Lattice-gas model driven by Hubbard electrons

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Self-consistent Monte Carlo simulations are undertaken for a lattice-gas model which is driven by the free energy of electrons described by a Hubbard model with electronic hopping restricted to ions at nearest-neighbor sites. Our previous work, an independent-electron tight-binding lattice-gas model (bcc or fcc), is modified to introduce two effects: the disorder of the dense system and, more importantly, the role of the electronic correlation. The first effect is achieved using an fcc lattice, but restricted so an occupied site can have no more than eight, instead of twelve, occupied nearest-neighbor sites. To treat correlations, the electronic intra-atomic repulsion is, at first, included via the Gutzwiller approximation at finite temperature; this approach is simple enough to be solved for all cases in the large, disordered systems used in our Monte Carlo simulations but can still give a good qualitative representation of the main effects of the electronic correlations. Then, the exact treatment of the Hubbard model for clusters with up to six atoms is integrated into the calculation. We obtain vapor-liquid coexistence curves and then, approximations to the electronic conductivities and paramagnetic susceptibilities at coexistence conditions. This simple model is, in part, motivated by experiments on the alkali-metal fluids. [S1063-651X(99)06809-9]

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INTRODUCTION

Correlations among fermions are of basic interest in treating many-body systems by considering effects which go beyond those arising from the Pauli principle. There are very few systems in which such effects can be treated exactly and even simplified models require approximate treatment. In the study of solids and fluids, especially those which may have metallic characteristics, the electron-electron interaction induces correlations which are important in the understanding of their electronic properties. Further, in fluids in which electron delocalization can take place, the structural and thermodynamic properties of the system are closely tied to electronic effects and thus will also reflect the role of electronic correlations. In this work, we wish to examine the influence of electron correlations on the structural, thermodynamic, and electronic properties of a simplified model of a fluid of monovalent atoms in which the electrons play the central role by providing the only system cohesion. Although this type of problem is intrinsically interesting from a theoretical point of view, its study is also motivated by our hope of obtaining a qualitative understanding which will allow interpretation of the properties of the alkali fluids; these materials have been extensively studied experimentally.

A simple model in which to study the influence of electron correlations is that suggested by Hubbard [1]. It consists in allowing electron transfer between atoms and considering a constant short-ranged electron-electron repulsion while neglecting all other effects of the interaction among electrons. Despite its apparent simplicity, the model is not susceptible to exact solution, except for small clusters of atoms and one-dimensional lattice systems [2]. Approximation methods have been reviewed [3]. This model has initially been shown to be useful in studying a rich spectrum of molecular mag-

netic properties. It has also been used to elucidate such solid-state properties as a metal-insulator transition and magnetic anomalies. Further, its study has been applied to systems with a statistical ''frozen-in'' disorder in order to study the joint effects of interaction and disorder (see, for example, Refs. [4] and [5]). Metal-insulator transitions are known to arise due to either or both effects. In a fluid, it is of interest to couple the interaction of electrons to a ''thermalized'' disorder of the atomic positions, rather than a ''frozen-in'' disorder. The statistical effects of such two types of ionic disorder are different and the qualitative conclusions on the effects of ionic disorder and electronic correlation on the electronic properties are in sharp contrast; a brief discussion is given in the last section.

In considering the experimental aspect of the motivation for this study, experiments on the alkali fluids, at phase coexistence, show several notable features [6]: (1) A pair-correlation function which, as the density is lowered, has a nearest-neighbor (nn) distance which is nearly fixed while the average coordination number decreases. (2) A vapor-liquid coexistence curve, scaled to the critical parameters, which is substantially more asymmetric than that of simple fluids, i.e., with a relatively denser liquid phase. (3) A metal-nonmetal transition which results on lowering the density sufficiently; at coexistence it takes place in the vapor: i.e., at the critical temperature, the conductivity shows a strong decrease on lowering the pressure, at pressures below the critical value. (4) A paramagnetic susceptibility which has the following dependence [7]: (i) At the lowest densities, a Curie behavior, typical of N neutral monovalent atoms: $N\mu_B^2/k_BT$, is observed. (ii) Then, as the density increases, at first there is a reduction from the Curie dependence. (iii) There follows a reapproach to the Curie values, in the liquid phase. (iv) Finally, a decrease towards an enhanced Pauli-Landau limit,

characteristic of a degenerate-electron system [8], is observed; it has a dependence on density with only a weak explicit temperature effect.

We have attempted a minimal model to study electron effects in a fluid and theoretically account for the above features qualitatively. To date, our simplest model was a self-consistent treatment of ions and electrons with the ionic configurations obtained from a Monte Carlo treatment based on a lattice gas, in which the ions partially occupy the sites of a chosen lattice. The system cohesion was purely electronic and resulted from a thermal occupation of the states from a one-electron tight-binding model [9]. The ionic configurations were driven by the electronic free energy which depended on those ionic positions. With reference to the above list of experimental features, that model has the following virtues: (1) The observed feature of the pair-correlation function automatically results from the lattice-gas model. (2) The coexistence curve asymmetry is obtained as a consequence of the fact that the effective ion-ion interactions are not pairwise additive, in contrast to the case for simple fluids. (3) The metal-nonmetal transition results since the electronic properties dominantly reflect the ionic structures, which fail to percolate at low density; the percolation threshold is found to occur at lower density than that for random ionic positions and occurs in the vapor, at coexistence. However, that model yields a paramagnetic susceptibility at odds with observations. The model results in the following behavior of the susceptibility. At low system density, the equilibrium system consists of isolated occupied sites which are charge neutral only in a statistical sense. Statistically, positive and negative ions are given the same weight as the neutral atom species but do not contribute to the paramagnetism. Thus, the model yields one-half of the Curie paramagnetism of neutral monovalent atoms. On increasing the density, clusters appear; as spin-paired electrons do not contribute to the paramagnetism, a reduction from the Curie result arises. At even higher density, the energy-level spacing near the chemical potential eventually decreases to values less than the thermal energy, causing a transition to the Pauli behavior. The model contains no mechanism which might result in any further features in the susceptibility. We undertook various attempts to include effects, in the one-electron model, which might result in a susceptibility bump [as in (4 *iii*)], such as allowing cluster charging, but all have failed. The charging mechanism was considered since Redmer and Warren [10] had reported a mean-field calculation, considering chemical equilibrium among a variety of atomic and molecular species, and their charged versions, which did yield such a bump, due mainly to the positive diatomic molecules. In our model, the physical space does not exist for a substantial fraction of small clusters, which are isolated from the rest of the system, if the overall site-occupation fraction is to correspond to the liquid phase at the values required for the observed susceptibility bump.

