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Thermodynamic and electronic properties of a tight-binding lattice-gas model

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Abstract. Thermodynamic and electronic properties are obtained for a lattice-gas model fluid with self-consistent, partial occupation of its sites; the self-consistency consists in obtaining ionic configurations from grand-canonical Monte Carlo simulations based on fits to the exact, electronic, tight-binding energies of isothermal ensembles of those same ionic configurations. The energy of an ion is found to be a concave-up function of its local coordination. Liquid–vapour coexistence densities and the electrical conductivity, which shows a metal–non-metal transition, have been obtained.

1. Introduction

The statistical mechanics of simple insulating liquids is a well developed subject, with different approaches being used to obtain the thermodynamics and the correlation structure from the pairwise additive interaction potential between atoms or molecules [1]. A quantum-mechanical study of the atomic or molecular structures provides the interatomic potential, but, in all other respects, the interaction is decoupled from the classical statistical-physics problem of obtaining the positions and correlations of the atoms. One of the more striking deviations from this *simple liquid* behaviour is provided by liquid metals, in which the conduction electrons are fully delocalized, and the system has to be treated as a mixture of ions (with classical statistics) and electrons (with Fermi–Dirac statistics). The study of dense liquid metals, near the triple-point temperature, has been based on a double perturbative expansion [2] around a *reference simple fluid* for the ions, and around the *jellium* model for the conduction electrons. The vapour, at coexistence with the liquid metal, has a qualitatively different electronic structure, with the valence electrons localized in neutral atoms or clusters. At low temperature, the vapour has extremely low density and is almost trivial. In the neighbourhood of the critical point, and of the metal–non-metal transition region, the interrelation between electronic delocalization and ionic structure becomes crucial, and the approaches valid at low temperature fail qualitatively.

Recent experimental data on the critical region of the alkali fluids [3] provide strong motivation for a more extensive theoretical study of these systems [4, 5]. Our main objective here is to set up a minimal model, including the main relevant features of the coupling between the electronic and the ionic structure, in order to analyse the statistical-physics

problem posed by these systems. We have reported [6] preliminary calculations using this approach. In our model, we forsake the ‘state-of-the-art’ description of liquid metals in condensed matter physics, and our model neglects aspects of the problem which are certainly relevant for some properties of these systems. However, we show that many qualitative effects of the coupling between electronic and ionic structures are already present in a very simple model. This approach allows the study of the critical region through Monte Carlo simulation with systems of large size, compared with those used in ‘state-of-the-art’ models, and helps in discerning the crucial features which yield a liquid–vapour coexistence curve and an electrical conductivity which show that the alkali fluids are qualitatively different from the simple fluids.

Even in a very simple model, the exploration of the liquid–vapour coexistence in the neighbourhood of the critical point requires large simulation boxes, which renders multiple exact solutions of the tight-binding problem rather expensive, computationally. Thus, for our Monte Carlo simulation, the electronic free energy will be determined using a mapping of the cohesive energies onto the local environment of each ion, an approach used in our previous work [7, 8] which finds stronger justification here. This mapping may be regarded as a simplified version of the *glue* model which was proposed and used to study the properties of solid and fluid metals in [9]. The main difference from that work is that, in the present case, the mapping is not an empirical form used to fit macroscopic parameters (cohesive energy, bulk modulus, etc) and then used to obtain other properties of the system. Here, the mapping is used to fit exact solutions for an ensemble of systems described at the microscopic level, and the goodness of the fit provides a direct check of its quality as a trial function, before its use to study thermodynamic properties of the system.

2. The tight-binding lattice-gas model

Our first simplification consists in using a lattice-gas model to represent the ionic structure. Thus, the ions are constrained to partially occupy the sites of a chosen lattice. The critical behaviour of such ‘lattice-gas’ models, with simple pair interactions, shows that they belong to the same universality class as simple fluids; so we may assume that the long-range fluctuations in the critical region are not qualitatively affected by this simplification. Although in the main body of this work the underlying lattice structure is taken to be body-centred cubic (bcc), since it has the same maximum coordination as is observed for the alkali fluids, we shall also investigate the face-centred cubic (fcc) structure to analyse the influence of the lattice on the results.

