Vacancy ordering transitions in one-dimensional lattice gas with Coulomb interactions

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Recently, physical properties of single crystals of quasi-one-dimensional sulfide KCu$_7$S$_4$ have been studied. These measurements show several anomalies, in which the “transition” temperatures and physical properties depend strongly on $x$. It was suggested that these transitions are most likely due to vacancy ordering involving Cu$^+$-ion diffusion along the Cu(2)-Cu(2) zigzag chains. In this paper we propose a long-range mean-field model to study vacancy ordering in a one-dimensional chain with 1/r Coulomb interactions. Our results indicate that phase transitions exist in a one-dimensional lattice gas system in which vacancy ordering is involved. The system has complex thermodynamic properties which are extremely sensitive to the occupancy. Each simple rational occupancy has a unique phase diagram.

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I. INTRODUCTION

Studies of one-dimensional (1D) systems are very rich.1–3 A large number of measurements of thermodynamic changes at phase transitions in quasi-one-dimensional materials have been made and compared with various theories. Theoretically, it is well known that 1D systems with short-range interactions do not exhibit phase transitions at finite temperature. Moreover, systems with infinite long-range interactions which fall off faster than $r^{-(d+2)}$ ($d$ is the dimension of the system) also do not exhibit any phase transitions.4–6 A class of models with interactions that fall off as the inverse square of the distance, called Calogero-Sutherland models (CSM), were proposed by Moser,7 Calogero,8 and Sutherland.9,10 Sutherland investigated exactly a system of either fermions or bosons. Exact but complex wave functions and correlation functions were obtained from a lattice version of CSM introduced by Haldane11 and Shastry.12 Inozemtsev proposed a hyperbolic exchange model, which is the second generalization of the inverse-square exchange model.13 However, to the best of our knowledge, there have been no studies of lattice-gas systems with interactions whose potential energy falls off as the inverse of the distance between the particles or spins until now.

Experimentally, there is a large and growing class of low-dimensional coinage metal ($M$) chalcogenides ($Q$) made of the pseudo-one-dimensional $M_xQ_4$ columns. Previous studies on these materials have showed that phase transitions with drastic changes in the transport and thermodynamic properties occur at low temperatures, and several exhibit hysteresis over a wide temperature range.14,15 In particular, measurements on KCu$_{7-x}$S$_4$ show several sharp anomalies associated with phase transitions at temperatures that depend on $x$.16,17 It was originally suggested that the phase transitions of KCu$_{7-x}$S$_4$ were due to charge-density-wave ordering,18 but later work showed that they are most likely due to vacancy ordering involving Cu$^+$-ion diffusion along the zigzag Cu(2)-Cu(2) chains between Cu$_4$Q$_4$ columns. This is because the stoichiometric KCu$_7$S$_4$ phase cannot be a metal according to the oxidation state (K$^+$(Cu$^+$)$^7$(S$^{2-}$))$_4$, which suggests that KCu$_7$S$_4$ has no partially filled bands, and the crystal structure of KCu$_{7-x}$S$_4$ contains vacancies that could order.19,17 This ordering would involve a diffusion process, in agreement with the experimental transport and thermodynamic measurements. Moreover, superlattice spots observed in TEM measurements are also consistent with an order-disorder transition.20 However, the vacancy ordering scenario is not obvious. Other compounds, such as K$_3$Cu$_8$S$_6$ (Refs. 21 and 22) and KCu$_3$S$_2$ (Refs. 23–25), whose structures contain Cu$_4$S$_4$ columns but have no structural vacancies, also exhibit low-temperature phase transitions.