Clearly, the above model is limited by the complete neglect of the intrinsically interesting electron-electron interactions. Further, published work has included speculations that the experiments have two features that are specifically at odds with our simplest model. First, that the metal-nonmetal transition is not percolative but rather correlation induced: of the Mott type [11]. Then, that the magnetic susceptibility

bump (4 *iii*) is also induced by electron correlations: a Brinkman-Rice [12] precursor of antiferromagnetism [13]. We label the above statements as speculative since a theoretical self-consistent model of a fluid with such interactions and disordered ionic topologies is lacking. There does exist work which treats ionic disorder and electron correlations. First, a filled lattice with an imposed Anderson-type [14] disorder in the site energies and Hubbard onsite terms [4]. Then, an off-lattice Hubbard model for the electrons with the ionic positions assumed to be either randomly distributed in space (labeled gaslike disorder) or correlated exclusively through hard-sphere interactions among the ions (labeled liquidlike disorder) [5]. Although such work claims to represent models suitable for the alkali fluids, the statistical ionic disorder is frozen in and thus is fully decoupled from the electronic structure; thus, we suggest that the correct statistical weighing of the relevant effects are not included in such models.

In this paper, we partially remedy our previous neglect of electron-electron interactions. A tight-binding Hubbard model for the electrons and a lattice gas for the ionic configurations are used. Once again, the electrons and ions are treated self-consistently. The Hubbard model is first treated using the variational Gutzwiller approximation [15], at nonzero temperature [16], and thermodynamic and electronic properties are obtained [17]. For strong electronic correlations, that approximation is then partially improved by integrating into the treatment an exact solution of the Hubbard model for clusters of up to six atoms; such a size is at the limits of normal computational power. Thus, we maintain our previous model but add ''thermalized'' disorder in the dense liquid and an approximate treatment of onsite electron-electron interactions. We reexamine the set of results on the asymmetry of the coexistence curve, the underlying cause of the metal-nonmetal transition, and the paramagnetic susceptibility.

HUBBARD MODEL AND GUTZWILLER APPROXIMATION

Our model is to be self-consistent in the treatment of ions and electrons. The ionic structures will be described within a lattice-gas model: the ions partially occupy the sites of an underlying lattice. We wish to consider a wide variety of disordered ionic configurations, to be able to describe a fluid which ranges from a low-density gas to a dense liquid. For each ionic configuration, the electrons, in the same number as the ions, are described by a single orbital associated with each ion and coupled, by a hopping matrix element $-t$, to the orbitals at nearest-neighbor (nn) sites which are also occupied by ions. The Hubbard Hamiltonian for the electrons also includes an onsite repulsion U between electrons on the same sites:

$$H = -t \sum_{(i,j)\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (1)$$

with c being the annihilation and n the number operators. As the relevant thermal energies turn out to be comparable to the energy scale t, we require the Helmholtz free energy,

with both the internal energy and an entropic contribution, of the electrons described by the above Hamiltonian:

$$F_{el} = \langle H \rangle - T S_{el}. \tag{2}$$

Note that the electronic Hamiltonian and its associated free energy depend on ionic configuration through the connectivity of occupied nn pairs (i,j). We later close the self-consistency, within the model, by taking F_{el} as the only energy for the ions in the lattice-gas configurations. The requirement of thermal equilibrium among ionic configurations then leads to our Monte Carlo procedure, weighing the probability of ionic configurations by the Boltzmann factor $e^{-F_{el}/k_B T}$. Also, mean electronic properties, such as electronic conductivities and paramagnetic susceptibilities, will arise from the Hubbard Hamiltonian with connectivities due to the most probable ionic configurations.

The thermodynamic self consistency, between ionic and electronic properties, demanded in our model is similar to that which might be expected in the alkali-metal fluids, although their realistic description should include the absence of a background lattice and other interactions, such as Coulombic and van der Waals ones, beyond those characterizing this simplest model. On the other hand, this self-consistency is quite different to that in the type of solid-state problems to which the Hubbard Hamiltonian has been applied, for either ordered cases or for those in which a frozen-in disorder of the diagonal or off-diagonal energies are considered. From a practical point of view, the self-consistency we demand poses a difficult problem. The Hubbard Hamiltonian can only be solved exactly for very small clusters and there is strong activity in the search for workable approximations for large clusters and bulk systems. However, in our model we require the solution to this Hamiltonian problem with connectivities ranging from isolated atoms to disordered bulk systems. Therefore, accounting for electronic correlations arising from the Hubbard Hamiltonian need to be treated in a simple approximation which compromises between the requirements of accuracy and of computational cost. We first examined an unrestricted-Hartree-Fock procedure for the Hubbard model. In that case, in the Hubbard term of the Hamiltonian, for each spin orientation, the opposite-spin electron occupation at each site is replaced by its mean-field average and, for fixed ionic connectivity, the electronic spin-dependent problem is iterated to self-consistency; this procedure is a first-order perturbative treatment of electron correlation effects. As U/t grows, it results in strong anomalies for small clusters (with spurious transitions to antiferromagnetic structures). Then, we proceeded to consider other approximations which, in principle, are not perturbative.

We begin with the Gutzwiller [15] variational approximation, with the Rice *et al.* [16] extension to finite temperature. In that case, each cluster is statistically neutral and is treated independently. Electronic double occupancy of sites is penalized by constructing wave functions with the amplitude of such terms reduced from the independent-electron value by a variational parameter; a cluster with a fixed fraction d of the ions having two electrons is examined. The possible values of d range from zero: one electron per site, a situation favored for large U/t, to the value it would take for uncorrelated electrons: $d = 0.25$. Cases in which a fraction n_σ of the

ions are occupied by spin-σ electrons may be considered; for the paramagnetic case $n_\sigma = 0.5$, but we shall later consider an alternative, due to the presence of a magnetic field, in order to calculate the susceptibility. The Gutzwiller approximation results in the following. The exact uncorrelated electronic spectrum (energies ϵ_k) is occupied thermally; this yields an average band energy per particle. Note that since the hopping Hamiltonian has zero trace, then the sum of ϵ_k, over the entire band, also vanishes; thus, the above average band energy is negative. The approximate cluster energy per atom (E), for fixed d, is obtained by adding the onsite correlation energy Ud to the above average, which is multiplied by a spin-dependent band-renormalization factor

$$q(\sigma, n_\sigma, d) = \{[(1 - n_\sigma - n_{-\sigma} + d)(n_\sigma - d)]^{1/2} + [d(n_{-\sigma} - d)]^{1/2}\}^2 / [n_\sigma(1 - n_\sigma)]. \tag{3}$$

Thus,

$$E(d) = Ud + \sum_{k\sigma} q(\sigma, n_\sigma, d) \epsilon_{k\sigma} f_{k\sigma}. \tag{4}$$

The function $f_{k\sigma}$ is the statistical thermal occupancy of the states. For the paramagnetic case, q varies monotonically from zero, at $d=0$, to unity, at $d=1/4$; thus, since the first term in $E(d)$ increases while the second decreases with d, a minimization is possible.