The electronic properties of our model are described by the simplest one-electron tight-binding Hamiltonian for each ionic configuration, with N ions partially occupying the M sites of the lattice. Thus, we postulate a single electronic orbital at each occupied lattice site (no orbitals at the empty sites) and the electronic hopping is restricted to nearest-neighbour (nn) occupied sites. The one-electron energies, ϵ_n , and wavefunctions, $\phi_n(i)$ (the probability amplitudes that an electron occupies the orbital on the ion at site i), depend on the ionic configuration. They are the $n = 1, \dots, N$ solutions of the eigenvalue equation

$$(\epsilon_a - \epsilon)\phi(i) - t \sum_j^{nn} \phi(j) = 0 \quad (1)$$

for $i = 1, \dots, N$ and with the sum over j extended to all of the occupied sites which are nn to site i , either directly or through the periodic boundary conditions imposed. The site energy, ϵ_a , corresponds to that of the atomic orbital, and t is the constant hopping parameter

for hopping between occupied nn sites. The one-electron eigenstates are to be occupied, using Fermi statistics, with probability

$$f_n = [\exp((\epsilon_n - \mu_e)/k_B T) + 1]^{-1}. \quad (2)$$

The electronic chemical potential μ_e is used to fix the total number of electrons to be equal to the total number of atoms. The only energy associated with each ionic configuration is the electronic free energy:

$$U = 2 \sum_{n=1}^N \epsilon_n f_n + k_B T [f_n \ln f_n + (1 - f_n) \ln(1 - f_n)]. \quad (3)$$

If orthonormal solutions to (1) are chosen, charge neutrality at each site is obtained. An obvious limitation of the present approach is the complete neglect of electron–electron interactions. It is noteworthy that this neglect results in an overestimate of the single-atom entropy, and an underestimate of the experimental dimer energy in comparison with the cohesion of the densest system. A similar model for expanded alkali metals was proposed by Franz [10] using a Cayley-tree approximation for the ionic configuration. Franz’s work did not study the thermodynamic properties of the system, decoupled the ionic and the electronic structure, and only calculated the electronic conductivity and the magnetic susceptibility.

Structural, thermodynamic, and electronic self-consistency demand that the probability of finding any ionic configuration be proportional to its Boltzmann factor, $\exp(-(U - N\mu)/k_B T)$, in a grand-canonical ensemble with chemical potential μ . The self-consistency requirement is the same for very rarefied ($N \ll M$) and for very dense ($N \approx M$) configurations, although their electronic states are very different. In all cases, the preferential double occupancy of the lower energy states provides the cohesive energy of the system. Once the underlying lattice structure is chosen, the only parameters in the model are ϵ_a and t . The parametrization is simplified by taking $\epsilon_a = 0$ as the energy origin, and using t as the energy scale.

3. Results and discussion

Monte Carlo methods can now be used to determine the equilibrium ionic structures in conjunction with the exact tight-binding electronic calculations. We have used simulation cubes with six, seven, and ten bcc cells on each side (432, 686, and 2000 sites, respectively) and periodic boundary conditions. But, as we have commented previously, this approach is computationally expensive and it is therefore interesting to first examine simple approximations to the problem of finding the statistical equilibrium configurations for the ions; these alternative procedures also allow the obtaining of further insight into the problem.

