in due course.

This paper belongs to the last of the mentioned groups. It is organized as follows. In Section 2 we provide the reader with the relevant informations, definitions, and notations. In Section 3 we begin our study of the ground states with the investigation of neutral systems. For such systems an interesting theorem has been obtained for large values of the coupling constant U,(6, 12) and this result was generally expected to be valid for all values of U. However, as we discuss in Section 3, the qualitative understanding of this theorem suggests that it can no longer be correct for small U. Since the theorem was established using the canonical formalism, we start our analysis with the canonical ensemble. Furthermore, to have some idea about the structure of the ground states, we consider first finite but large systems for which we can use existing computer programs to compute explicitly the ground-state energies for all possible configurations and thus find the configuration with minimal energy. We then consider infinite systems and study all the periodic configurations with periods less than some specific values. This analysis will show that for sufficiently small coupling constant U there appear phenomena of segregation (phase separation) and thus the grand canonical formalism is better adapted to the problem. In Section 4 we then describe the results obtained in the grand canonical formalism for neutral as well as nonneutral systems. Finally in Section 5 we summarize our observations, conclusions, and conjectures.

2. DEFINITIONS AND NOTATIONS

The object of this work is to study the ground-state properties of the one-dimensional spinless Falicov–Kimball model. This model describes a system of itinerant spinless quantum fermions interacting with classical ions on a one-dimensional lattice Λ. Whenever the lattice has a finite number $|\Lambda|$ of lattice sites we impose periodic boundary conditions. The Hamiltonian is

$$H_\Lambda = \sum_{x \in \Lambda} (-a_x^* a_{x+1} - a_{x+1}^* a_x - Uw(x) a_x^* a_x) \tag{1}$$

where a_x^*, a_x are the creation and annihilation operators of itinerant spinless electrons and $w(x) = 0$ or 1 is the number of ions at the lattice site x. The total number of electrons $N_e = \sum_{x \in \Lambda} a_x^* a_x$ and the total number of ions (in the configuration w) $N_i(w)=\sum_{x\in\Lambda} w(x)$ are the conserved quantities. The function $w(x)$, $x\in\Lambda$, is called the ion configuration. The electrons can hop only between nearest neighbor sites and the corresponding kinetic energy matrix elements are set to unity. Therefore in H_Λ there is only one independent parameter expressed in these units: the electron–ion interaction U.

For a given configuration $w(x)$ the Hamiltonian (1) is the second quantized form of the one-particle operator whose matrix elements are

$$h_{xy}=-t_{xy}-Uw(x)\delta_{xy} \tag{2}$$

where

$$t_{xy}=\begin{cases}1 & \text{if } y=x\pm 1\\ 0 & \text{otherwise}\end{cases} \tag{3}$$

In the following, when we speak of the spectrum of the configuration w we mean the spectrum of this one-particle Hamiltonian. The bands (gaps) in this spectrum are referred to as the bands (gaps) of the configuration w. The ground-state energy $E^U(w;N_e)$ of the system (1) corresponding to N_e electrons and the ion configuration w is equal to the sum of the N_e lowest energy levels of the single-particle Hamiltonian (2).

Applying to (1) the unitary hole–particle transformation with respect to the ions, we obtain

$$E^{(U)}(w^*;N_e)=E^{(-U)}(w;N_e)-UN_e \tag{4}$$

where $w^*(x)=1-w(x)$, while with respect the the electrons we get

$$E^{(U)}(w;N_e)=E^{(-U)}(w;|\Lambda|-N_e)-UN_i(w) \tag{5}$$

Therefore we can reduce the range of N_e and N_i considered and arbitrarily fix the sign of U (in the sequel we drop the superscript U from E). We choose $U>0$, i.e., the particles attract each other at the same lattice site.

We study also the infinite systems in the thermodynamic limit. The limit is taken in such a way that the particle densities per site $N_e/|\Lambda|$, $N_i/|\Lambda|$ and the ground-state energy density $E(w;N_e)/|\Lambda|$ tend to the electron density ρ_e, the ion density ρ_i, and the ground-state energy density $e(w;\rho_e)$. For the periodic ion configuration w the Green function of the tight-binding Schrödinger equation and consequently the density of states $n(w)$, ρ_e, and $e(w;\rho_e)$ can be determined exactly.(19) However, the corresponding formulas contain the band edges of the spectrum of w, which are zeros of the polynomial whose order coincides with the period of w. At this point it is necessary to perform numerical calculations.

The problem we want to investigate is to find the *ground-state configurations* (g.s.c.), i.e., the zero-temperature phase diagram. In the canonical formalism one is given the electron and ion densities (ρ_e, ρ_i) and the task is to find the configurations $\bar{w}$ that minimize the energy $E(w, N_e)$, $N_i(w) = N_i$, or the energy density $e(w, \rho_e)$, $\rho_i(w) = \rho_i$. In the following sections we shall construct "restricted phase diagrams," which amounts to minimizing the set of functions $e(w, \rho_e)$, where w runs over some specified class of admissible configurations, for example, the class of all periodic configurations with period smaller than some fixed value. Since the minimum of a set of convex functions is not necessarily convex, one has to take the convex envelope of the minimum. For those values ρ_e where the convex envelope does not coincide with the minimum of the $e(w, \rho_e)$, the g.s.c. is then a mixture of two or more configurations. The configuration w of ions in the mixture w_1 & w_2 is defined as follows: the finite lattice Λ is partitioned into two parts Λ_1 and Λ_2; the restriction of w to Λ_1 and Λ_2 is w_1 and w_2 with $|\Lambda_1|/|\Lambda| = \alpha$ and

$$\rho_i = \alpha\rho_i(w_1) + (1-\alpha)\,\rho_i(w_2) \tag{6}$$

The thermodynamic limit is then taken, keeping α fixed.

In the grand canonical formalism one is given the electron and ion chemical potentials (μ_e, μ_i) and the task is to find the configurations $\bar{w}$ that minimize the free energy density

$$f(w; \mu_e, \mu_i) = e(w; \mu_e) - \mu_e\rho_e(w; \mu_e) - \mu_i\rho_i(w) \tag{7}$$

Again we shall construct "restricted phase diagrams," which amounts to minimizing $f(w; \mu_e, \mu_i)$ over some class of configurations. In this case there is no need to take the convex envelope since the free energy density (7) is a concave function of the chemical potentials.

In the following sections we shall consider special classes of configurations. It is useful to define them here and to introduce an appropriate notation. There are two translationally invariant configurations: the *full configuration*, denoted by $+$, where all the sites of the lattice are occupied $(\rho_i = 1)$, and the *empty configuration*, denoted by $-$, with no ions $(\rho_i = 0)$. The unique band of the empty configuration extends from -2 to 2 (while the band of the full configuration is translated by $-U$). At the Fermi level μ_F the electron density is

$$\rho_e(-; \mu_F) = \begin{cases} 0 & \text{if } \mu_F \leqslant -2 \\ \pi^{-1}\arccos(-\mu_F/2) & \text{if } |\mu_F| \leqslant 2 \\ 1 & \text{if } \mu_F \geqslant 2 \end{cases} \tag{8}$$

and the corresponding ground-state energy density is

$$e(-;\mu_F)=\begin{cases}-\pi^{-1}(4-\mu_F^2)^{1/2} & \text{if } |\mu_F|\leqslant 2\\ 0 & \text{otherwise}\end{cases} \tag{9}$$

A periodic ion configuration that does not belong to one of the two classes considered, with period q and p ions per unit cell ($\rho_i=p/q$), is denoted by p/q.

The unit cell of the *crenel configuration* $\{p/q\}$ consists of p consecutive sites occupied by the ions, while the remaining $q-p$ sites are empty. The *atomic most homogeneous configuration* with $\rho_i=p/q$ is denoted by $[p/q]$. In this configuration the ions in the unit cell are distributed in such a manner that the distances between two consecutive ions are either d or $d+1$ with $d\leqslant q/p<d+1$. Furthermore, the distribution of the distances d and $d+1$ has to be most homogeneous.(12, 20) More precisely, with p relatively prime to q, the position of the ions in the unit cell is given by k_j solutions of the equations $pk_j=j \bmod q$, $j=0, 1,..., p-1$.

Similarly we define the *n-molecule most homogeneous configuration* $[p/q]_n$, $n\geqslant 2$, where $\rho_i=p/q$ and p is a multiple of n. This configuration is defined in the same way as $[p/q]$, but replacing "ion" by "n-molecule" that consists of n consecutive ions. More precisely, with p/n relatively prime to q, the position of the ions in the unit cell is given by k_j solutions of the equations $(p/n)k_j=j \bmod q$, $j=0, 1,..., p-1$. In particular, $[n/q]_n$ is identical with $\{n/q\}$. In the following we denote the n-molecules by H_n.

The following example illustrates the above definitions: for $p=6$ and $q=10$ the unit cell for the crenel configuration $\{6/10\}$ is [●●●●●●○○○○], for the atomic most homogeneous configuration $[6/10]$ it is [●●○●○●●○●○], i.e., it is the extension of the unit cell corresponding to $[3/5]$, for the 2-molecule most homogeneous configuration $[6/10]_2$ it is [●●○○●●○●●○], and for the 3-molecule most homogeneous configuration $[6/10]_3$ it is [●●●○○●●●○○]. Finally, as an example of a periodic configuration 6/10 that is not a member of the above-mentioned classes we can take the one with the unit cell [●●○●●○●○●○]. The list of all the periodic ion configurations that enter into our phase diagrams is given in Table I.