However, for nonzero temperature, entropy effects also need to be included before minimizing. The entropy for free fermions, required to reproduce Landau Fermi-liquid behavior, needs to be weighed by a factor w_k which accounts for nonorthogonality of the variational wave functions at fixed d. The free energy per particle [16] is then given by

$$F(d) = E(d) + k_B T \sum_{k\sigma} w_k [f_{k\sigma} \ln f_{k\sigma} + (1 - f_{k\sigma}) \ln(1 - f_{k\sigma})]. \tag{5}$$

Minimizing this free energy, at first with respect to n_σ, yields the probability that each state is occupied:

$$f_{k\sigma} = \{\exp[q(\epsilon_{k\sigma} - \mu_e)/(w_k k_B T)] + 1\}^{-1}. \tag{6}$$

In the above expression, μ_e is the electronic chemical potential which is chosen so each cluster is, statistically, charge neutral. We proceed by taking the unknown entropy weight function equal to a constant $(w_k = w)$, which is obtained from the sum rule arising from the total number of degrees of freedom at fixed d. Then,

$$w = [(1 - 2d)\ln(1/2 - d) + 2d \ln(d)]/(-\ln 4). \tag{7}$$

Finally, F is to be minimized, using d, to find the average fractional double occupancy of the cluster and to later allow calculation of the equilibrium thermodynamic properties of the system.

In using the Gutzwiller approximation to the Hubbard model, we want to be able to examine the effects due to electron correlations yet we must be careful to avoid qualitative inaccuracies due to the approximation. We have explored the effects of the onsite electron-electron interactions through calculations of the coexistence curve, fractional

double occupancy, electronic conductivity, and magnetic susceptibility, for $0 \leq U/t \leq 6$. This range covers the region in which the effects of the electron-electron interaction become qualitatively important. For instance, the exact Hubbard calculation of the dimer energy shows that if $U/t = 6$ the binding energy is reduced substantially, to 0.30 times its $U = 0$ value. Within the Gutzwiller approximation, the effect of the electron-electron repulsion is always overestimated. Thus, the approximate ground state binding energies of the dimer are reduced with respect to the exact values by factors of 0.91, 0.42, and 0.21, for $U/t = 2$, 4.5, and 6, respectively. For larger clusters and for the temperatures relevant to us, both the effect due to U and its inherent overestimation by the Gutzwiller approximation are strongly reduced. In summary, we may take $U/t = 4.5$ as a representative value for which the effect of the electron-electron interaction is already important and the Gutzwiller approximation is still reasonably accurate, while for $U/t = 6$ the approximation has already become qualitatively inaccurate for small clusters and the small cluster corrections presented later become necessary. The range $0 \leq U/t \leq 6$ can also be made reasonable from an experimental point of view for the alkali fluids. If we compare the calculated binding energy per particle of the dimer relative to that of the bulk fluid (using the model), we obtain too large a value for $U = 0$ and too small a value for $U/t = 6$.

LATTICE-GAS SIMULATIONS

The underlying lattice will be taken to be fcc but the partial occupation by ions is to be restricted so that no ion can have in excess of eight, rather than twelve, occupied nn; this value reflects the experimental situation in the alkali fluids. The lattice-filling restriction results in a disordered system even in the high-density limit. Self-consistency of the electronic states and ionic positions is then sought as follows. For each isotherm of interest, and starting with a set of random realizations of ionic positions for a variety of lattice fillings (restricted as to the number of occupied nn), we obtain the exact uncorrelated electronic states for each realization in the set. The electronic free energy is then calculated for each cluster and minimized with respect to d. The sum over disconnected clusters yields the total electronic free energy. Finally, to simplify the Monte Carlo calculations of equilibrium ionic configurations, these total electronic free energies are assumed to be a sum of an energy for each ion, which depends on the disordered local environment only through the number of its occupied nn. For a set of configurations, letting

$$F = \sum_{k=0}^{8} N_k u_k(T), \qquad (8)$$

with N_k being the fraction of ions with k occupied nn in each configuration, allows the coefficients $u_k(T)$ to be obtained from a least-squares fit to the free energies of the set of configurations. These coefficients, for an ensemble of random occupations, are used as the energies for an ion with k occupied nn in grand-canonical Monte Carlo simulations. Isothermal spectra of configurations obtained by the Monte Carlo procedure are then used to recalculate F and reobtain
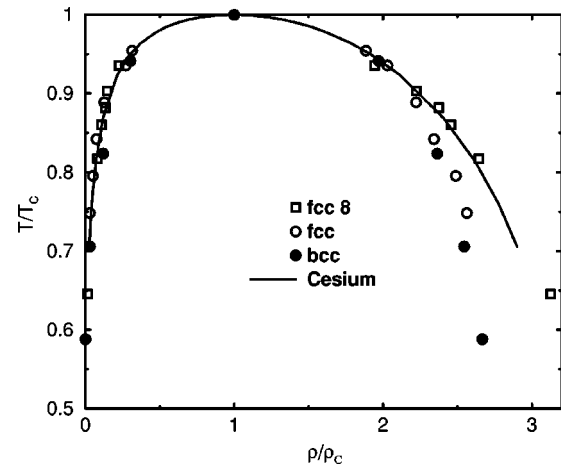

FIG. 1. Comparison of the reduced phase diagrams obtained previously for bcc (full circles) and fcc (open circles) lattices, $U = 0$ see Ref. [9], with the present results (squares) for the fcc lattice restricted so no ion can have more than eight occupied nn sites, also $U = 0$. The experimental Cs data (line), from Ref. [6], is also shown.

the coefficients $u_k(T)$; new Monte Carlo simulations are then performed. This process is repeated until it converges to yield a self-consistent "thermalized" disorder. The average accuracy obtained from the fits is found to be of 0.4%, if $U = 0$, and it decreases to 2%, for $U/t = 6$ treated using the Gutzwiller approximation.