To resolve a possible vacancy ordering model in a one-dimensional chain, we initiated a numerical study on this subject. Although in general there is a similarity between spins and occupation numbers, here we have a fixed number of vacancies, independent of any driving force. We consider a system in which $N_s$ ions are evenly distributed over $N_t$ lattice sites with Coulomb 1/r repulsive interactions (so that the occupancy $n_{av}$ of the system is $N_s/N_t$). Although the Coulomb interaction would be shielded in the conducting crystals, any interaction that had a 1/r dependence would give the same results. For simplicity, we ignore the zigzag nature in the real structure of KCu$_{7-x}$S$_4$. As a result, the 1D chain partially occupied with Cu$^+$ ions is illustrated as a straight line lattice gas with open boundary conditions. The corresponding Hamiltonian can be written as
\[ H = \sum_{i=1}^{N_S} \sum_{j \neq i} \frac{J}{|j-i|} n_in_j, \]

where \( J \) is the Coulomb potential energy between two nearest-neighbor particles, and \( n_i (n_i = 0 \text{ or } 1) \) is the particle number of site \( i \). Instead of periodic boundary conditions conventionally employed for 1D systems, we have used open boundary conditions for the following reasons: (1) long-range Coulomb repulsive interactions with infinite neighbors would cause the Hamiltonian to diverge, (2) the length of a real KCu\(_7\)S\(_8\) sample is about 1 mm, i.e., \( N_s \) is on the order of 10\(^5\) given the Cu-Cu van der Waals distance of approximately 3 Å, and thus numerically calculable with modern high speed computers.

In this paper we propose a long-range mean-field (LRMF) method to study the 1D lattice-gas systems with occupancies \( n_{av} \). We denote the average particle number of the \( N_w \) segments on both the right and left sides, so that \( N_i/N_w = (2N_a + 1) \), the local mean field acting on the \( i \)th particle is

\[ h_i = J \sum_{j=1}^{N_S} \sum_{i=1}^{N_W} \langle n_j \rangle \left( \frac{1}{jN_w - i + 1} + \frac{1}{jN_w + i - 1} \right). \]

The value of \( h_i \) in terms of \( J \) can be numerically calculated for a very large \( N_s \). The LRMF Hamiltonian is then described by

\[ H_{MF} = J \sum_{j=1}^{N_S} \sum_{i=1}^{N_W} \langle n_j \rangle \left( \frac{1}{jN_w - i + 1} + \frac{1}{jN_w + i - 1} \right) \]

As \( N_s, N_v, N_w, \) and the temperature \( T \) are given, we can numerically calculate the self-consistent solutions of \( \langle n_i \rangle \) by adding over \( \langle n_i \rangle \)'s with \( N_w \) elements and summing over \( \langle n_i \rangle \)'s equals to \( N_v \).

Since the x-ray diffraction patterns are determined by the average particle number distributions, intuitively each element in \( \{ \langle n_i \rangle \} \) is a member of a reasonable set of order parameters. For convenience, we further define a useful order index \( q \) by

\[ q = \frac{\sum_{i=1}^{N_w} (\langle n_i \rangle - n_{av})^2}{N_w(1-n_{av})^2 + (N_v-N_w)n_{av}^2}, \]

where the values of \( q \) range from 0 to 1. When \( q = 0 \), all the \( \langle n_i \rangle \) are equal to \( n_{av} \), which corresponds to the state at very high temperature. When \( q = 1 \), the system is completely ordered, \( \langle n_i \rangle = 0 \) or 1, corresponding to the state at absolute zero. The internal energy of the considered segment is defined by

\[ E = \frac{\text{Tr} \left[ J \sum_{j} \sum_{i=1}^{N_W} \langle n_j \rangle \left( \frac{1}{jN_w - i + 1} + \frac{1}{jN_w + i - 1} \right) \exp(-H_{MF}/kT) \right]}{\text{Tr}[\exp(-H_{MF}/kT)]}. \]
away from one end is about 1%, and 4% for one-tenth away with \( N_s = 600,000 \). Therefore, except for the portions near the two ends in the 1D lattice-gas system, most of the segments exhibit almost the same thermodynamic properties as the center segment, i.e., although we only consider the center segment, the results can be roughly presented as the properties of the whole 1D lattice-gas system.