3.1. Mean-field approximation

The simplest approximation which relates the electronic and thermodynamic properties of our model is a macroscopic mean-field treatment. In this approximation, electronic feedback to the structure is ignored and the ions occupy the lattice sites randomly. It is only required that the lattice occupation have a mean density $\rho = N/M$ and that a single ion per lattice site be allowed. We then obtain the electronic free energy $U(T)$ in (3), for a spectrum of realizations of the randomly disordered lattice-site occupations which range from nearly empty to nearly full lattices. An exact diagonalization is carried out for each realization; the electronic structure is found to depend on the specific realization. Results for the energy per ion, $u = U/N$, as a function of the mean density are presented in figure 1 for the bcc

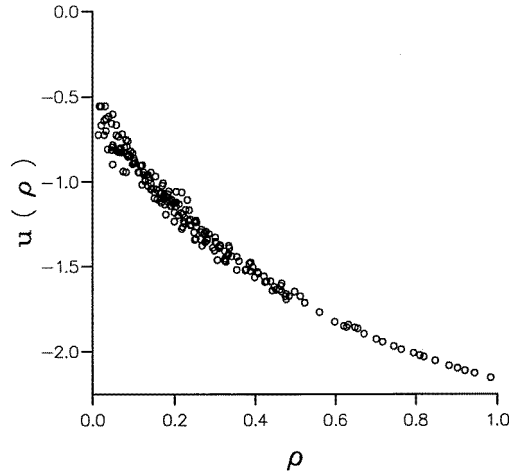


Figure 1. The electronic free energy per ion (in units of t) as a function of the mean fractional-occupation density of the bcc lattice, from a random-occupation ensemble and with the electronic entropy corresponding to $k_B T/t = 0.4$.

lattice; a typical example with $k_B T/t = 0.4$ was chosen for this figure. The values of u , for different realizations with the same value of ρ , have a substantial scatter around their mean value $\bar{u}(\rho, T)$, particularly at low densities. This scatter should scale out with an inverse power of the lattice size; in our finite system, the scatter reflects the energies of ionic configurations with the same number of ions distributed in different (random) patterns. Each isotherm of the average energy per particle is a concave-up function. This functional shape is strikingly different from the straight-line dependence obtained for pair-interacting systems. Our lattice model, at this level of approximation, is equivalent to a description of the electronic properties in continuous models of a fluid, with the correlation structure being that of a system of hard spheres [4, 5, 11]. Such calculations only take into account the packing restrictions, without accounting for fluctuations in the clustering. The difference between the present approach and those for which references are given above is that now we explore the thermodynamic implications of that electronic band structure, with the bold assumption that it provides the only cohesive energy.

In this mean-field approximation, the Helmholtz free energy per ion is obtained from $\bar{u}(\rho, T)$ minus T times the ideal-lattice-gas entropy contribution at each density:

$$F/N = \bar{u}(\rho, T) + k_B T \left[\ln(\rho) + \frac{(1-\rho)}{\rho} \ln(1-\rho) \right]. \quad (4)$$

Equation (4) can now be used to obtain a liquid–vapour coexistence curve; the result is shown as a solid line in figure 2. The critical temperature is found to be $k_B T_c^{mf}/t = 0.56$. The coexistence curve obtained exhibits an asymmetry between the densities of the coexisting vapour, ρ_v , and liquid, ρ_l . The asymmetry obtained contrasts with the fully symmetric results, $\rho_v = 1 - \rho_l$, appropriate to a lattice gas with nn pair interactions. In that latter case, we know that the mean-field approximation overestimates the critical temperature by about 20%. In the following sections we shall examine what results arise from fluctuations with our tight-binding lattice-gas model.

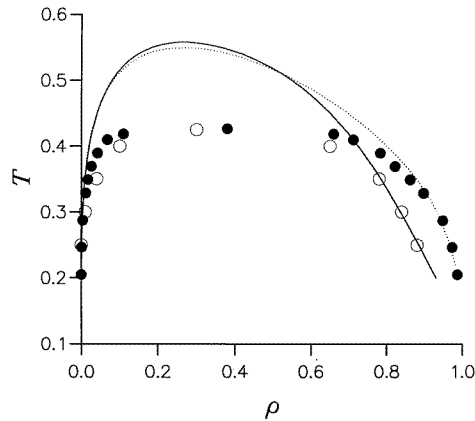


Figure 2. Liquid–vapour coexistence curves, with the temperature in units of t/k_B , versus the fractional-occupation density of the lattice, ρ . The lines are the results of mean-field calculations, equation (4), with the solid one for bcc structure and the dotted one for fcc structure (with an electronic hopping of $0.82t$). The open circles are the self-consistent bcc Monte Carlo results, obtained using the coefficients in equation (5); similarly, the full circles are the fcc results (with an electronic hopping of $0.82t$).