Our grand-canonical Monte Carlo simulations, for each chosen value of the Hubbard parameter, consist in searching for the equilibrium fractional occupation of the lattice (the density ρ), and equilibrium configurations, at fixed temperature (T) and ionic chemical potential μ, using the previously determined site energies $u_k(T)$ and carrying out the self-consistent iterations. If the temperature is sufficiently low, jumps in density are obtained, corresponding to near-coexistence conditions. Suitable averaging procedures are then used.

In Fig. 1, as our first set of results, we compare the reduced vapor-liquid coexistence curves calculated for the case in which the electrons are uncorrelated ($U = 0$): for the bcc and fcc lattices (no filling restriction, from Fig. 6 of Ref. [9]) and those for the fcc lattice restricted so no ion can have more than eight nn, the last case includes a disordered system even at the highest densities; the experimental data for Cs is also shown. In choosing the restricted fcc model, the shape of the phase diagram is brought into an improved agreement with experiment for the higher density liquid branch; this is a modest improvement we sought. It might be noted that background lattice causes the critical temperature to only change slightly in going from a bcc lattice, where $k_B T_c/t$ equals 0.42, to the restricted-occupancy fcc case, in which the value is 0.45.

GUTZWILLER APPROXIMATION RESULTS

A. Coexistence

The vapor-liquid coexistence curves, obtained with our Monte Carlo simulations, for $U = 0$ and Gutzwiller result for $U/t = 4.5$ are shown in Fig. 2, together with the corrected results, discussed later, of the approximation for $U/t = 6$.
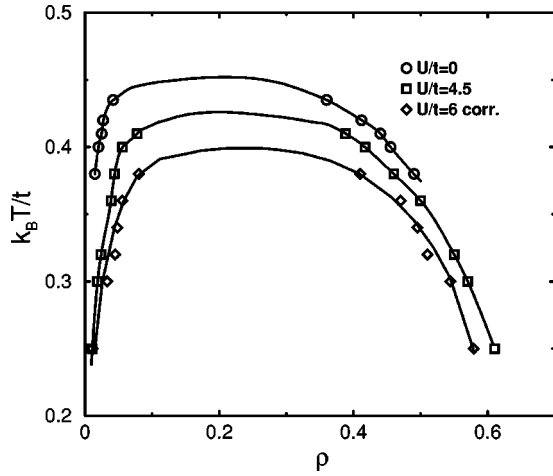
FIG. 2. Calculated self-consistent vapor-liquid coexistence curves with $k_B T$ in units of the hopping matrix element t and ρ being the fractional occupancy of the fcc lattice, for various values of U (in units of t), in the Gutzwiller approximation. The case $U/t = 6$ has all clusters with six or less atoms treated exactly. The lines are merely guides to the eye.

They show critical temperatures which decrease weakly with U. This is in qualitative agreement with our expectations, since the only driving force for condensation in our model is the electronic delocalization, which tends to be restricted by the electron-electron interaction. The decrease of $k_B T_c / t$, with U/t, is not very important; we obtain values of 0.40, for $U/t = 6$, and 0.43, for $U/t = 4.5$, to be compared with 0.45, for $U = 0$. These differences are comparable to those produced by using the restricted fcc instead of the bcc lattice at $U = 0$.

The second effect observed in Fig. 2 is that the coexisting vapor densities increase with U/t, partially decreasing the asymmetry of the liquid-vapor coexistence curve. This effect is also to be expected since for $U = 0$ the vapor phase has a large proportion of dimers and other small clusters, with large binding energies per atom. Increasing U/t decreases these binding energies and the coefficients u_k in Eq. (8) become more linear with k, thus approaching the bond-additive behavior of simple fluids which results in a symmetric phase coexistence. Thus, while the critical temperature is not affected substantially by either the filling restriction on the lattice or by these electron correlation effects, the latter effects attenuate the difference between the present case and models of simple fluids.

With coexistence ionic configurations having been obtained with the Monte Carlo process, we may explore, in some detail, the average electronic properties corresponding to such coexistence conditions. Let us consider first the behavior of d in the Gutzwiller approximation, it is presented in Fig. 3 as function of the density along the coexistence curve for $U/t = 6$. This double occupancy fraction is always below the uncorrelated value $d = 0.25$, but the difference depends strongly on the density. At intermediate and high densities d is nearly constant and its dominant effect is the effective reduction of the band energy by the factor q. In the vapor side, d depends strongly on density and approaches the $d = 0$ limit, in which the electrons would be fully localized and the ions in a cluster would behave as independent atoms.
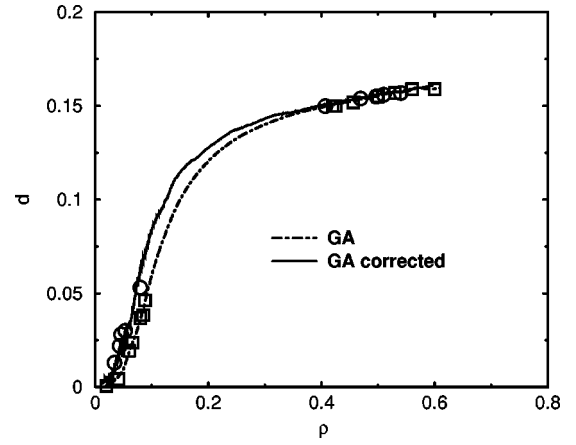

FIG. 3. Calculated mean values of the fractional double occupancy of sites, d, as a function of the fractional occupation of the fcc lattice (ρ), at temperatures corresponding to the calculated coexistence curve, for $U/t = 6$. Results are shown for the Gutzwiller approximation (GA) and for the case in which clusters of 6 atoms or less are treated exactly. The lines are obtained by averaging over all obtained configurations, either at high or low density, at the chemical potential corresponding to coexistence while the points limit the average to configurations whose densities are in a narrow band about those corresponding to each coexisting phase; it can be seen that both procedures give the same results.

This result shows that the electronic properties may in principle be strongly changed by the electron-electron interaction in the range of U/t considered here. As will be shown, this change indeed takes place for the magnetic susceptibility but not for the electrical conductivity.