III. RESULTS

In all of our calculations, we set the total sites \( N_s \) in the 1D system to be 600,000 and the sites in the considered segment \( N_w \) to be on the order of 20. It is worth mentioning that the difference is less then 0.01% between results of \( N_s = 120,000 \) and 600,000. Our calculations show that the thermodynamic properties of the 1D lattice-gas system with vacancy ordering are very sensitive to the occupancy \( n_{av} \). This result corresponds well to the experimental findings on quasi-one-dimensional KCu$_2$S$_4$ in which the physical properties depend strongly on \( x \). We found that \( \langle n_i \rangle \) quickly converge to a single self-consistent solution at high temperatures, but only a few sets of solutions for \( \langle n_i \rangle \) are possible at low temperatures for a particular \( n_{av} \). Each of the self-consistent solutions of \( \langle n_i \rangle \) at low temperatures corresponds to a possible metastable state in the system. When a set of \( \langle n_i \rangle \) with a lower free energy appears at some temperature, a phase transition will occur. Another interesting feature is that the distributions of the average particle numbers \( \{ n_i \} \) are periodic, i.e., if \( n_{av} \) can be written as the simplest fractional form \( n_{av} = q/p \) then the \( N_w \) elements in \( \{ n_i \} \) repeat themselves every \( p \) sites. Therefore, it is convenient to represent a state by only one period, that is \( \{ n_i \} \) where \( i = 0 \) to \( p \) for a particular \( n_{av} = q/p \). In the following, we will present the results for \( n_{av} = \frac{1}{2}, \frac{3}{5}, \frac{4}{5}, \) and \( \frac{5}{6} \).

A. \( n_{av} = 1/2 \)

Figure 1 shows the free energies for \( N_w = 12, 16, \) and 20 \( (N_s = 6, 8, \) and 10), respectively. For \( T \geq 0.14 \) J/k, the \( \{ n_i \} \) has a single numerical solution with all the \( \langle n_i \rangle \)'s being 0.5. This state apparently corresponds to the completely disordered state. For \( T \leq 0.14 \) J/k, another possible solution appears with lower free energy and the \( \langle n_i \rangle \) changing their values continuously from \( \{ n_i \} = \{ 0.5, 0.5, 0.5, 0.5, \ldots \} \) to \( \{ n_i \} = \{ 1, 0.1, 0.1, \ldots \} \) as the temperature decreases from about \( T = 0.14 \) J/k to \( T = 0 \) K. The \( \{ n_i \} = \{ 1, 0.1, 0.1, \ldots \} \) solution at absolute zero corresponds to the completely ordered state. Apparently, a second-order (continuous), order-disorder transition occurs at about \( T = 0.14 \) J/k in this system as the system changes from the ordered state to the disordered state at this temperature. The lower free-energy state at low temperatures has average particle numbers repeating themselves every two sites, i.e., the period of \( \{ n_i \} \) is 2, the denominator of \( n_{av} = 1/2 \) as we mentioned above. It can be easily seen in Fig. 1 that the general features of the free energies of various \( N_w \) are very similar, except for small quantitative shifts. Figure 2 shows the results for the internal energies of the possible stable states with \( N_w = 12 \) and 16, and again there are similar features for different \( N_w \). The
B. $n_{av}=2/3$

Figure 4 shows the free energies of all the stable states we found with $N_w = 12, 15, \text{ or } 18$. There are two phase transitions in this system with a second-order (continuous) phase transition at about $T = 0.1 \text{ J/k}$ and a first-order transition with a discontinuous $dF/dT$ at about $T = 0.04 \text{ J/k}$. Figure 5 shows the internal energies per site with $n_{av} = 2/3$ and $N_w = 12$. The upper panel inset shows the specific heats per site. There are two stable states near $T = 0$, as shown in detail in the lower panel inset. The lower internal energy state corresponds to $\langle n_i \rangle = \{1,1,0\}$, and the higher internal energy state corresponds to $\{1,0.5,0.5\}$.

![Figure 3](image1.png)

**FIG. 3.** The order indexes with $n_{av} = 0.5$ and $N_w = 12$. For the high temperature $\langle n_i \rangle = \{0.5,0.5\}$ phase, $q = 0$ for all $T$. Below the critical temperature, the particle number is periodically distributed with a period of two sites. $q$ approaches 1 as $T$ approaches absolute zero, while the system becomes completely ordered with $\langle n_i \rangle = \{1,0\}$.