The only aperiodic configurations that we shall consider are those that constitute a mixture of two or three periodic configurations described above. In particular, a mixture of the full and empty configurations is the so-called *segregated configuration*(6) where all the ions clump together. This segregated configuration is the g.s.c. when ρ_e/ρ_i is sufficiently small (Section 4). Other mixtures of the form $w\,\&\,-$, where w is a periodic configuration, will play an important role in our studies of neutral systems (Section 3). The density of states fo the mixture $w\,\&\,-$ is

$$n_\alpha(\mu)=\alpha n(w;\mu)+(1-\alpha)\,n(-;\mu) \tag{10}$$

Table I. Periodic Ion Configurations That Appear in the Restricted Phase Diagrams

ρ_e	ρ_i	Unit cell	ρ_e	ρ_i	Unit cell	ρ_e	ρ_i	Unit cell	ρ_e	ρ_i	Unit cell
1/11	$[2/11]_2$		1/5	$[2/5]_2$		2/7	[5/7]	●●●○●●○	5/12	8/12	●●●●○●○●●○●○
	$[3/11]_3$			$[3/5]_3$		3/10	[3/10]	●○○○●○○●○○		9/12	●●●●○●●●●○●○
1/10	$[2/10]_2$		4/19	[4/19]			4/10	●●○○●○○●○○	3/7	2/7	●○●○○○○
	$[3/10]_3$		3/14	[3/14]			5/10	●●○○●●○●○○		[3/7]	●○●○●○○
	$[4/10]_4$		2/9	[2/9]	●○○○○●○○○		$[6/10]_2$	●●○○●●○●●○		4/7	●○●○●●○
	$[5/10]_5$			3/9	●●○○○●○○○	1/3	[1/3]			5/7	●○●○●●●
1/9	$[2/9]_2$			$[4/9]_2$	●●○○●●○○○		$[2/3]_2$		4/9	3/9	●○●○●○○○○
	$[3/9]_3$			5/9	●●○○●●●○○	3/8	2/8	●○○●○○○○		[4/9]	●○●○●○●○○
	$[4/9]_4$			$[6/9]_3$	●●●○●●●○○		[3/8]	●○○●○○●○		5/9	●○●○●○●●○
1/8	$[2/8]_2$		1/4	[1/4]			4/8	●●○●○○●○		6/9	●○●○●●●●○
	$[3/8]_3$			$[2/4]_2$			5/8	●●○●●○●○	5/11	3/11	●○●○●○○○○○○
	$[4/8]_4$		3/11	[3/11]	●○○○●○○○●○○		$[6/8]_2$	●●○●●○●●		4/11	●○●○●○●○○○○
1/7	$[2/7]_2$			4/11	●●○○●○○○●○○	2/5	1/5	●○○○○		[5/11]	●○●○●○●○●○○
	$[3/7]_3$			5/11	●●○○●●○○●○○		[2/5]	●○○●○		[6/11]	●○●○●○●○●○●
	$[4/7]_4$			$[6/11]_2$	●●○○●●○○●●○		3/5	●●○●○		7/11	●●●○●○●○●○●
1/6	$[2/6]_2$			7/11	●●●○●●○○●●○		$[4/5]_2$	●●○●●		8/11	●●●●●○●○●○●
	$[3/6]_3$		2/7	[2/7]	●○○○●○○	5/12	[5/12]	●○○●○●○○●○●○	1/2	[1/2]	
2/11	$[4/11]_2$	●●○○○●●○○○○		3/7	●●○○●○○		6/12	●●○●○●○○●○●○			
1/5	[1/5]			$[4/7]_2$	●●○○●●○		[7/12]	●●○●○●●○●○●○			

where

$$n(-;\mu)=\pi^{-1}\,\mathrm{Re}(4-\mu^2)^{-1/2} \tag{11}$$

and $n(w;\mu)$ is given in ref. 19. Consequently, the electron and ion densities are

$$\rho_e=\alpha\rho_e(w)+(1-\alpha)\,\rho_e(-), \qquad \rho_i=\alpha p/q \tag{12}$$

where

$$\rho_e(w)=\rho_e(w;\mu_F)=\int_{-\infty}^{\mu_F} n(w;\mu)\,d\mu \tag{13}$$

and $\rho_e(-)$ is given by Eq. (8). Similarly, the energy density of this mixture is

$$e=\alpha e(w)+(1-\alpha)\,e(-) \tag{14}$$

where

$$e(w)=e(w;\mu_F)=\int_{-\infty}^{\mu_F} \mu\, n(w;\mu)\,d\mu \tag{15}$$

and $e(-)$ is given by Eq. (9).

The mixture of the configuration $w=p/q$ and the empty configuration is denoted $p/q\,\&\,-$ or p/q & *vacuum* (if the Fermi level μ_F is smaller than -2).

As a rule our considerations and our results refer to the infinite system. Only the preliminary results of Section 3, necessary to guide the future analysis and to see if finite-size effects are important, were obtained for finite systems (Fig. 4 and Tables III, V, and VI).

3. NEUTRAL SYSTEMS. PHASE DIAGRAMS IN THE CANONICAL ENSEMBLE

In this section we study the ground-state properties of the neutral systems in the canonical ensemble. If the system is finite we thus take $N_e=N_i=N$ and we are interested in the configurations $\bar{w}$ that minimize the energy $E(w;N)$.

If the system is infinite, then $\rho_e=\rho_i=\rho$ and the problem is to find the configurations $\bar{w}$ that minimize the energy density $e(w;\rho)$. We shall first consider only periodic configurations with $\rho=p/q$, p and q being relatively prime integers.

For large U and rational densities it was first conjectured(6) and then rigorously proved that the g.s.c. is the most homogeneous configuration of atoms.(12) Since this result was established using the perturbation series of $e(w)$ in powers of U^{-1}, the question naturally arises whether the restriction to large U is technical or fundamental. Until now it has been usually conjectured that such a theorem should be valid for all values of U.(12, 21) Indeed, the results of Kennedy and Lieb(3) and Brandt and Schmidt(4) for the half-filled-band case ($\rho = 1/2$) and the numerical studies of Freericks and Falicov(6) for $\rho = 1/2$, $1/3$ seemed to support this conjecture.

However, the analysis of a finite number of ions and electrons on an infinite lattice (with $N_e = N_i$), while providing a qualitative explanation of this result, suggests also that it cannot remain valid for small U. Indeed, for large U and to leading order in U^{-1} the energy of the neutral system is given by an effective two-body potential of the form $2(d+1)\exp[-\lambda(2d+1)]$, where d is the distance between the ions.(16) In other words, for large U an equal number of ions and electrons will form neutral atoms which repel each other with an effective two-body potential that is convex and decreasing. Using the result of Hubbard,(20) we thus conclude that for large U the g.s.c. of the neutral system with a finite density should be the most homogeneous configuration.

On the other hand, one can easily check that for $U \leqslant 2/\sqrt{3}$ the energy of the neutral 2-molecule is smaller than the energy of two neutral atoms that are infinitely separated. Indeed the ground-state energy E^{atom} of the neutral atom is

$$E^{\text{atom}} = -(4+U^2)^{1/2} \tag{16}$$

while the energy $E^{\text{2-molecule}}$ of the neutral 2-molecule is

$$E^{\text{2-molecule}} = \begin{cases} -2\dfrac{U^3}{U^2-1} & \text{if } U \geqslant 2 \\ -\dfrac{(U+2)^2}{U+1} & \text{if } U \leqslant 2 \end{cases} \tag{17}$$

Moreover for $U \leqslant 2$ the 2-molecule has only one bound state.

More data are contained in Fig. 1, where the energy of two ions and two electrons on the infinite lattice is shown as a function of the distance between the ions for different values of U. For large values of U the ground state consists of two neutral atoms at infinite distance. On the other hand, for small values of U this happens when one 2-molecule with one bound electron and one diffusion electron is formed. Similarly, Fig. 2 shows that the ion configuration that minimizes the energy of three ions and three

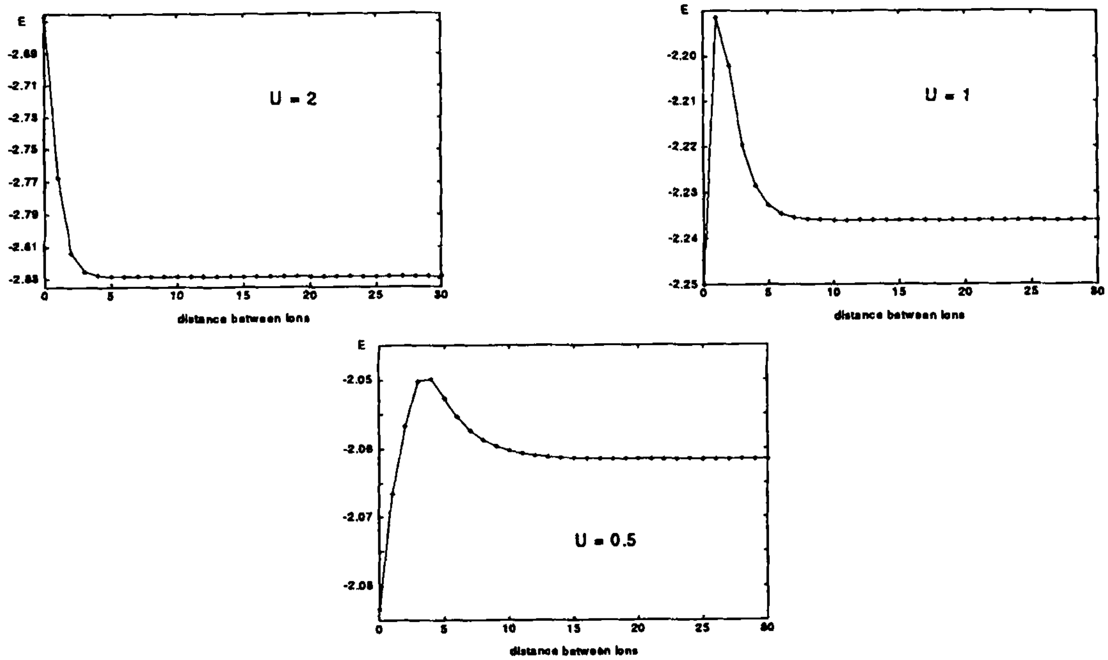

Fig. 1. Energy per ion for two ions and two electrons versus the distance between the ions.