B. Electrical conductivity

We first focus on the electrical conductivity of the system. It should be noticed that the case of interest to us, a high-temperature disordered system, contrasts with the usual application of the Hubbard model for low-temperature solid-state systems. Whereas in those latter cases the electronic states retain their phase coherence for long distances before it is disrupted by scattering, in our case this distance is expected to be short. In the cases of interest to us, we take, as a reasonable estimate, a phase-coherence length equal to the nn distance in the lattice.

As in our previous work [9], we consider two different approximations to estimate the electrical conductivity, first the "classical" approach by Nield *et al.* [20], based on the connectivity of the ions in each configuration: occupied nn sites in the lattice are connected by unit resistors, and the macroscopic conductivity is obtained from using Kirchoff's laws to obtain the resistance of each configuration and then averaging over configurations. Alternatively, though still assuming a loss of phase memory (due to scattering) after a nn hop, a quantum estimate for the conductivity can be obtained. This approach is a variant of the randomized-phase model of Hindley [18] in the Kubo-Greenwood formula [19], modified for the disordered topology of hopping sites in our model. The system is again described as a network of classical resistors, but now with each bond, between occupied nn sites i and j, having a variable conductance given by

$$1/R_{i,j} \propto \sum_{m \neq n} \frac{\partial f_n}{\partial \epsilon_n} |\phi_n(i)|^2 |\phi_m(j)|^2 \delta(\epsilon_n - \epsilon_m). \qquad (9)$$

The subscripts m and n refer to different electronic states which have the same energy, for the elastic scattering case. The conductivity is then obtained as in the previous case. Also, in this approach, small clusters cannot have any influence on metallic behavior, as they are connected by infinite resistance to other clusters. Then, percolation of the ionic structures is a prerequisite for metallic conductivities. In our finite size system, the condition of elastic scattering is relaxed, with the delta function being replaced by a Gaussian of variance equal to $0.16t$; the precise Gaussian-width value has little importance to the results of the nonzero U cases, if it is small compared to U. The required energies and amplitudes were obtained from the exact diagonalizations of the uncorrelated-electron model for typical equilibrium configurations at the thermodynamic parameters and U values of interest. The results for $U=0$ showed that the thermally averaged conductivity depended mainly on the connectivity of the ions, and the metal-insulator transition was determined by the prerequisite of ionic percolation, without important changes due to the quantum effects.

The usual mean-field treatment of the randomized-phase model [18,5] should be contrasted with our approach. In that usual treatment, the macroscopic conductivity is taken to be proportional to our $1/R_{ij}$ averaged over all possible ionic configurations. At high density, when the disorder is weak, the values of $1/R_{ij}$ are indeed all similar and, since the connectivity is high, this approach would give results which are close to our solutions, using Kirchoff's laws, for the network of classical resistors R_{ij}. However, at lower density, the mean-field approach will completely fail to describe the transition to a nonpercolative regime, as the topological disorder in the connectivity is washed out on averaging $1/R_{ij}$ over ionic configurations.

For nonvanishing U, in addition to the configurations being used, the term with the partial derivative of the Fermi function contains the effects of electronic correlations, in an averaged sense, since it depends on the fractional double occupancy d. Equivalently, the correlation dependence of the conductance can be understood from its dependence on the average electron occupation of the two sites, a pair of probabilities which are assumed to be uncorrelated spatially. If U/t is nonvanishing, the only energy-conserving transport arises from propagating an empty or a doubly occupied site; both possibilities vanish if $d=0$. That is, this transport is possible if the neighboring pair of sites either have one of them singly or doubly occupied and the other empty (the electron can then jump to the empty site). In contrast, if the site pair is occupied by electrons of opposite spin, or the jump proceeds from a doubly occupied to an empty site, the transport causes an energy change of U. Also, if the neighboring pair of sites have parallel-spin electrons the transport is forbidden by the Pauli principle. The average probability of all possibilities are easily obtained from the definition that a fraction d of the ions are doubly occupied, that due to charge neutrality there is also a fraction d which are empty, and that the remaining ions must then have equal fractions of sites occupied by spin-up and spin-down electrons. This ar-
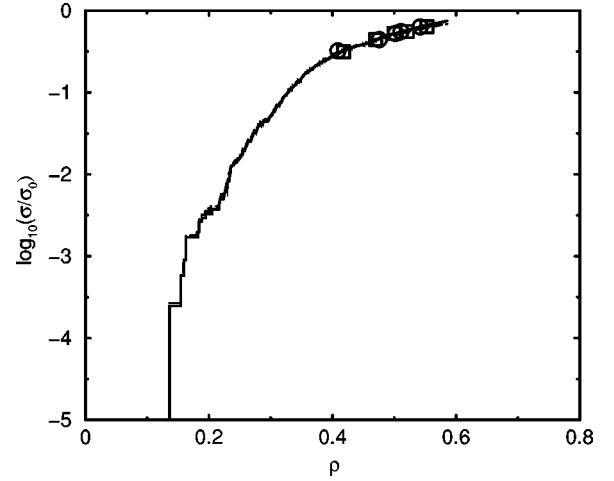

FIG. 4. Electrical conductivity, normalized to the value at the restricted maximum filling of the fcc lattice, logarithmic scale, vs fractional occupation of the lattice. The conditions correspond to the Gutzwiller approximation, the calculated coexistence curve, and $U/t=6$. All pairs of occupied nn sites are replaced by a constant resistor in the classical case (open circles) or by resistors with the variable conductances of Eq. (9) in the quantum case (squares). The points and line have the same meaning as in Fig. 3.

gument yields the same d dependence as does the partial derivative of the Fermi function.

The quantum approach to the conductivity takes electron correlations into account, through the decreasing values of d in the Gutzwiller approximation. It also partially considers disorder-induced electron wave function effects, through the site amplitudes in Eq. (9). Thus, the "classical" conductivity of any percolating ionic configuration may be reduced, and even taken to zero, by the joint effect of disorder and correlation on the electronic structure, with a Mott-Anderson transition. For some particular ionic configurations, near the obtained percolation threshold, the results of the Kubo-Greenwood calculation could show a strong dispersion in the conductances of the different bonds due to correlations and interference effects. The overall system resistance would then be very different from that due to setting all "bond resistors" equal to their mean value, as is done in the simplest approach. Indeed, Franz [21], using a Cayley-tree approximation for the ionic configuration and an independent-electron Kubo-Greenwood formula for the conductivity, obtained a critical density for quantum percolation which is higher than that for classical percolation.