![Figure 4](image2.png)

**FIG. 4.** The free energies per site with $n_{av} = 2/3$ and $N_w = 12, 15, \text{ and } 18$. There are two phase transitions in this system; one second-order at about $T = 0.1 \text{ J/k}$ and one first-order at about $T = 0.04 \text{ J/k}$.

![Figure 5](image3.png)

**FIG. 5.** The internal energies per site with $n_{av} = 2/3$ and $N_w = 12$. The upper panel inset shows the specific heats per site. There are two stable states near $T = 0$, as shown in detail in the lower panel inset. The lower internal energy state corresponds to $\langle n_i \rangle = \{1,1,0\}$, and the higher internal energy state corresponds to $\{1,0.5,0.5\}$.

T. C. KING, Y. K. KUO, M. J. SKOVE, AND S.-J. HWU PHYSICAL REVIEW B 63 045405

045405-4
C. $n_{av}=3/4$

Figure 7 shows the free energies of all possible stable states with $N_w=12 (N_o=9)$. Five phase transitions exist in this system, with two second-order transitions at higher temperature and three first-order transitions at lower temperature. The inset of Fig. 7 shows the fine structure of the two lowest temperature first-order phase transitions. The internal energies of all possible stable states are shown in Fig. 8; the inset shows the specific heats, where each peak corresponds to a phase transition. The order indexes of all possible states are shown in Fig. 9. There are two possible solutions between $0.032 \leq kT/J \leq 0.065$, as shown clearly in Fig. 7 (two second-order phase transitions occurs at these two tempera-

FIG. 6. The order indexes with $n_{av}=2/3$ and $N_w=12$. A significant difference from the case of $n_{av}=1/2$ is that the $q$ values in this system is never zero. This means that the average particle number distribution will never be exactly uniform for any finite $T$.

FIG. 7. The free energies per site with $n_{av}=0.75$ and $N_w=12$. Five phase transitions with two second-order transitions at higher temperature and three first-order transitions at lower temperature exist in this system. The inset shows the fine structure of the two lowest temperature phase transitions.

FIG. 8. The internal energies per site with $n_{av}=0.75$ and $N_w=12$. The inset shows the specific heats, where each peak corresponds to a phase transition.

FIG. 9. The order indexes with $n_{av}=0.75$ and $N_w=12$. The lowest free-energy state is represented by diamond symbols. Near $T=0$, the $q=1/3$ state corresponds to the $\{n_i\} = \{1,1,0.5,0.5\}$ and the $q=1$ state corresponds to $\{1,1,1,0\}$. The inset shows the fine structure at about $T=0.02 J/k$. 
However, the order indexes for these two states are indistinguishable within this temperature region. The inset of Fig. 9 shows the fine structure of the two lowest temperature phase transitions where the lowest free energy state is in diamond symbols. In the region near $kT/J \approx 0.016$, the repetition patterns from the top to the bottom curve are $\{n_i\} = \{0.999,0.889,0.225,0.888\}$, $\{0.973,0.995,0.701,0.331\}$, and $\{0.986,0.514,0.514,0.986\}$, respectively, while near $kT/J \approx 0.0196$, $\{n_i\} = \{0.996,0.884,0.304,0.816\}$, $\{0.993,0.737,0.343,0.927\}$, and $\{0.976,0.524,0.524,0.976\}$. Near $T = 0$, the $q = 1/3$ corresponds to the state $\{1,1,0.5,0.5\}$ and $q = 1$ corresponds to $\{1,1,1,0\}$.

D. $n_{av} = 4/5$

Figure 10 shows the free energies of all possible stable states with $N_w = 10 (N_o = 8)$. There are five phase transitions in this system. In this case, the three higher temperature phase transitions are second order and the two lower temperature ones are first order. The inset of Fig. 10 shows the details of the first-order phase transition at about $T = 0.0124 J/k$. Figure 11 shows the internal energies of all possible stable states with $N_w = 10$; the specific heats of this system are shown in the inset. The order indexes of all possible stable states are shown in Fig. 12. Near $T = 0$, $q = 0.375$ corresponds to the state $\{1,1,0.5,0.5\}$ and $q = 1$ corresponds to the state $\{1,1,1,0\}$.