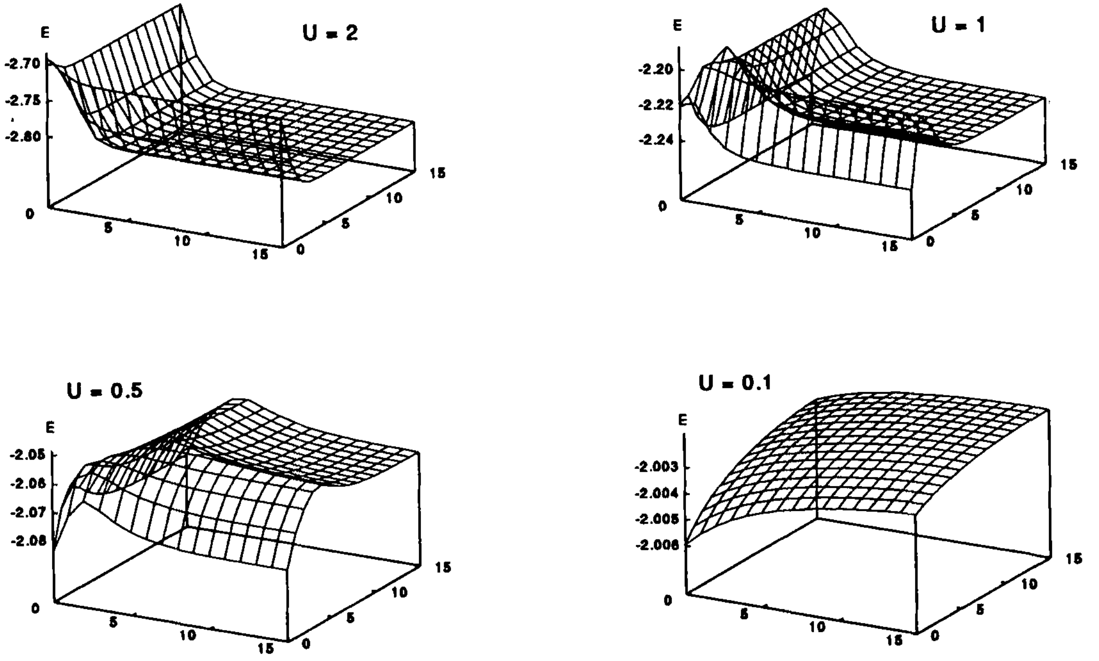

Fig. 2. Energy per ion for three ions and three electrons versus the two distances between the ions.

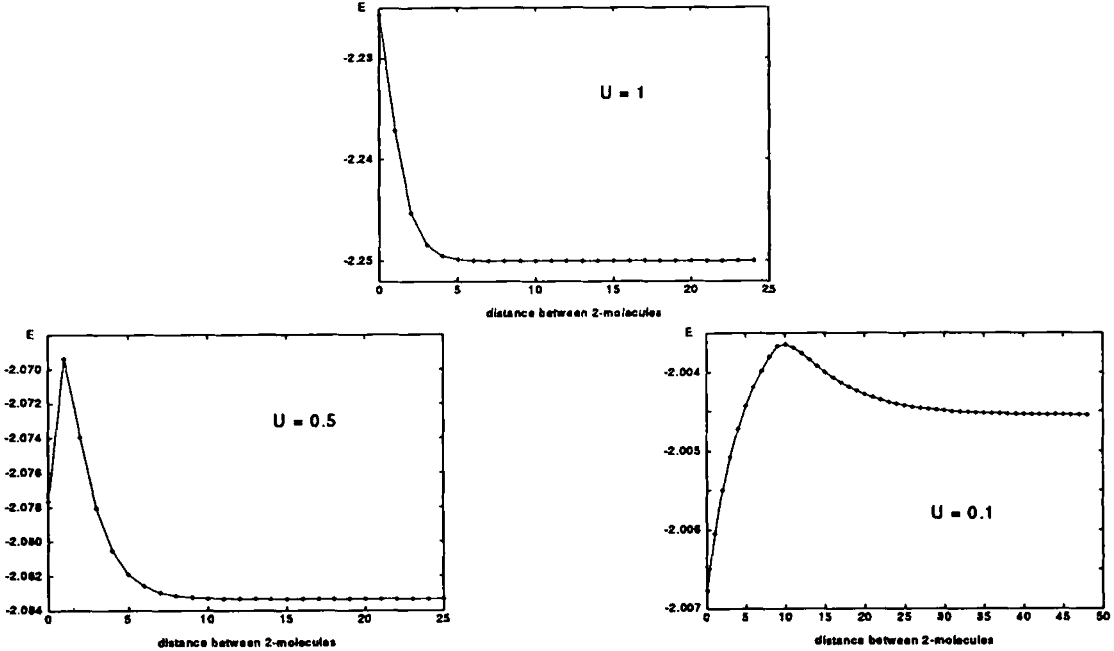

Fig. 3. Energy per ion for two 2-molecules and four electrons versus the distance between the molecules.

electrons depends on the value of U. There are three kinds of ground states: (1) three neutral atoms at infinite distance (U large), (2) one 2-molecule with one bound state and one neutral atom at infinite distance, and (3) one 3-molecule with one bound state (U small).

Finally we can see in Fig. 3 that the energy between two 2-molecules (and four electrons) presents the same properties as the energy between two ions: for sufficiently large U it is convex and decreasing and thus the ground state consists of two 2-molecules infinitely separated, while for U sufficiently small the ground state consists of one 4-molecule with one bound state. Although we have not checked it, we expect that the energy between two n-molecules (and $2n$ electrons) has similar properties. To conclude the above considerations of neutral systems with a finite number of ions, let us find the n-molecule with the lowest energy per ion as a function of U. The result is shown in Table II. We note that for each n-molecule there is an interval of U where its energy is minimal. Moreover, in this interval the n-molecule has only one bound state. We then conjecture that for given U, the neutral system with zero density of particles will form n-molecules, with $n = n(U)$, which are infinitely separated.

The above results suggest that, for sufficiently small U, the neutral systems with *nonzero density* might realize their ground state by forming n-molecules, $n > 1$, that are most homogeneously distributed. To test this idea we have considered a finite system of 512 sites and studied the restricted phase diagram for configurations of the form $[p/q]_n$. For example, for $\rho_i = 9/128$ ($N_i = N_e = 36$) we have considered the ion configurations whose unit cells are displayed in Table III. The results are given in Fig. 4. To determine the finite-size effect, the transition line between the atomic configurations H_1 and the 2-molecule configurations H_2 has been computed for a system of 200 sites and no significant difference was observed. We also

Table II. *n*-Molecules with Smallest Energy per Ion versus *U*

U interval	Type of n-molecule
$(1.155, \infty)$	H_1
$(0.511, 1.155)$	H_2
$(0.280, 0.511)$	H_3
$(0.175, 0.280)$	H_4
$(0.119, 0.175)$	H_5
$(0.086, 0.119)$	H_6
$(0.065, 0.086)$	H_7
$(0.051, 0.065)$	H_8
$(0.041, 0.051)$	H_9

Table III. Periodic Configurations for p = 9/128 Taken into Account in Fig. 4[a]

Type of molecule	Unit cell
H_1	(•)(13○)(•)(13○)(•)(13○)(•)(14○)(•)(13○)(•)(13○) (•)(13○)(•)(13○)(•)(14○)
H_2	(2•)(26○)(2•)(27○)(2•)(26○)(2•)(27○)(2•)(26○) (2•)(27○)(2•)(26○)(2•)(27○)(2•)(26○)
H_3	(3•)(39○)(3•)(40○)(3•)(40○)
H_4	(4•)(52○)(4•)(53○)(4•)(53○)(4•)(53○)(4•)(53○) (4•)(53○)(4•)(53○)(4•)(53○)(4•)(53○)

[a] In our notation, for instance (3•) stands for three consecutive sites occupied by ions, while (3○) stands for three consecutive empty sites.

compared the energy of the finite system with the energy of the corresponding periodic configuration of the infinite system (e.g., see Tables V and VI). From this analysis we can thus conclude that the usual conjecture concerning the ground state of a neutral system (mentioned at the beginning of this section) cannot be correct: for sufficiently small U and sufficiently small densities the most homogeneous configuration of atoms cannot be the ground-state configuration.

Of course from this analysis we cannot conclude that the molecular configurations $[p/q]_n$ are the true g.s.c. Therefore for some special values

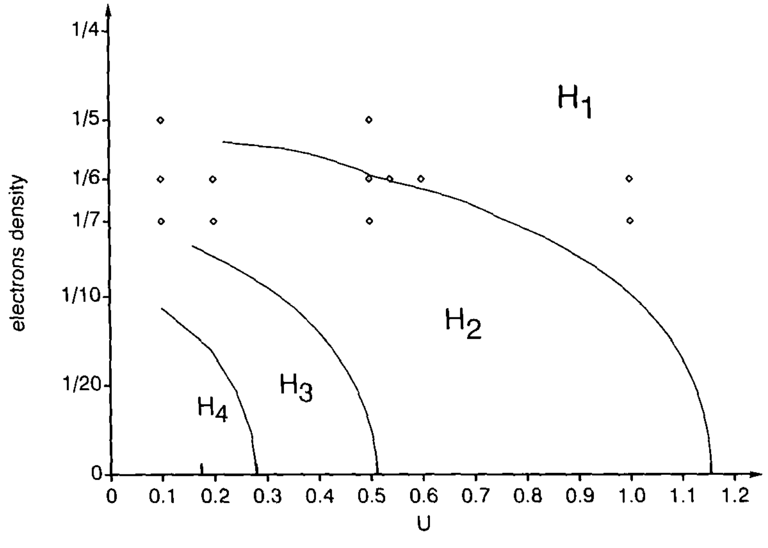

Fig. 4. Restricted phase diagram with respect to n-molecule most homogeneous configurations, $n \leqslant 4$, over the lattice of 512 sites. The points are special values discussed in the text.

of U and ρ (Fig. 4), and for an *infinite system*, we have computed the energies of *all* the periodic configurations with period smaller than or equal to some Q. The configurations $\bar{w}_p$ with the smallest energy and their energy are given in Table IV.

Clearly, for sufficiently small U and ρ the most homogeneous configurations of atoms or molecules are not the g.s.c. These results show that Theorem 1 of Freericks and Falicov(6) is not always correct: for $\rho = p/q$ there exist periodic configurations whose energy is smaller than the energy of atomic configurations and whose period is larger than q (similar results hold true for smaller values of U). However, we shall see in the sequel that, if the true g.s.c. is periodic, then it is given by the construction of Freericks and Falicov(6) and this remains true in the nonneutral case ($\rho_e \neq \rho_i$).

Furthermore, Table IV shows that for small densities and small U the particles tend to arrange themselves into molecules (as was the case at zero density) and lead us to think that the g.s.c. could be mixtures of periodic configurations of molecules and the empty configuration. To check this guess we have considered a system of six ions and six electrons on a lattice of 42 sites, i.e., $\rho = 1/7$. The energies of all ion configurations have been computed and the g.s.c. selected (see Table V). We see that the g.s.c. of this finite system ($\rho = 1/7$) are the mixtures of $\{2/7\}$ & $-$ or $\{2/6\}$ & $-$. However, Fig. 4 suggest that the mixture of $\{3/6\}$ & $-$ could come into competition if the lattice were sufficiently large. We have thus computed the energies of these three mixtures for a lattice of 420 sites and for the infinite lattice (see Table VI).