It is found, in the statistical sampling of ionic configurations from our model, that the dominant configurations do give global resistances which are well described by the simplest version of the Nield model: a constant resistor. The conductivity resulting from our procedure is shown in Fig. 4, for the fluid at coexistence, with $U/t=6$ and ionic configurations obtained using the Gutzwiller approximation; also, a comparison is shown with the simplest model. As can be seen, there is good agreement between the alternate methods. These results for $U/t=6$ are in reasonable agreement with our previous $U=0$ work (compare with Fig. 5 in Ref. [9]), noting the difference in density normalization and the fact that the present results are at coexistence while the previous ones were for a near-critical isotherm. Thus, percolation of
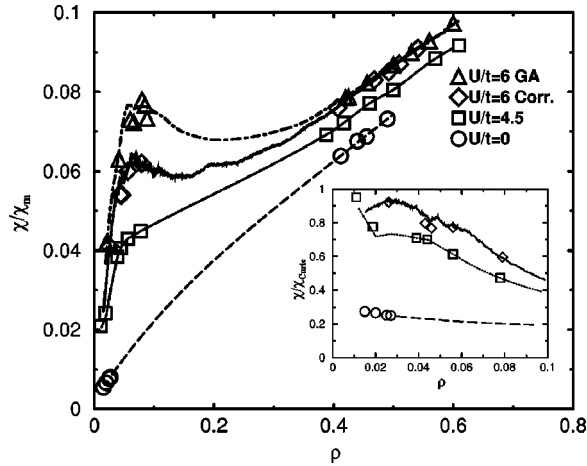
FIG. 5. Volume paramagnetic susceptibility (Gaussian units) vs fractional filling of the fcc lattice. χ_m is the volume μ_B^2/t divided by that of the unit cell in the fcc lattice. The conditions correspond to the Gutzwiller approximation and the calculated coexistence curves, for various values of U (in units of t). The case $U/t=6$ is also shown when small clusters are treated exactly. The symbols correspond to grand canonical averages and the lines to (smoothed) histograms of Monte Carlo averages. Also shown, see inset, are the susceptibilities normalized to the Curie result; at low densities the ratio tends to unity, except for $U=0$ when it tends to 0.5.

the ionic structures, at coexistence, causes the nonmetal-metal transition in the present calculation and thus, presumably, in the alkali fluids.

C. Magnetic susceptibility

Next, the volume susceptibility can be obtained by adding a magnetic field to the free energy calculations (see Ref. [16]). At coexistence, the calculated susceptibilities are shown, for several values of U/t, in Fig. 5. The units used are μ_B^2/t times a density renormalization: the experimental density of the dense liquid divided by the maximum (restricted) fractional filling of the fcc lattice. The insert to this figure shows the susceptibility normalized to the appropriate Curie value. The first qualitative change, due to the electron-electron interaction, is that, for isolated atoms, we recover the low-temperature Curie law $\chi_{\text{Curie}}=N\mu_B^2/k_BT$. In the $U=0$ case, this result was reduced by a factor of 2 by the unphysical statistical weight given to the charged ions. It is noteworthy that as U/t increases the density range in which the Curie law is valid grows beyond that at which isolated atoms are the main species. This effect is due to the decreasing values of d, which in the limit $d=0$ would give the full Curie result for any configuration of the ions. As the system density increases, the electronic degeneracy increases and the magnetic susceptibility tends to the Pauli-like behavior: roughly independent of T and controlled by the density of states at the Fermi level. The results for $U/t=4.5$, along the coexistence curve, show a rather sharp change on departing from the Curie law, towards the Pauli regime, around $\rho=0.04$, on the vapor side of coexistence. The comparison of the $U=0$ and the $U/t=4.5$ results, at high density, show a moderate enhancement of the magnetic susceptibility due to the electron correlation, but the effect is not as important as that in the low density regime.

The results for $U/t=6$, within the Gutzwiller approximation, yield an even larger range of validity for the Curie law. With increasing density, χ has a maximum value at $\rho=0.06$, then a shallow minimum, as both d and the electron degeneracy increase, and finally the susceptibility tends to the Pauli behavior in the liquid. The experimental results also present a local maximum, but there it is observed well within the liquid regime. Within our calculation d never decreases in that region and the calculated susceptibility in the liquid is well below the Curie result. On analyzing the contributions to our calculated χ in the shoulder region, there is a very large contribution from small clusters, an effect which might be an artifact of the approximation. In the temperature range of interest, the Gutzwiller approximation gives $d=0$ for dimers and noncompact trimers if $U/t\gtrsim4.7$, while exact calculations for the same clusters result in a small but finite value of d and a magnetic susceptibility below the Curie limit. Moreover, the $d=0$ result in the Gutzwiller approximation is obtained sharply at large enough U/t, as an unphysical phase transition, while the exact results always change smoothly for any U. This fact confirms that $U/t=6$ may be beyond the range of qualitative accuracy for the Gutzwiller approximation, so that the observed shoulder structure could be an artifact. In the next section we seek a correction for small clusters and check its effects on the properties derived from the model.

SMALL CLUSTER CORRECTIONS

As noted, the Gutzwiller approximation, for large U/t, results in qualitative anomalies, with respect to exact results, in the behavior of d for selected small clusters and such anomalies have an observable effect on their calculated susceptibilities. However, for any cluster with N atoms the exact solution of the Hubbard Hamiltonian may be obtained through the diagonalization of a $4^N \times 4^N$ matrix, though the problem is complicated by the fact that the number of configurations for N-site clusters also grows rapidly with N. Thus, we undertook to carry out a corrective program using exact solutions of the Hubbard model for all cluster configurations which contain up to six atoms; this limit was determined by practical computational limitations, but it includes all the cases in which the Gutzwiller approximation for $U/t=6$ seems to be qualitatively wrong.