3.2. Monte Carlo simulation

In our model, the electronic free energy is determined by first solving (1) and then occupying the states thermally to obtain the results of (3). Naturally, the eigenvalue equations depend on the ionic correlations through the distribution of occupied sites. In turn, as previously mentioned, the distribution of site occupations is a function of the Boltzmann factors, which depend on the results of (3). Thus, this is a closed system with the distribution of site occupations and the electronic free energy requiring self-consistent determination for each set of thermodynamic conditions.

It seems reasonable to attempt a description of the electronic free energy (3) for each value of T , and representative ensembles of site occupations, as a function of the nn environments of the occupied sites [7, 8]. Thus, we try a least-squares fit, to such ensembles of realizations, with a trial form:

$$U(T) = \sum_{k=0}^{k_{max}} u_k(T) N_k \quad (5)$$

where N_k are the number of ions with k occupied nn in each realization and k_{max} is the coordination number of the lattice. Ions with $k = 0$ represent isolated atoms; equation (3) yields $u_0 = -2k_B T \ln 2$. As previously noted, the entropy contribution for isolated atoms is overestimated (by a factor of two) in the present tight-binding model. The remaining coefficients u_k (for $k = 1, k_{max}$) are free, fitting parameters at each temperature.

For each isotherm, with $k_B T/t$ taking values between 0 and 0.5, we begin by using the trial function (5) to fit results from the exact diagonalizations for the random ensemble of realizations used in the mean-field approximation, at a spectrum of occupation densities. Then, using the coefficients $u_k(T)$ obtained as the site energies for particles with k occupied nn sites, grand-canonical Monte Carlo simulations are performed to obtain equilibrium configurations and densities as functions of the chemical potential along the isotherm. Then, the process is iterated. A modest sample of equilibrium configurations, from those obtained

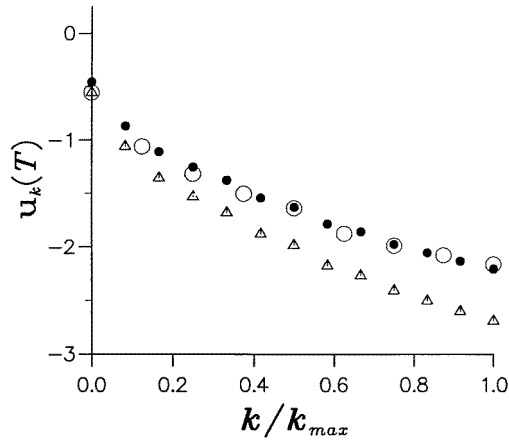


Figure 3. Self-consistent results at $k_B T/t = 0.4$ for the fitting parameters $u_k(T)$, giving the energy (in units of t) of a particle with k occupied nn sites, versus k normalized to the lattice coordination. Open circles are for the bcc lattice with hopping parameter t , triangles are for the fcc lattice with hopping parameter t , and full circles are for the fcc lattice with hopping parameter $0.82t$.

at the chosen temperature and a spectrum of the possible system densities, are again exactly diagonalized. In contrast to the case for the previous mean-field approach, the ion positions are no longer random ones but are correlated with the electronic energy as a function of the local configuration. The states are occupied using the Fermi function, and new parameters $u_k(T)$ are obtained from a least-squares fit to the new electronic free energies as a function of the possible fractional occupation of the lattice. Monte Carlo simulations are again performed with the new site energies. The procedure is repeated to self-consistency at each temperature of interest. We then proceed to obtain the self-consistent phase coexistence and the electronic properties of the system. The fits, using equation (5), are very good, with relative differences always less than 2%. An example, obtained as described, of the coefficients u_k for the bcc structure and with $k_B T/t = 0.4$, a near-critical isotherm, is shown as open circles in figure 3. Such results clearly demonstrate the non-linear dependence of the coefficients on the index k , expected from the non-additive character of the interactions. A system with nn pair interactions would be represented exactly by (5) with coefficients u_k proportional to the index k .