Table IV. Canonical Restricted Phase Diagram for an Infinite Chain and Special Values of (U, ρ)[a]

U	ρ	Period $\leqslant Q$	Unit cell	Energy	Energy ($[1/p]$)
0.10	1/5	20	●○○○○	−0.378 561	
0.10	1/6	24	●●○○○○●●(16○)	−0.321 413	−0.321 386
0.10	1/7	21	●●●(18○)	−0.278 539	−0.278 511
0.20	1/6	24	●●○○○○●●(16○)	−0.325 073	−0.324 972
0.20	1/7	21	●●○○○○○●(13○)	−0.281 342	−0.281 238
0.50	1/5	20	●○○○○	−0.401 926	
0.50	1/6	24	●●○○○●●(17○)	−0.338 876	−0.338 655
0.50	1/7	21	●●○○○○○●(13○)	−0.292 371	−0.291 988
0.54	1/6	18	●●○○○○●(11○)	−0.340 847	−0.340 815
0.60	1/6	18	●○○○○○	−0.344 206	
1.00	1/6	24	●○○○○○	−0.371 472	
1.00	1/7	21	●○○○○○○	−0.318 390	

[a] The ground-state configurations were selected among all the periodic configurations whose period does not exceed Q.

Table V. Ground-State Configurations of Neutral System with 42 Sites and Density $\rho = 1/7$

U	Unit cell	Energy
0.1	••(5○)••(5○)••(26○)	−0.278 265
0.2	••(4○)••(4○)••(28○)	−0.281 258

These new and surprising results show that for sufficiently small values of U and ρ the g.s.c. is indeed a mixture of some periodic configuration with the empty configuration. We have thus looked at the restricted phase diagram for all configurations that are mixtures of the empty configuration and a periodic configuration with period $q \leqslant 7$ for $\rho = 1/5$, $1/6$, $1/7$ and period $q \leqslant 10$ for $\rho = 1/10$. Note that, in particular, the most homogeneous configurations are among those considered. Table VII shows that the configurations minimizing the energy are mixtures of $\{p/q\}$ & $-$ (i.e., crenel configurations followed by the empty configurations) or the most homogeneous configurations of atoms. This observation suggests we restrict our attention to those configurations that are either most homogeneous or mixtures of the form $\{p/q\}$ & $-$. We have thus constructed the restricted phase diagram for all configurations that are either most homogeneous or mixtures of $\{p/q\}$ & $-$ with $q \leqslant 10$. This has been done in the range $U \in [0.01, 1.2]$, $\rho \in [0.1, 0.3]$, taking steps $\Delta U = 0.05$, $\Delta\rho = 0.005$. We have also considered the values of ρ (in the above range) of the form a/b with $b \leqslant 29$. In the domains that have not been expected to appear (e.g., $\{3/6\}$, between $\{2/6\}$ and $\{2/7\}$) finer steps were used: $\Delta U = 0.01$,

Table VI. Energy Density of the Mixture $\{p/q\}$ & $-$ for the Neutral System with Density $\rho = 1/7$, for a Lattice of 420 Sites, and for an Infinite Lattice, Compared with the Energy Density of the Atomic Most Homogeneous Configuration $[1/7]$

U	Configuration	Energy ($L = 420$)	Energy ($L = \infty$)
0.1	$\{2/7\}$ & $-$	−0.278 580	−0.278 679
	$\{3/6\}$ & $-$	−0.278 538	−0.278 535
	$\{2/6\}$ & $-$	−0.278 500	−0.278 500
	$[1/7]$		−0.278 511
0.2	$\{3/6\}$ & $-$	−0.281 470	−0.281 490
	$\{2/6\}$ & $-$	−0.281 452	−0.281 455
	$\{2/7\}$ & $-$	−0.281 441	−0.281 439
	$[1/7]$		−0.281 238

Table VII. Restricted Phase Diagram for Mixtures of the Form p/q & – (Infinite Lattice)

ρ	$U=0.1$	$U=0.2$	$U=0.3$	$U=0.4$	$U=0.5$	$U=0.6$	$U=0.7$	$U=0.8$	$U=0.9$	$U=1.0$	$U=1.1$
1/5	{2/5}	{2/5}	H_1	H_1	H_1	H_1	H_1	H_1	H_1	H_1	H_1
1/6	{2/6}	{2/6}	{2/5}	{2/5}	{2/5}	{2/5}	{2/5}	H_1	H_1	H_1	H_1
1/7	{2/7}	{3/6}	{2/6}	{2/6}	{2/6}	{2/6}	{2/5}	{2/5}	{2/5}	H_1	H_1
1/10	{3/9}	{3/8}	{3/8}	{2/8}	{2/7}	{2/7}	{2/7}	{2/6}	{2/6}	{2/6}	H_1

$\Delta\rho = 0.001$. Finally, the transition lines separating different domains of 2-molecules have been computed explicitly. The results are summarized in Fig. 5.

To achieve a better understanding of the transition we have fixed $U = 0.6$ and we have found that for $\rho \in [0.14, 0.15]$ the mixture of $\{2/5\}$ & $\{2/6\}$ & – has lower energy than $\{2/5\}$ & – or $\{2/6\}$ & –. Similarly for $\rho \in [0.18, 0.19]$ the mixture $\{1/5\}$ & $\{2/5\}$ & – has smaller energy than $\{1/5\}$ & – or $\{2/5\}$ & –. Therefore the transition lines should be replaced by transition boundaries with mixtures of one or two periodic molecular configurations and the empty configuration. Our investigations of the grand canonical phase diagram, described in the sequel, suggest that between two domains $[p/q]_n$ & – and $[p'/q']_n$ & – there is the domain $[(p+p')/(q+q')]_n$ & – and so on. On the other hand, between two adjacent domains $[p/q]_n$ & – and $[p'/q']_{n+1}$ & – there is a mixture $[p/q]_n$ & $[p'/q']_{n+1}$ & –.

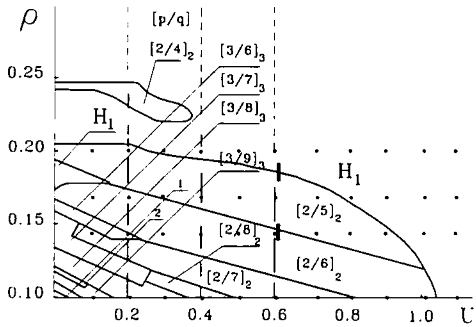

Fig. 5. Restricted phase diagram of the infinite neutral system in the canonical ensemble. All the mixtures of the form $\{p/q\}$ & –, with $q \leqslant 10$, and the atomic most homogeneous configurations whose period does not exceed 30 were taken into account. The dots correspond to the entries of Table VII. The configurations found in the grand canonical analysis are located at the vertical segments. The fat vertical segments represent the mixtures $\{1/5\}$ & $\{2/5\}$ & – and $\{2/5\}$ & $\{2/6\}$ & –. The domains labeled 1 and 2 are $[4/9]_4$ and $[4/8]_4$, respectively.

Let us summarize our observations. For neutral systems $(\rho_e = \rho_i = \rho)$ and for $U \leqslant 2/\sqrt{3}$ there is a critical density $\rho_c(U)$ such that for $\rho > \rho_c(U)$ the g.s.c. is atomic most homogeneous (as for $U > 2/\sqrt{3}$) and thus the g.s.c. varies from point to point. On the other hand, for $\rho < \rho_c(U)$, larger and larger molecules appear, and the g.s.c. remains a mixture of the periodic n-molecule configuration $[p/q]_n$ and the empty configuration, over a certain range of densities. As ρ decreases, the period q increases discontinuously until a value where a mixture $[p/q]_{(n+1)}$ & $-$ takes over.

Furthermore, if the g.s.c. is atomic most homogeneous, then the system is an insulator, while if the g.s.c. is a mixture, the system is a conductor. We thus have a transition from an insulator to a conductor as U decreases.

We now give an interpretation of our observations. We have already noticed that a finite number of ions and electrons on an infinite lattice will tend to make n-molecules (with one bound state only) which repel each other. For finite densities $\rho_i = \rho_e = \rho$ we would like to understand why the g.s.c. is a mixture of a periodic and the empty configuration and what is the physical mechanism responsible for the period q. Looking at the band structures of the periodic configurations $\{n/q\}$, we notice that the Fermi level μ_F of the mixture $\{n/q\}$ & $-$, corresponding to ρ, is in the gap between the first two bands (Fig. 6) and thus we have

$$\rho_i = \rho = \alpha \frac{n}{q}, \qquad \rho_e = \rho = \alpha \frac{1}{q} + (1-\alpha)\, \rho_e(-\,;\mu_F) \tag{18}$$

Thus

$$\rho_e^{\{n/q\}} = \alpha \frac{1}{q} = \frac{\rho}{n}, \qquad \rho_e(-\,;\mu_F) = \rho \frac{n-1}{n-\rho q} \tag{19}$$

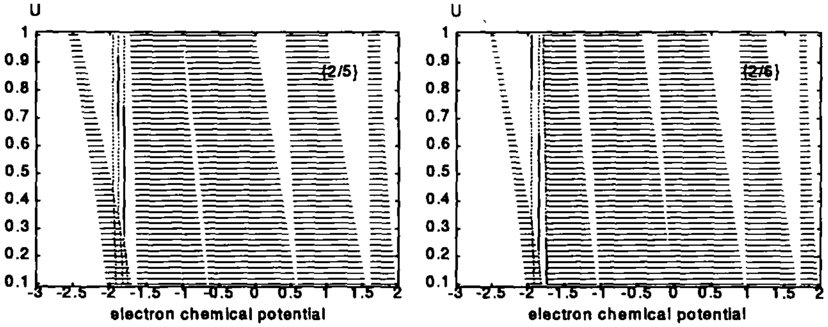

Fig. 6. Band structure of the configurations $\{2/5\}$ and $\{2/6\}$ for U between 0.1 and 1.0. The vertical lines show the location of the Fermi level for the densities $\rho = 1/10$, $1/7$, and $1/6$.

i.e., there is one electron per molecule in a bound state associated with the periodic ion configuration, while the remaining $\rho(n-1)/n$ electrons are in the extended states associated with the empty configuration of the ions. The corresponding energy density of the system is

$$e = \frac{\rho}{n}\left(qe^{(1)}(\{n/q\}) - 2(n-1)\frac{\sin y}{y}\right) \tag{20}$$

where $e^{(1)}(\{n/q\})$ is the energy density of the first band of the configuration $\{n/q\}$ and $y = \pi\rho(n-1)/(n-\rho q)$. Given ρ and n, the first term decreases as q increases, which can be seen as a consequence of the effective repulsion between n-molecules due to the bound electrons. On the other hand, the second term increases as q increases, which reflects the fact that the electrons in the empty space tend to increase the volume occupied. Therefore the period q that minimizes the energy density results from the competition between the effective repulsive force between the molecules and the pressure exerted by the electrons in the empty configuration of the ions.