The exact energy of clusters is, of course, lower than that obtained using the variational Gutzwiller approximation. Taking into account all the possible configurations of each cluster in the lattice, we calculate $F(T,N)/t$, the thermal average of the free energy per atom as a function of the cluster size N, both with the exact solution of the Hubbard Hamiltonian and with the Gutzwiller approximation (GA), for $N=1$ to 6 and $U/t=6$. An example of the results, for $k_BT/t=0.36$, is shown in Fig. 6. The free-energy difference per site, $\Delta f(T,N)/t=(F_{\text{exact}}-F_{\text{GA}})/t$, is also shown in the inset of Fig. 6, plotted vs N^{-1}. As may be expected, it vanishes for the monomer but is larger for dimers $N=2$ than for larger clusters. In fact for $N=3$ to 6 the difference becomes nearly constant, as should be the case in the thermodynamic limit of large clusters since both F_{exact} and F_{GA} are extensive variables. Thus, we may extrapolate this free-energy-per-site correction to any larger cluster or compact phase for which
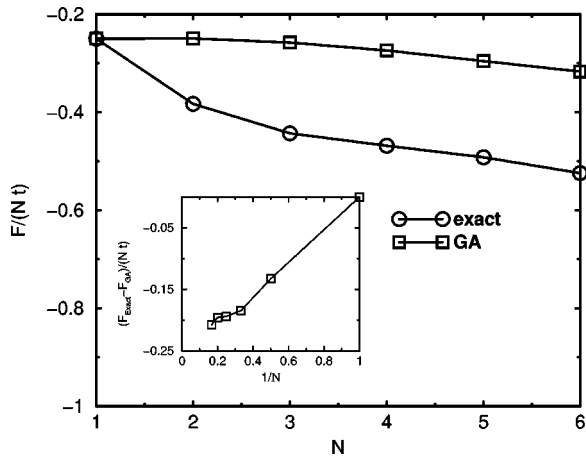
FIG. 6. Free energies per particle, in units of t, vs number of atoms per cluster (N), calculated using typical configurations obtained from the parametrization $U/t=6$ and $k_B T/t=0.36$. The circles are obtained from exact treatment of clusters with up to six atoms. The squares are our previous results, treating all clusters in the Gutzwiller approximation (GA). The inset shows the errors in the approximation plotted vs N^{-1}; for clusters with $N \geq 6$ we have extrapolated this result, by taking the error to be a constant.

the exact solution of the Hubbard Hamiltonian is beyond our computational capability. In this way, we assume that a reasonable way to proceed is to shift the free energies per occupied site of the Gutzwiller approximation by a constant term, $\Delta f(T)$, in all the clusters with $N \geq 6$, while for smaller clusters the energy is calculated exactly. Notice that without this shift, of the free energy of large clusters, the use of the exact solution for $N \leq 6$ followed by the result of the GA method for $N > 6$ yields a discontinuity in the mean energy of the clusters, as a function of N, and would produce unphysical anomalies in the ionic correlation structure of the vapor. Moreover, in the liquid branch the correction is only a rigid shift of the free energy per site. The shift does not change the equation of state nor the ion-correlation structure, which should still be that of the GA. Following this procedure results in sets of $u_k(T)$ which produce fits of the same quality as had been obtained previously.

The effects of these corrective procedures at $U/t=6$ are observable, but not very important, in the calculations of the phase diagram (not shown). Their effect on the calculated average double occupancy d, along the coexistence curve, is shown in Fig. 3; treating the small clusters exactly yields a small increase in the vapor phase. However, the calculated electrical conductivities, along the respective coexistence lines, have unobservable differences, as could be expected since the conductivity only depends on the percolating clusters for which the corrective procedure is only a rigid shift of the energies. A larger difference appears in the magnetic susceptibility, which was the property most sensitive to the electron-electron interaction. The artifact of having $d=0$ for dimers and open trimers, in the GA for $U/t>4.7$, is now corrected and the shoulder in the volume susceptibility becomes smoother. Figure 5 also shows the susceptibility, at coexistence, with the small cluster corrections for $U/t=6$. However, these changes do not alter any of our qualitative conclusions, which appear to be the true properties of the

model and not an artifact of the approximation used to solve the Hubbard Hamiltonian.

SUMMARY AND FINAL REMARKS

Our model is based on a self-consistent treatment of coupled ions and electrons. It considers the ions within a lattice gas, with thermal equilibrium configurations determined using Monte Carlo simulations. The ionic positions are driven by the electronic free energy. The electrons are assumed to obey a Hubbard model with hopping limited to ionic positions at nn sites. The approximation used to treat the electrons is that of Gutzwiller, and Rice *et al.* The model has allowed us to reproduce several features observed experimentally in the alkali-metal fluids. First, the asymmetry and general shape of the reduced coexistence curve. Furthermore, a choice of the hopping parameter t of order 0.5 eV for Cs, which increases monotonically for Rb, K, and Na, gives reasonable approximations to the observed values of the dimer and bulk liquid cohesive energies, and also to the critical temperatures. Also, the general behavior of the electrical conductivities, at coexistence conditions, are reproduced.

The effects of the on-site electron-electron interactions, up to $U/t=6$, do not change the qualitative behavior of the vapor-liquid coexistence or of the nonmetal-metal transition. That transition is still driven by the classical percolation of the ionic clusters, as in the $U=0$ case. The possibility of a Mott-Anderson transition, with the localization of the electronic states by the joint effects of disorder and correlation, is present in our treatment of the model but turns out to be of little importance for the conductivity thermally averaged over the relevant ionic configurations. Clearly, the contrast between the ''classical'' percolation of the ions and electronic percolation is sharper in our model than in more realistic descriptions of a fluid, as we consider the hopping element to be either zero or t, with the disorder appearing only through the connectivity of the orbitals. The presence of disorder in the values of t would enhance the Anderson localization and links with lower values of t would enhance the effects of U in a Mott transition.

The above effects of disorder in the values of hopping matrix element can be partially seen in the disordered off-lattice Hubbard models of Koslowski, Rowan, and Logan [5]. Those models use a hopping matrix element $t(r_{ij})$ having an exponential decay, with ion separation, and a Hubbard term which is treated using the unrestricted-Hartree-Fock approximation. The work analyzes the density of electron states arising from a '''gaslike'' (uncorrelated) or ''liquidlike'' (with hard-sphere correlations) disorder in the ionic structures. In that work, the electrical conductivity is then calculated within the mean-field treatment of the connectivity discussed previously, so that there is no possibility of a transition to a nonpercolative regime. Such a transition, in fact, could never appear with their long-ranged hopping matrix element. Their conductivity results (with a frozen disorder and at zero temperature) depend on the density of states at the Fermi level and on their estimate of the degree of localization of these states. In contrast to our conclusions, the role of the electron-electron correlation is crucial to the conductivity calculated in those models, since the dominant density dependence appears through the square of the density of

states (per unit volume) at the Fermi level. For $U=0$ and as the density is lowered, the electronic band becomes very narrow with a high density of delocalized states at the Fermi level. The result is an unphysical growth of the conductivity with decreasing density, which can only be avoided by taking $U>0$ and having the electron correlation split the narrow band.