Our simulation boxes are too small to allow a detailed study of the critical region. However, the overall features of the self-consistent liquid–vapour coexistence curve have been obtained; the results are shown as open circles in figure 2. The critical temperature, in units of the hopping parameter, is reduced to about 0.42 from the previous mean-field result of 0.56.

We have sought further proof that the number of occupied nn to the occupied sites is the important factor in determining the electronic energy of our system; that is, that the fitting method (equation (5)) gives high-accuracy results. As a test, after equilibration, we have generated one hundred ionic configurations from successive, complete, Monte Carlo sweeps of our lattice, at fixed temperature and chemical potential. The exact electronic energy for each of the configurations was obtained and compared to that of the fitting method, using the previous set of fixed u_k for the chosen temperature. We have chosen a temperature $k_B T/t = 0.4$ and a chemical potential $\mu/t = -2.275$ as the conditions for performing

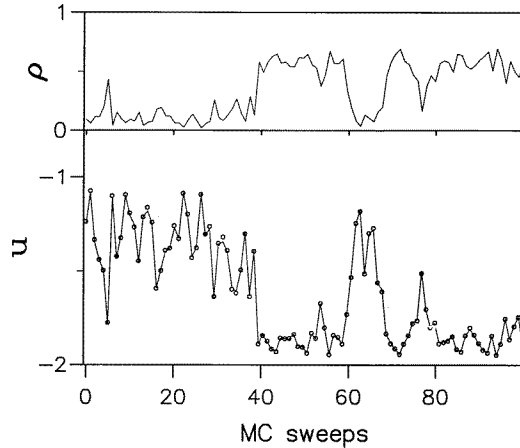


Figure 4. The fractional-occupation density (upper panel) and electronic free energy of the system (in units of t , lower panel) for configurations resulting, after equilibration, from one hundred, successive, complete, Monte Carlo sweeps of the bcc lattice. The thermodynamic conditions are close to those appropriate to the critical point: $k_B T/t = 0.4$ and $\mu/t = -2.275$. The solid lines (to guide the eye) join the resulting densities and also the electronic energies obtained from exact diagonalizations of the ionic configurations. The circles give the electronic energies from the fit of equation (5) to the energies of the isothermal ensemble, i.e. from the fixed set $u_i(T)$ used in the Monte Carlo simulation.

the grand-canonical Monte Carlo simulations. These conditions are near the critical point, where the density has very strong fluctuations and the ionic configurations change from isolated clusters to complex percolating structures. The fractional-occupation density was observed to indeed have large fluctuations, as shown in the upper panel of figure 4 (the line connecting the results for each sweep is shown to guide the eye). For each of the ionic configurations obtained, the electronic energies per ion are also shown in the lower panel of figure 4; results are exhibited for both the exact diagonalizations of each ionic configuration (connected by a solid line) and points arising from the fit of equation (5). The accuracy achieved by the fit of equation (5) can be seen to be impressive, even in this case which has large critical fluctuations.

The above results show that the description of the electronic free energy in terms of the local coordination of each ion (5) is able to give accurate results for ionic configurations with very different kinds of disorder. These results support our previous use of this map [7, 8], in which the coefficients of (5) were first calculated assuming that the ionic correlation function was that of a hard-sphere system and then were used to obtain alternatively correlated structures with strong clustering effects.