4. PHASE DIAGRAMS IN THE GRAND CANONICAL ENSEMBLE

To obtain a better understanding of the phases at zero temperature, and to avoid the difficulties associated with mixtures that one has to consider in the canonical approach, we shall now investigate the *infinite system* in the grand canonical formalism. The problem is the following: given the chemical potentials (μ_e, μ_i), what is the configuration $\bar{w}$ that minimizes the free energy density $f(w; \mu_e, \mu_i)$?

In the following we consider only periodic configurations and we construct the phase diagrams restricted to periodic configurations with period smaller than or equal to 10, for interaction U taking values 0.6, 0.4, 0.2. Using the symmetry properties and the known results,(15) we can restrict our investigation to the region $\mu_e \in [-2-U, -U/2]$, $\mu_i \in [-U/2, 0]$. We have thus constructed the restricted phase diagrams in the following manner: for fixed μ_e and given w, the free energy is a linear function of μ_i. We can therefore calculate exactly the interval of μ_i for which the configuration $\bar{w}$ yields the minimum of the free energy (among all the configurations whose period does not exceed 10). This was done taking steps $\Delta\mu_e = 0.05$ and $\Delta\mu_e = 0.025$ in the case $U = 0.2$. Near the endpoint $(\mu_e = \mu_e^*)$ and near the transition lines finer steps were taken. The resulting phase diagrams are presented in Figs. 7, 9, 11, and 12. To study these diagrams we have also computed the band edges of all configurations that appear in Fig. 7 and we have marked the intervals of μ_e in which they are g.s.c. (see Fig. 8).

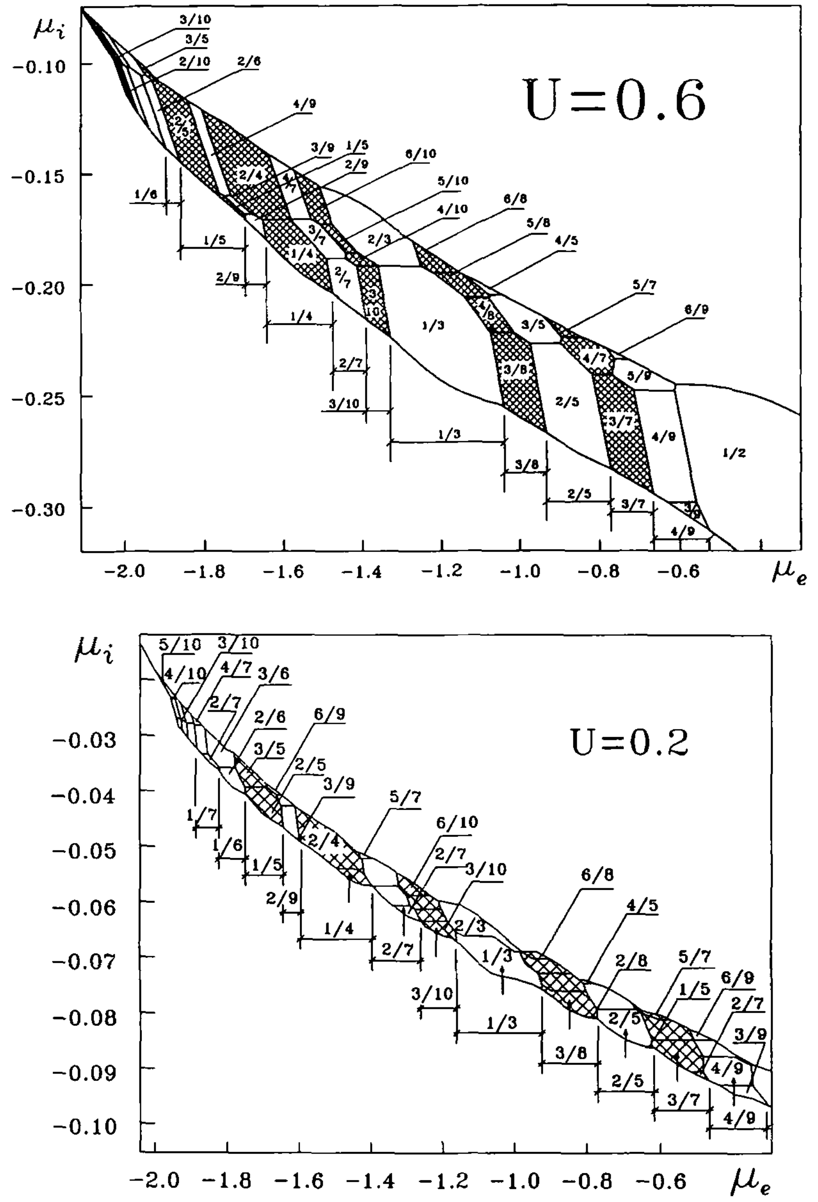

Fig. 7. Restricted phase diagram of the infinite chain in the grand canonical ensemble. All the periodic configurations whose period does not exceed 10 were taken into account. In the lower part of the diagram p/q indicates the electron density. In the different domains p/q indicates the ion density. For $\rho_e = p/q$ only $\rho_i = \tilde{p}/q$ appear.

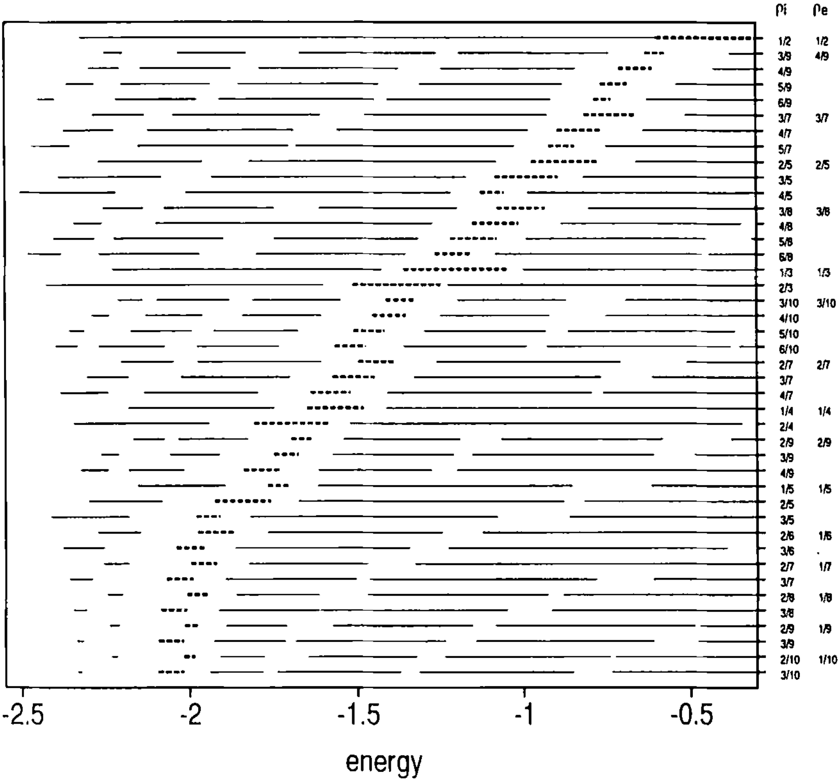

Fig. 8. Bands of the g.s.c. that appear in the grand canonical phase diagram (Fig. 7) for $U = 0.6$. The continuous horizontal lines mark the extents of the bands, the dashed segments the μ_e extents of the corresponding g.s.c.

Our analysis of the restricted phase diagrams, together with the information on the band structure, shows that the (μ_e, μ_i) plane is divided into three main domains: D_+, where the full configuration is the g.s.c.; D_-, where the empty configuration is the g.s.c.; and D, where the g.s.c. is different from the full or empty configuration. In the range $\mu_e \leqslant -U-2$ we already know[15] that for $\mu_i > 0$ the g.s.c. is the full configuration, for $\mu_i < 0$ the g.s.c. is the empty configuration, and for $\mu_i = 0$ all configurations have the same energy. For $-U-2 < \mu_e \leqslant \mu_e^*$, where $\mu_e^* < -2$ (see Fig. 12), the domains D_+ and D_- are separated by the curve

$$f(+; \mu_e, \mu_i) = f(-; \mu_e, \mu_i) = 0 \tag{21}$$

i.e.,

$$\begin{aligned} \pi\mu_i &= -(4-\tilde{\mu}_e^2)^{1/2} - \tilde{\mu}_e \arccos(-\tilde{\mu}_e/2) \\ \tilde{\mu}_e &= \mu_e + U \end{aligned} \tag{22}$$

A point (μ_e, μ_i) on this curve corresponds to a mixture of the full configuration with electron density

$$\rho_e(+, \mu_e) = \pi^{-1} \arccos(-\tilde{\mu}_e/2) \tag{23}$$

and the empty configuration with $\rho_e(-; \mu_e) = 0$ (vacuum). This is the so-called segregated configuration, in which all the ions clump together.$^{(6)}$ Along the curve (22) we have

$$\rho_e/\rho_i \leqslant \rho_e(+; \mu_e^*) \tag{24}$$

In other words, for densities ρ_e and ρ_i satisfying inequality (24) the g.s.c. is the segregated configuration. The problem of determining the value of μ_e^* will be addressed later.

Figure 8 shows that for each configuration $\bar{w}$ appearing in the phase diagrams (Fig. 7) the Fermi level is located in a gap of the corresponding spectrum. This property has also been observed for $U = 0.4$, while for $U = 0.2$ it does not seem to be true, since the boundary between two domains with $\rho_e = p/q$ and $\rho_i = p'/q$, $(p'+1)/q$, is not always a straight-line segment. However, we have checked that this property is indeed satisfied when we consider configurations with larger periods.