In our model, or in any other disordered model with short-ranged hopping, a ''mean-field'' treatment of the connectivity would give similar results to those of Koslowski *et al.* However, we know that such an approach must fail at low enough density, as the systems goes to the percolation transition which is defined by a change from the existence to the absence of a path, through the ionic configurations, in which all hopping jumps are nonvanishing. When the connectivity of each ionic configuration is taken into account, through the classical network of resistors R_{ij} defined in Eq. (9), the ''classical'' percolation becomes a prerequisite for the quantum percolation of the electronic wave functions, even at $U=0$. Our separate treatment of each isolated cluster may be formally regarded as the result of a Mott transition produced by a high ratio between the correlation energy of a cluster and a very low hopping element between separated clusters, which is implicitly included in our model regardless of the value of U. It seems that the existence of well defined ''clusters,'' with a nearly constant distance between nearest neighbors, is a true characteristic of the alkali fluids, so that our choice of either t or zero for the hopping matrix elements is qualitatively justified. Taking a nonzero value for U makes very little difference in the electrical conductivity of our model, as the main effect of the electronic correlation is already included through the classical percolation requirement; in contrast, a choice of $U\neq0$ is crucial in models with an unbounded range for the hopping element. However, we have shown that the classical percolation depends strongly on requiring a self-consistent treatment of the ionic disorder. The metal-nonmetal transition in our model is located well within the vapor phase at coexistence (in agreement with the experimental observations), but only when the strong ionic correlations are included through the self-consistent thermalized disorder. We would obtain a percolation threshold (i.e., a metal-nonmetal transition) quite close to the critical density, at higher density than our present results, if we assumed, as do Kowslowski *et al.*, that the ionic disorder is random and frozen. A future calculation with a continuum description of the fluid, and with thermalized ionic disorder, would allow a comparison of the results for $U=0$ and a short-ranged matrix element $[t(r_{ij})=0$ for r_{ij} larger than some distance] with those with a long-ranged $t(r_{ij})$ but $U>0$. Meanwhile, we conclude that the present model gives a qualitatively accurate description of the threshold for metallic conductivity, ascribing it, in a physically intuitive description, to the ionic percolation.

The main effect of the electron correlation, in our model, appears in the magnetic susceptibility, which for $U=0$ failed to reproduce the Curie law for the low temperature dilute vapor. With $U/t=6$, the Curie law is obeyed by isolated atoms and, in fact, by the coexisting vapor, up to nearly the critical temperature. This result is a combined effect of two factors: lower cluster binding energies and a stronger influence of the electronic correlation in small clusters. In the

liquid branch of the coexistence curve, the susceptibility goes to a Pauli-like dependence, becoming nearly independent of T, but with some enhancement of the $U=0$ results due to electron correlations. The global structure of the magnetic susceptibility per unit volume, along the vapor-liquid coexistence curve, has a weak shoulder joining the regions with the Curie and the Pauli behavior. These results do not change qualitatively on using an exact treatment of the Hubbard Hamiltonian for clusters up to six atoms. Thus, we may conclude that they are true characteristics of the model and not artifacts of the Gutzwiller, and Rice *et al.*, approximation.

In contrast to our results, Chapman and March [13] used the GA to suggest a qualitative explanation for the experimentally observed magnetic susceptibility bump in cesium; also, they assumed that the nonmetal-metal transition takes place at a density which is smaller, but close to, that of the susceptibility bump . However, in the experimental results the local maximum of χ appears well within the liquid branch, at a density which is nearly double the critical one, while the nonmetal-metal transition is in the vapor. In our model both the susceptibility bump and the nonmetal-metal transition appear in the vapor, at about half the critical density.

It is noteworthy that the tight-binding approach, with a single orbital per site and a value of t which reproduces the critical temperature, gives a density of states at the Fermi level, for the dense liquid, which is two or three times smaller than that obtained with a nearly-free-electron model, and an effective mass near the free electron value, which presumably describes the dense fluid reasonably well. This difference partly accounts for the fact that the paramagnetic susceptibility in the Pauli regime is observed to be larger than that calculated in this model. Qualitatively, one is tempted to say that our model should be modified to have a larger number of electronic states and that then joining the Curie to the Pauli susceptibilities would carry the calculated susceptibility bump into the liquid phase. However, such an argument ignores the basic conceptual problem of how to obtain a nearly Curie susceptibility, in the liquid, at the same conditions which produce a large electrical conductivity (with a short mean free path).

Another experimental observation which cannot be reproduced by this tight-binding model is the Knight shift data [22]. Those data, when coupled with the measured susceptibility, for Cs at coexistence, yield an electron density at the nuclei, for those electrons which contribute to the susceptibility, which, for the bulk liquid, is near half of that in the free atom. As the liquid is expanded the electron density at the nuclei decreases with decreasing density, at first slowly and then more rapidly, to a minimum of near a third the atomic value. Then, that electron density presumably increases monotonically to the atomic value in the dilute vapor. The increasing tendency has only been observed near the minimum. The minimum value is achieved at a liquid density corresponding to that at which the susceptibility is observed to have a maximum. The single-orbital tight-binding model not only gives a density of states at the Fermi level which is too small but, neglecting overlap of the functions at the various sites, it gives an average electron density at the nuclei which is always the atomic value.

We conclude that the present model offers a good qualitative description of the liquid-vapor coexistence and electrical conductivity of the alkali fluids. These properties depend strongly on the self-consistency between the ionic and the electronic structures. The use of hopping matrix elements restricted to nearest-neighbor ions provides an interpretation of the metal-nonmetal transition as due to a classical percolation of the ionic structures. We have shown here that this interpretation is qualitatively correct even for high values of the electron-electron repulsion. The results for the electrical conductivity depend weakly on U, with the main dependence on density appearing through the ionic connectivity. Regarding the magnetic susceptibility, the model appears to have the correct trends but our self-consistent calculations show that all the experimental results cannot be directly explained using the Gutzwiller, and Rice *et al.*, approach, as had been suggested by Chapman and March. An extension of the model to include more orbitals and thus increase of the density of states in the liquid may affect this problem and also allow an estimate of the observed Knight shift, but such a suggestion requires further investigation and probably some new physics.

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