3.3. The influence of the underlying lattice

In order to study the influence of the choice of the underlying lattice structure on the thermodynamic properties of the model, we have compared results obtained using a fcc lattice with the previous ones which were based on the bcc lattice. For the fcc system, we have used simulation parallelepipeds of five by five by ten cubic cells (1000 sites), and periodic boundary conditions. To compare the phase diagrams for a given fluid obtained by using different background lattices, we must first consider how to establish that the fluid is

the same one. We assume that a given fluid is specified by its density and cohesive energy, at $T = 0$, when the lattice is completely full. As the coordination number is different for bcc (8) and fcc (12) lattices, equating the fluid densities in the two systems is easily accomplished by a change in the lattice constant. This parameter does not appear explicitly in the calculations, since all of the results are given as depending on the filling fraction. The zero-temperature cohesive energies per ion of the completely full lattices are $u^{fcc} = -2.516t$ and $u^{bcc} = -2.064t$, if the same hopping t is used. To make these cohesions equal, with t defining hopping in the bcc system, we set $t^{fcc} = 0.82t$. At non-zero temperatures, all thermal energies will be left scaled to the t for the bcc system, while the fcc electronic energy calculations will take into account the modified hopping parameter.

Figure 3 shows that the fcc parameters u_k (triangles), obtained self-consistently for the example of a near-critical isotherm, $k_B T/t = 0.4$, are quite different from those for the bcc lattice (open circles), if scaled to the same t . However, when the fcc calculation uses, for the electronic energy calculations, a hopping parameter of $0.82t$ (full circles), the curve almost coincides with the bcc data. Further, in figure 2 we also show the fcc liquid–vapour coexistence curves obtained using the electronic hopping $t^{fcc} = 0.82t$. The fcc mean-field approximation (dotted line) yields a critical temperature $k_B T_C^{mf}/t = 0.55$. The liquid–vapour coexistence obtained with the self-consistent map (full circles) has a critical temperature $k_B T_C/t = 0.42$. Self-consistency yields a similar reduction from the mean-field result for both lattices. These coexistence curves also exhibit an asymmetry between the liquid and vapour branches. When we compare, in figure 2, the self-consistent fcc liquid–vapour coexistence curve (with the electronic hopping of $0.82t$) with the previous bcc result, the two curves can be seen to be quite similar; the main discrepancy is in the liquid branch, due to the lattice-coordination difference. Given these comparisons, we conclude that the choice of background lattice does not strongly affect the thermodynamic properties calculated for the fluid under consideration.

3.4. Electrical conductivity

Our model, although extremely simplified, allows the electrons to couple with the ionic structure. The effects of this coupling are crucial to the electronic structure of the model. Mean-field methods with random occupation of the lattice, like sophisticated treatments in which the electronic density of states in a liquid is obtained assuming hard-sphere ionic correlation functions [4], would give an electronic density of states which is independent of the temperature. In self-consistent calculations, the electronic structure will reflect the dramatic change in the ionic correlations accompanying the thermodynamic phase change. This self-consistent interdependence of the electronic and ionic structures should dominate the electronic properties of the system. We examine some of the consequences of this coupling below, returning to the bcc lattice model.

We have explored the relationship between electrical conductivity and ionic structure. The experimental signature of a metal–non-metal transition in these systems is a decrease of several orders of magnitude in the conductivity of the expanded fluid. In our previous work [7, 8], we suggested that such behaviour is dominantly driven by the onset of a lack of percolation of the ionic cluster structure leading to a lack of macroscopic delocalization of valence electrons, rather than by other features such as a transition to a non-metal due to the Fermi level moving into a regime in which the disorder leads to interference-induced (Anderson-type) electronic localization. The present model allows a probing of that assumption, since the electronic wavefunctions can be found for any ionic structure.

In our model, it is obvious that the ionic percolation sets a lower bound in density for

the existence of metallic conductivity. We can begin to estimate a quantitative measure of the ionic percolation effects on the electrical conductivity through the Kirchhoff's law model proposed by Nield *et al* [12]. Given an ionic structure, this simplest approximation replaces each pair of occupied nn sites by a classical, fixed-value resistor. The resistance of the resulting network is calculated along the various directions in the simulation box. The value of the 'bond resistance' may be fixed to obtain the experimental conductivity in the dense liquid (near the triple point) and then the predictions of the model, along the coexistence curve or along any isotherm, can be compared to the experimental data for the alkali fluids, to see whether similar features are obtained.