Figure 7 shows that the domain D consists of connected subdomains $D_{(\rho_e, \rho_i)}$ characterized by some periodic configuration of the ions and by a fixed density of electrons ρ_e (since the Fermi level is in the gap). We note that for given densities (ρ_e, ρ_i), if there is a periodic g.s.c. corresponding to this density, then it is associated with one connected domain $D_{(\rho_e, \rho_i)}$. This is a consequence of the fact that the free energy surface is concave and at zero temperature it is piecewise affine. It turns out also that the configuration of the ions can be determined by the following procedure given by Freericks and Falicov$^{(6)}$:

Let $\rho_e = p/q$, with p relatively prime to q and $\rho_i = p_i/q$, where p_i may not be relatively prime to q. Define the integer k_j by the relation $pk_j = j \bmod q$, $j = 0, 1, 2, \ldots$. Then the position of the ions in the unit cell is given by k_j with $j = 0, 1, 2, \ldots, p_i - 1$.

The following structure of D is remarkable: the union D_{ρ_e} of the domains $D_{(\rho_e, \rho_i)}$ corresponding to the same electron density $\rho_e = p/q$ constitutes a connected region. In this region the ion density takes on the values p'/q, $(p'+1)/q, \ldots, p''/q$, for some p' and $p'' \geqslant p'$ (see Fig. 9).

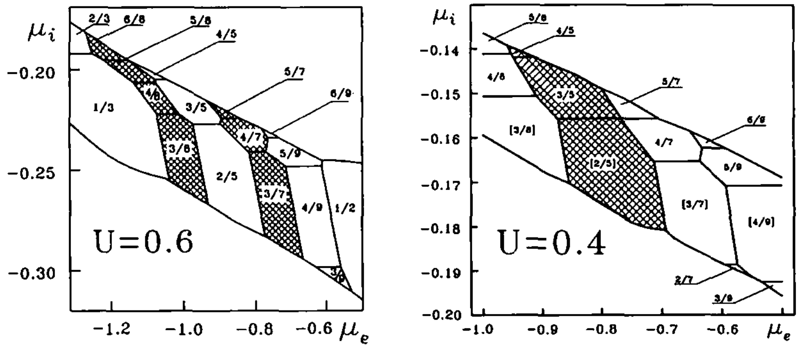

Fig. 9. Domains D_{ρ_e} with $\rho_e = 3/8$, 2/5, 3/7, and 4/9.

Moreover, the unit cell of the configuration associated with the ion density $\rho_i = (p+1)/q$ can be obtained by adding one ion to the unit cell of the configuration associated with $\rho_i = p/q$.

Another property of D is related to the observation that the domains D_n where the ion configurations consist of n-molecules with fixed n are in general connected regions whose size decreases as n increases. There is a relatively large domain D_1 corresponding to neutral atoms ($\rho_e = \rho_i = \rho$) with ρ ranging from some $\rho_{\min}(U)$ to $1 - \rho_{\min}(U)$, a smaller domain D_2 corresponding to 2-molecules with $\rho_i = 2\rho_e$, and consecutively domains D_n corresponding to n-molecules, where $n = 2, 3, \dots, N(U)$, with $\rho_i = n\rho_e$ (i.e., in all the domains D_n there is one electron per molecule). In each domain D_m, $m = 1, \dots, N(U)$, the ion density satisfies the inequality $\rho_{\min}^{(m)}(U) \leqslant \rho_i \leqslant \rho_{\max}^{(m)}(U)$. Furthermore, the minimal value $\rho_{\min}^{(m)}(U)$ is zero for all m between some $n(U)$ and $N(U)$ [in the cases considered we had $n(U) = N(U) - 1$] and for those m the boundary between D_m and the vacuum ($\rho_e = \rho_i = 0$, i.e., $\mu_e \leqslant -2$) is linear. Between two domains D_n and D_{n+1} the periodic configurations are such that their unit cells contain n- and $(n+1)$-molecules only. Between D_n and the vacuum the unit cells consist of atoms and holes followed by a sequence of empty sites, while between D_n and the full configuration the unit cells consist of atoms and holes followed by a sequence of occupied sites.

We note also that all the domains D_{ρ_e} (with a given electron density) that appear in .the restricted phase diagrams follow the Aubry sequence (Farey's tree, Fig. 10)$^{(22)}$ with respect to ρ_e and exhibit a devil's staircase structure with respect to their size (Fig. 11).

We therefore arrive at the conjecture that to all electron densities between zero and one there correspond, according to the Aubry sequence,

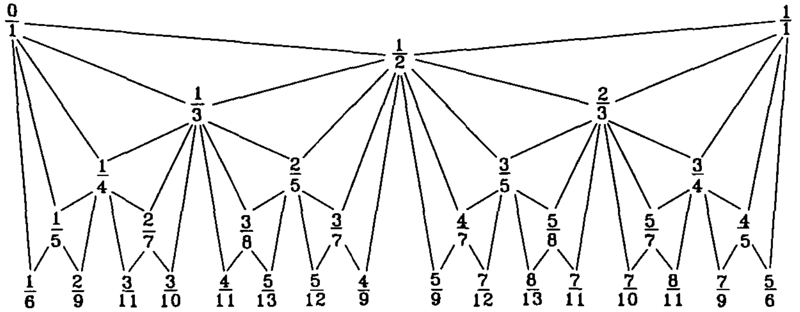

Fig. 10. Farey tree (or Aubry sequence) for electrons.

the domain D_{ρ_e} which present a fractal structure known as the devil's staircase.(23)

Similar observations can be made with respect to the structure of the domains D_n of n-molecules. The ion densities in these domains appear to follow the "n-molecule Aubry sequence," which is similar to the Aubry sequence, but starts with $0/n$ and n/n and one has to consider rationals p/q with $p = 0 \bmod n$ (see Fig. 10). This property can be understood as resulting from an effective two-body interaction between n-molecules that is convex and decreasing (as was the case for the effective two-body interaction between the atoms for large U). However, because of the effective k-body interaction, we do not have the exact devil's staircase of Burkov.(22) In the neutral case this effect was already observed in ref. 18, where the periodic g.s.c. up to period 6 and for large U was studied. To check the above conjecture we have taken into account some periodic configurations with period larger than 10. The results are shown in Fig. 11.

An inspection of the phase diagrams (and Fig. 12) yields a more detailed picture of the neutral case discussed within the canonical formalism. For $U < 2/\sqrt{3}$ the domain corresponding to nontrivial neutral configurations ($\rho_e = \rho_i$) consists of the domain D_1 ending at the point B, together with the curve AB, boundary between the empty and the periodic configurations for $\mu_e \geqslant -2$. .Along the curve AB the density increases monotonically from zero to $\rho_{\min}(U)$. At each point on this curve the g.s.c. is a mixture $[p/q]_n \,\&\, -$ or $[p/q]_n \,\&\, [p'/q']_{n+1} \,\&\, -$. Furthermore, at each point the density is different (because of the weight of the vacuum, not because of the periodic g.s.c.). In the domain D_1 the density is piecewise constant, increasing from $\rho_{\min}(U)$ to $1 - \rho_{\min}(U)$, with a devil's staircase structure. The results for $\rho_e = \rho_i$ and $U = 0.6$, 0.4, 0.2 have been reported in Fig. 5.

We conclude this section with an argument leading to an equation for μ_e^*, the μ_e coordinate of the point where the coexistence line of the empty and full configurations joins the domain D. The reduced phase diagrams show that for $\mu_e \in [\mu_e^*, -2]$ the boundary of D with the vacuum $(\rho_e = \rho_i = 0)$ is piecewise linear and corresponds to the configurations of the form $[n/\infty]_n$. On the other hand, our considerations in the canonical formalism have shown that for a finite number of ions the g.s.c. of a neutral system consists of n-molecules (where n is U-dependent) with one bound electron and $n-1$ diffusion electrons. For $\mu_e < -2$ there is no diffusion

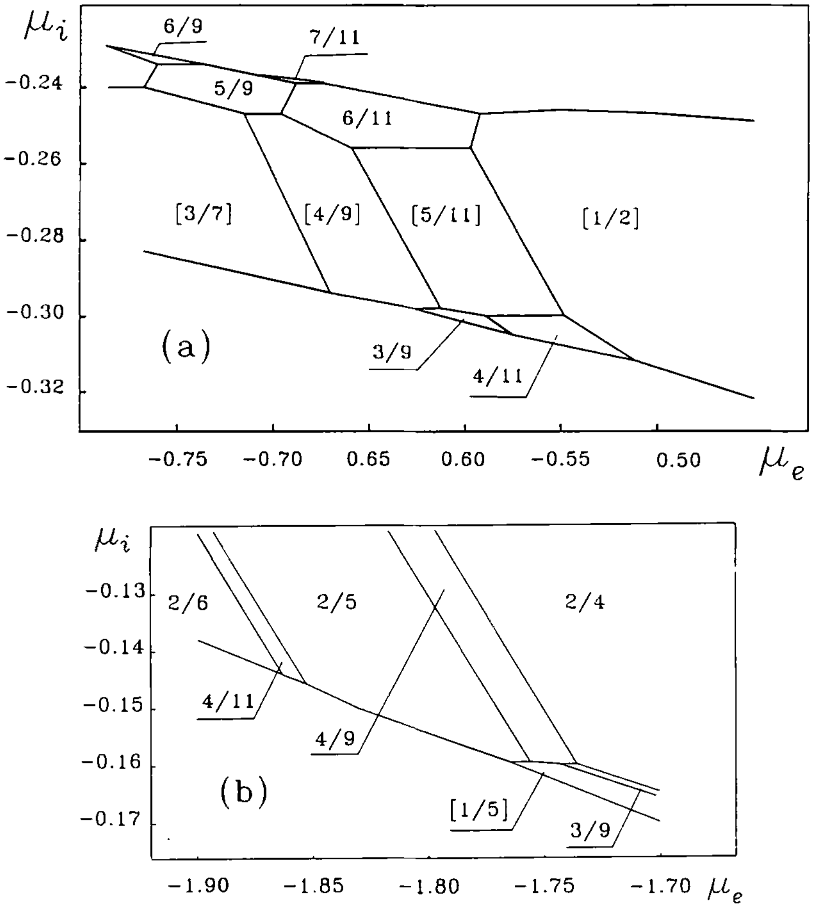

Fig. 11. Test of the conjecture regarding the Aubry sequence and the devil's staircase. (a) $U = 0.6$, (b) $U = 0.6$, (c) $U = 0.2$, (d) μ_e extents of the domains contained in D_1.