In all of our calculations, we found that the $\{n_i\}$ and $q$ change continuously at second-order phase transitions but discontinuously at first-order phase transitions. For example, for the case of $n_{av} = 3/4$ and $N_w = 12$, a second-order phase transition occurs at $T_{C1} = 0.066 J/k$. For the temperature just above $T_{C1}$, there is only one state of $\{n_i\} = \{0.865,0.635,0.635,0.865\}$. For the temperature just below the $T_{C1}$, there are two possible metastable states with the higher free-energy state $\{n_i\} = \{0.871,0.638,0.629,0.662\}$ and lower free-energy state $\{0.984,0.516,0.516,0.984\}$, respectively. For the same case, a first-order phase transition occurs at $T_{C5} = 0.016 J/k$. For temperatures just above $T_{C5}$, there are two possible stable states with the higher free-energy state $\{0.984,0.516,0.516,0.984\}$ and lower free-energy state $\{0.998,0.877,0.248,0.877\}$. For temperatures just below the $T_{C5}$, there are three possible stable states. From the highest order
IV. SUMMARY AND DISCUSSION

We propose a LRMF method to study 1D lattice-gas models with 1/r Coulomb interactions. Our calculations show that the system has complex thermodynamic properties and that the properties of the phase transitions are extremely sensitive to the occupancy \( n_{av} \). This result qualitatively agrees with experimental findings in the quasi-one-dimensional KCu\(_{7-n}\)S\(_4\) system, in which the physical properties depend strongly on \( x \). We found that the ensemble of average particle numbers \( \{n_i\} \) quickly converge to a single self-consistent solution at high temperatures, but several possible solutions for \( \{n_i\} \) are available at low temperatures for any \( n_{av} \). This in turn supports the possible scenario of vacancy ordering in the Cu ion zigzag chain in the KCu\(_{7-n}\)S\(_4\) system. Moreover, many possible states with similar free energies at low temperatures could be responsible for the observed thermal hysteresis of the anomalies in the ac heat capacity and resistivity in these materials. However, we cannot address the frequency dependence of the ac heat capacity until diffusion time is included in our model. Besides, the zigzag nature of the real KCu\(_{7-n}\)S\(_4\) structure and interchain interactions also need to be considered to more precisely describe the properties of the KCu\(_{7-n}\)S\(_4\) system.

The temperature-dependent \( \{n_i\} \) shows that the system is in dynamic equilibrium except at \( T=0 \). That means the particles keep jumping and moving in the 1D lattice at any finite temperatures. It is well known that thermal fluctuations are important near the critical temperatures especially in 1D systems and the effect of fluctuations on these vacancy ordering transitions in a 1D lattice-gas system is of physical interest. However, the fluctuations were not considered in the LRMF method we introduced in this paper. A full Monte Carlo simulation with fluctuations in the title system is underway for comparison.

Other interesting features of our calculations are as follows: (1) the critical temperatures for the second-order transitions are always higher than the first-order ones for a particular \( n_{av} \); (2) the average particle number distribution is not uniform at our highest temperature except for \( n_{av} = 1/2 \); (3) the average particle numbers \( \langle n_i \rangle \) within a segment are distributed periodically, with the period of the distribution depending crucially on \( n_{av}(=q/p) \) (this is exactly what has been seen in TEM [20] and temperature-dependent x-ray superlattice patterns [26] on the KCu\(_{7-n}\)S\(_4\) system); (4) the thermodynamic properties are more complex for larger values of \( p \). We found that for the same \( N_w \), the states with more chaotic \( \{n_i\} \) distribution always have lower free energy. Even though the values of \( \{n_i\} \) change as the temperature varies, the regularity of each state still holds.

The LRMF method we proposed is a simple but useful method. With further modifications, the LRMF method can be widely used to study various lattice systems with long-range interactions, even two- or three-dimensional lattice systems. For examples, the ferromagnetic and antiferromagnetic quantum systems with long-range interactions are suitable for our next study.

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