The above method neglects the effects of electronic wavefunctions, which may preclude electronic conduction even if the ionic structure percolates throughout the system. The excellent congruence between the results obtained in our previous work [7, 8] and data for fluid caesium suggested that electron localization, due to disorder-induced interference effects (Anderson-type effects, in contrast to a lack of percolation), was not important in the conductivity of expanded alkali metals. In the present model, we may compare the results of the above simplest Nield model with a quantum estimate for the conductivity—for example, the results of assuming a loss of phase memory (due to scattering) after a nn hop. This alternative is a variant of the randomized-phase model of Hindley [13] in the Kubo–Greenwood formula [14], modified for the disordered topology of hopping sites in our model. In this alternative approach, the conductance between occupied nn sites i and j is given by

$$1/R_{i,j} \propto \sum_{m \neq n} \frac{\partial f_n}{\partial \epsilon_n} |\phi_n(i)|^2 |\phi_m(j)|^2 \delta(\epsilon_n - \epsilon_m) \quad (6)$$

which requires a non-zero product, at nn sites, of different electronic states, m and n , which have the same energy, for this elastic scattering case. In our finite-size system, the condition of elastic scattering will be relaxed, with the delta function being replaced by a Gaussian of variance equal to $0.16t$. Actually, the precise Gaussian-width value has little importance to the results, except near complete filling of the lattice. The required energies and amplitudes are obtained from the exact diagonalizations for typical equilibrium configurations for the thermodynamic parameters of interest. Results for the macroscopic conductivity are then obtained as in the Nield model but using (6) for each 'bond resistor'. This approach partially takes into account electron-wavefunction effects on the conductivity. We have used it, with phase-memory-loss scattering after a nn hop, to include the strong scattering to be expected in a hot disordered fluid.

For some particular ionic configurations, near the percolation threshold obtained, the results of the Kubo–Greenwood calculation could show a strong dispersion in the conductances of the different bonds due to interference effects, which would then be reflected in an overall resistance very different from that due to setting all 'bond resistors' equal to their mean value, as is done in the simplest approach. For example, Franz [10], using a Cayley-tree approximation for the ionic configuration and our Kubo–Greenwood formula for the conductivity, obtains a critical density for quantum percolation which is higher than that for classical percolation. However, in the statistical sampling of ionic configurations from our model, it was found that most configurations do give global resistances which are well described by the simplest version of the Kirchhoff's law model. An example of the results of each of our two procedures is shown in figure 5, for a near-critical isotherm of the bcc lattice. As can be seen, there is good agreement between the alternative methods, which indirectly supports our previous hypothesis that the non-metal–metal transition in the alkali fluids is mainly driven by the onset of percolation of ionic structures.

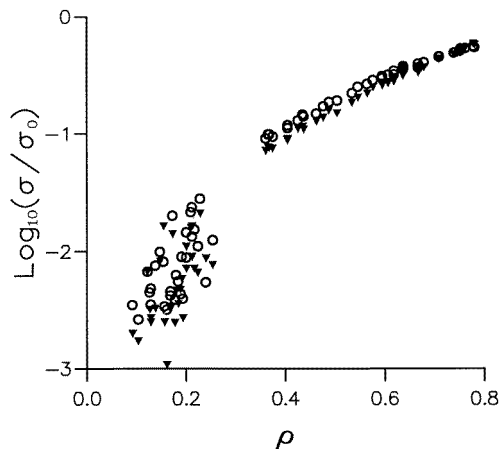


Figure 5. Electrical conductivity estimates σ for the bcc lattice, normalized to the conductivity at full lattice occupation σ_0 , on a logarithmic scale, versus the density, for the isotherm $k_B T/t = 0.4$. The full triangles are obtained using the Greenwood–Kubo quantum values of the bond resistors (equation (6)); the open circles are the results of using a fixed-bond resistor; both approaches then use the Kirchhoff model for a spectrum of Monte Carlo configurations.