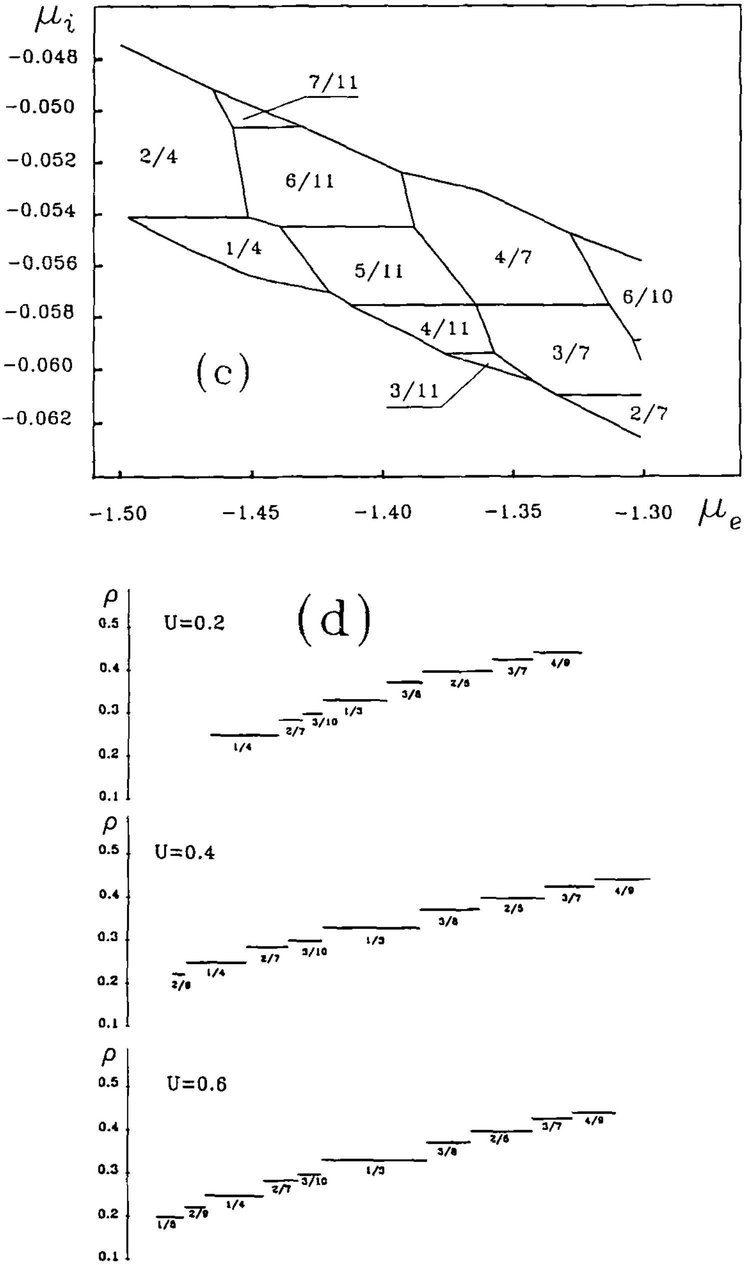

Fig. 11. (*Continued*)

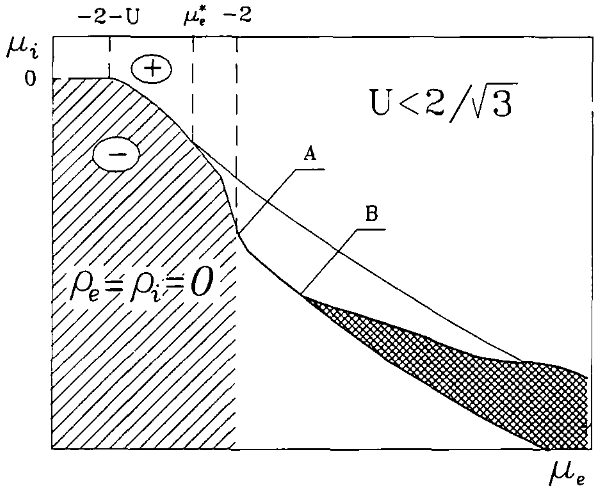

Fig. 12. The region of the (μ_e, μ_i) plane where the system is neutral $(\rho_e=\rho_i)$. In the hatched area the g.s.c. are periodic, while at the curve *AB* the g.s.c. are mixtures of periodic configurations with the empty configuration.

electrons and we then have only n-molecules with one electron. The free energy per ion is thus

$$f(H_n; \mu_e, \mu_i) = \frac{E_0^{(n)} - \mu_e}{n} - \mu_i \tag{25}$$

where $E_0^{(n)}$ is the energy of the n-molecule ground state. On the other hand, the free energy of the vacuum is zero. Therefore the boundary of the vacuum domain (for $\mu_e \leqslant -2$) is given by the concave envelope of the functions of μ_e,

$$f(+; \mu_e, \mu_i) = 0, \qquad f(H_n; \mu_e, \mu_i) = 0, \qquad \text{i.e.,} \quad \mu_i^{(n)} = (E_0^{(n)} - \mu_e)/n \tag{26}$$

For $\mu_e = -2$ the value $n(U)$ that corresponds to the minimum of the sequence $(E_0^{(n)} + 2)/n$ is equal to the number of ions in the molecule at zero density (Table II). Since the function given by $f(H_n; \mu_e, \mu_i) = 0$ has the slope $-1/n$, it is sufficient to construct the concave envelope of the functions given by Eq. (26) with $n \geqslant n(U)$. These functions are plotted in Fig. 13. In particular it appears that for $U \geqslant 2.65$ the value of μ_e^* is determined by $f(H_1; \mu_e, \mu_i) = 0$, i.e.,

$$\mu_i = -(4 + U^2)^{1/2} - \mu_e \tag{27}$$

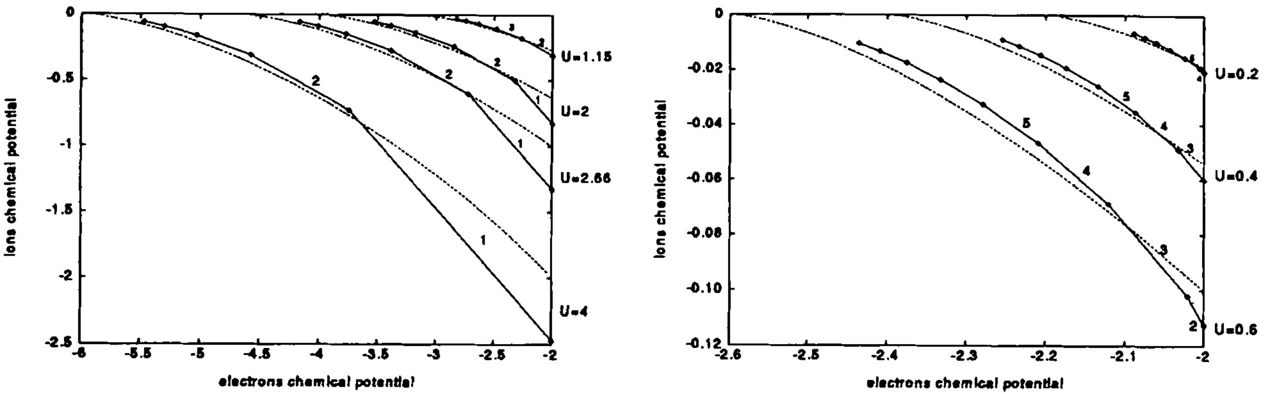

Fig. 13. Graphs of the functions defined by Eq. (26).

which together with Eq. (22) gives, for $U \geqslant 2.65$, the following equation for μ_e^*:

$$(4+U^2)^{1/2} = U + (1/\pi)\{[4-(\mu_e^*+U)^2]^{1/2} - (\mu_e^*+U)\arccos[(\mu_e^*+U)/2]\} \tag{28}$$

Therefore the line of coexistence between the full and empty configurations (i.e., the segregated configuration) appears for μ_e in the range $(-2-U, \mu_e^*)$. The corresponding densities given by (8) and (12) are

$$\rho_e = \frac{\rho_i}{\pi}\arccos[-(\mu_e+U)/2] \tag{29}$$

Consequently the maximum $b(U)$ of the ratio ρ_e/ρ_i is given by

$$\frac{\rho_e}{\rho_i} \leqslant \frac{1}{\pi}\arccos[-(\mu_e^*+U)/2] = b(U) \tag{30}$$

which together with (28) yields for $U \geqslant 2.65$ the following equation for $b(U)$:

$$(4+U^2)^{1/2} - U = \frac{2}{\pi}\sin[\pi b(U)] + 2[1-b(U)]\cos[\pi b(U)] \tag{31}$$

For $U \to \infty$ the leading term in the asymptotic expansion of $b(U)$ is $1-(3/\pi^2 U)^{1/3}$. The plot of $b(U)$ is shown in Fig. 14 together with the upper and lower bounds derived by Brandt.[13] To the precision of Fig. 14, the curve obtained by Freericks and Falicov[6] almost coincides with our curve and only a few points have been reported.

Finally we add a remark concerning the canonical phase diagrams obtained by Freericks and Falicov.[6] Let us take $U=0.6$. For the densities $\rho_e = 1/3$, $\rho_i = 1/2$ the unit cell of the g.s.c. in ref. 6 is [●●○●○○]; the energy density of the corresponding g.s.c. is equal to -0.667401. We found that the even mixture $[1/3]\,\&\,[2/3]$ has the energy density -0.668167. Similarly, for the densities $\rho_e = 1/2$, $\rho_i = 1/3$ the unit cell of the g.s.c. in ref. 6 has the length 6 and consists of two occupied sites separated by one empty site, the other sites being empty. The energy density of the corresponding g.s.c. is equal to -0.753835. We found that the mixture $[1/2]\,\&\,-$ has the energy density -0.754651.

In conclusion, to be physically meaningful, an incoherent phase diagram [in the plane (ρ_e, U) and for fixed ρ_i] must take into account mixtures of configurations with different ion densities. The same remark, as we have already seen, applies to the neutral case.

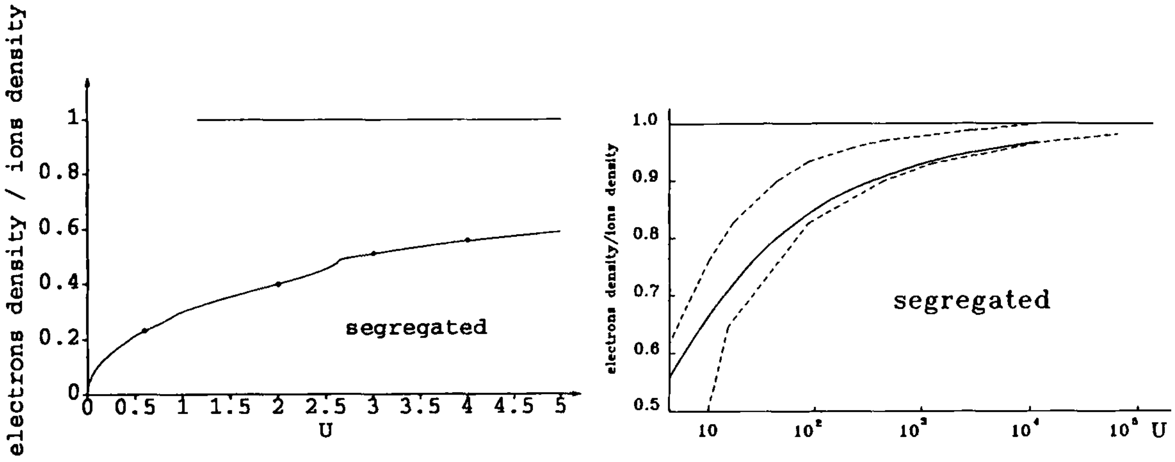

Fig. 14. Canonical phase diagram. For $U > 2/\sqrt{3}$ and $\rho_e = \rho_i$ the g.s.c. is the atomic most homogeneous configuration. The boundary of the segregated configuration, shown as the straight line, was computed from Eq. (30). The irregular curves represent the bounds obtained in ref. 13, while the diamonds represent numerical results of ref. 6.

5. CONCLUSIONS

Our analysis of the zero-temperature restricted phase diagrams of the spinless Falicov–Kimball model has revealed several new and surprising effects.

In the case of *neutral systems* we have seen that for $U > 2/\sqrt{3}$ the ground-state configuration is, as expected, atomic most homogeneous and the system is an insulator. However, for $U < 2/\sqrt{3}$ this remains true only for densities ρ which are not too small or not too large. Indeed there is a critical density $\rho_c(U)$ such that for $\rho < \rho_c(U)$ [or $\rho > 1 - \rho_c(U)$] the ground state presents entirely different properties. We observed three new phenomena:

1. *Phase separation*: the ground-state configuration is a mixture of a periodic configuration and the empty configuration, i.e., all ions are distributed periodically in one semi-infinite half-space, while the other half-space is free of ions.

2. *Formation of n-molecules*: the ions form clusters where n consecutive lattice sites are occupied and these clusters are most homogeneously distributed over the occupied half-space.

3. *Changes in conducting properties*: the Fermi level is located in the band of the empty configuration and therefore an extra electron can be added at no cost in the energy.

As the density ρ decreases, the following infinite sequence of phase diagram transformations is observed. In the first stage the weight of the half-space with no ions increases while the unit cell in the half-space occupied by the ions remains unchanged. In the second stage, at a sufficiently small density the distances between the molecules jump to a larger value (modification of the unit cell but not of the size of the molecules). Then the two stages repeat themselves until the value of the density is reached where a transition from n-molecules to $(n+1)$-molecules occurs. After this transition the first two stages repeat themselves again, but now with ion configurations containing $(n+1)$-molecules, and so on. For a given potential U there is a largest admissible size $N(U)$ of the molecules that can be formed. After the $N(U)$-molecules have been formed the remainder of the sequence consists of the first two stages repeating themselves indefinitely.

These phenomena were interpreted as consequences of the fact that for small U the n-molecules have only one bound electron, the other $n-1$ electrons being diffusive. The g.s.c. appears then to result from the competition between a strictly convex effective repulsion between the molecules and the pressure exerted by the "free" electrons.

On the other hand, for any density ρ, $\rho_c(U) < \rho < 1 - \rho_c(U)$, the ground-state configuration is periodic most homogeneous and the system is an insulator. Furthermore, in the plane of the chemical potentials the density in the neutral domain appears to follow the Aubry sequence and the sizes of phase domains show the devil's staircase structure.

We pass now to the *nonneutral systems*. In this case we have found that for $\rho_e < \rho_i b(U)$, where $b(U)$ is given by the construction described in Section 4 [while for $U \geqslant 2.65$ it is given by (31)], the g.s.c. is the segregated configuration and the system is a conductor. The form of $b(U)$ has been checked to be in agreement with our numerical results, the numerical results given in ref. 6, and the bounds given in ref. 13.

For densities ρ_e and ρ_i such that $\rho_i b(U) < \rho_e < 1/2$, the set of periodic g.s.c. decomposes mostly into sequences for which $\rho_i = n\rho_e$, $1 \leqslant n \leqslant N(U)$. Given such a sequence, then for any ρ_i between $\rho^n_{\mathrm{min}}(U)$ and $\rho^n_{\mathrm{max}}(U)$, the ground state consists of n-molecules which are most homogeneously distributed over the lattice, with one electron per molecule.

For general values of (ρ_e, ρ_i) we came to the conclusion that for any electron density $\rho_e = p/q$, with p relatively prime to q, there are periodic ground states with ion densities $\rho_i = \tilde{p}/q$, where $\tilde{p}$ is any integer satisfying $p' \leqslant \tilde{p} \leqslant p''$. If ρ_i is such that $\tilde{p}/q < \rho_i < (\tilde{p}+1)/q$, the ground-state configuration is a mixture of the two phases with density $\tilde{p}/q$ and $(\tilde{p}+1)/q$ (for $\rho_i > p''/q$ it is a mixture of a periodic and the full configuration); for $\rho_i < p'/q$ it is a mixture of a periodic and the empty configuration. In any case if the ground state is periodic, then the system is an insulator.

The restricted phase diagram presents the following general properties. The nontrivial part of the (μ_e, μ_i) plane, i.e., $-(U+2) < \mu_e < 2$, decomposes into three connected domains D_-, D_+, and D, corresponding, respectively, to the empty, full, and periodic translationally noninvariant configurations. The domains D_- and D_+ are separated by the domain D, contained in the vertical stripe $[\mu_e^*, -(U+\mu_e^*)]$, where $\mu_e^* = \mu_e^*(U) < \min\{-2, -U/2\}$, and by two curves which correspond to the segregated phase (see Fig. 12). There are two partitions of D into connected subdomains that are of importance in the analysis of the restricted phase diagrams. In the first partition there appear subdomains D_n, where the ions in the g.s.c. form n-molecules with one electron per molecule ($\rho_i = n\rho_e$). In each domain D_n the ion density follows the Farey tree order (Aubry sequence) and the domains of distinct periodic configurations exhibit the devil's staircase structure. The second partition consists of the subdomains D_{ρ_e}, where the electron density has a definite rational value $\rho_e = p/q$. These domains form "curved stripes" going across D from the boundary with D_- to the boundary with D_+. The ion densities in these domains constitute the sequence p'/q, $(p'+1)/q, \ldots, p''/q$, for some $p' < p''$ that depend on ρ_e and U.

Finally, we have seen that Theorem 1 of ref. 6 is partially incorrect and at the same time seems to be more general. We conjecture that this theorem should be valid for all U in the form: Given $\rho_e = p/q$, with p relatively prime to q, and $\rho_i = \tilde{p}/q$, then if the ground state is periodic, it is given by the Freericks–Falicov method.

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REFERENCES

1. L. M. Falicov and J. C. Kimball, *Phys. Rev. Lett.* **22**:997 (1969).
2. D. I. Khomskii, in *Quantum Theory of Solids*, I. M. Lifshits, ed. (Mir, Moscow, 1982).
3. T. Kennedy and E. H. Lieb, *Physica A* **138**:320 (1986).
4. U. Brandt and R. Schmidt, *Z. Phys. B* **63**:45 (1986).
5. J. Jędrzejewski, J. Lach, and R. Lyżwa, *Physica A* **154**:529 (1989).
6. J. K. Freericks and L. M. Falicov, *Phys. Rev. B* **41**:2163 (1990).
7. U. Brandt and R. Schmidt, *Z. Phys. B* **67**:43 (1987).
8. Ch. Gruber, J. Iwański, J. Jędrzejewski, and P. Lemberger, *Phys. Rev. B* **41**:2198 (1990).
9. J. L. Lebowitz and N. Macris, preprint, Ecole Polytechnique Fédérale de Lausanne.
10. A. Messager and S. Miracle-Sole, preprint, Marseille University.
11. Ch. Gruber, *Helv. Phys. Acta* **64**:668 (1991).
12. P. Lemberger, *J. Phys. A* **25**:715 (1992).
13. U. Brandt, *J. Low Temp. Phys.* **84**:477 (1991).
14. M. Barma and V. Subrahmanyam, *Phase Trans. B* **16**:303 (1989).
15. Ch. Gruber, J. Jędrzejewski, and P. Lemberger, *J. Stat. Phys.* **66**:913 (1992).
16. Ch. Gruber, J. L. Lebowitz, and N. Macris, *Europhys. Lett.* **21**:389 (1993); *Phys. Rev. B* **48**:4312 (1993).
17. T. Kennedy, The state of matter, *Adv. Ser. in Math. Phys.* **20**:42 (1994).
18. J. Lach, R. Lyżwa, and J. Jędrzejewski, *Phys. Rev. B* **48**:10783 (1993); *Acta Phys. Polon. A* **84**:327 (1993).
19. R. Lyżwa, *Phys. Lett. A* **164**:323 (1992); *Physica A* **192**:231 (1993).
20. J. Hubbard, *Phys. Rev. B* **17**:494 (1978).
21. E. H. Lieb, private communication.
22. S. Aubry, *J. Phys. Lett.* (Paris) **44**:L-247 (1983).
23. R. Bruinsma and P. Bak, *Phys. Rev. B* **27**:5824 (1983).