4. Summary

We have presented a tight-binding lattice-gas model, which can be solved to obtain its structural and thermodynamic properties. The model takes into account the inhomogeneity of statistical configurations of the system, driven by non-additive interactions due to valence-electron delocalization. A self-consistent procedure is used to determine the equilibrium structures: Monte Carlo simulations coupled to exact diagonalizations and site-energy fittings.

As previously noted, the first qualitative consequence of the feedback from the electronic to the ionic structures in our model is the existence of a vapour–liquid phase transition. At low temperatures, random distributions of the ions, assumed in studies with frozen disorder, are thermodynamically unstable. The instability can cause a condensation into drops of dense liquid at coexistence with a vapour at lower density. The qualitative features of the condensation which results from our model, driven by the electronic band energy, will be compared with experimental alkali-fluid data. Although the extreme simplicity of the present model should preclude expectations of quantitative agreement, the phase diagrams in figure 6, our self-consistent results (full and open circles, for bcc and fcc structures respectively) and experimental data for Cs (solid line), all in units of the critical temperatures and densities, show an appealing similarity. The strong asymmetry, observed in the experiments, between the coexisting vapour and liquid densities is also quite clear in the results from our model; we emphasize this feature by showing the ‘diameter function’ from the fcc calculation. This asymmetry contrasts with the coexistence curve results of lattice-gas models with additive nn pair interactions, also shown in figure 6.

Our second qualitative result is that, in this model, equilibrium density fluctuations influence the phase diagram only weakly. The critical temperature in the mean-field approximation is about 20% higher than the value obtained in the Monte Carlo simulation. This difference is similar to that obtained for usual models of simple fluids, with pair interactions in three dimensions. However, such a modest difference contrasts with the

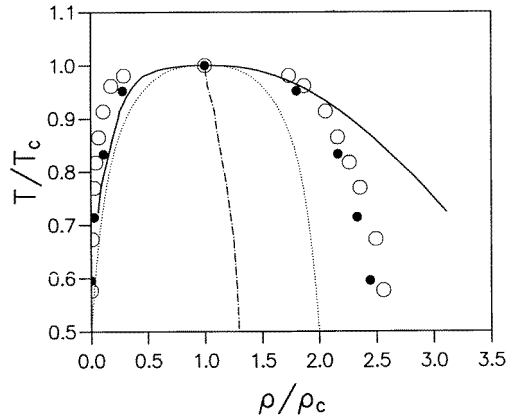


Figure 6. Reduced liquid–vapour coexistence curves, temperatures and densities scaled to their critical values. The full line is a fit to experimental data for Cs. The circles are the self-consistent Monte Carlo results from the present model; the full circles are for bcc structure, and the open circles are for fcc structure. The chain line shows the diameter function $\rho_d = (\rho_L + \rho_V)/2$ for the self-consistent Monte Carlo results for the fcc lattice. The dotted line is the result for a bcc lattice-gas model with additive nn pair interactions.

much larger effect—a ratio of almost a factor of three—in our previous work using pseudopotentials [7, 8]. The origin of this contrast is that in the previous work both the ion–ion and the ion–electron correlations are neglected in the mean-field perturbative treatment using the homogeneous electron gas as a reference. The poor description of ion–electron correlations, even after the perturbation of the reference system, is the principal cause of the high critical temperature which results. In contrast, in the present tight-binding model, ion–electron correlations are treated exactly, there are no direct ion–ion interactions to be affected by the correlations of the ionic structure, and the difference between the mean-field treatment (a random filling of the lattice sites) and the simulation is only due to corrections of the electronic energy due to the effects of ion–ion correlations.

The electrical conductivity of the system was estimated, using a quantum-resistor network and the self-consistent ionic structures. The metal–non-metal transition was then probed in a manner which is consistent with the previous structural treatment. It appears that the main reason for the material becoming non-metallic, on reducing its density, is the lack of percolation of its self-consistent ionic structure, rather than this being due to more complicated interference-induced electron localization effects.

The present model has provided confirmation that an energy mapping which reflects the local coordination of each particle gives a good description of the system. Thus, we have verified that the approach followed in our previous work [7, 8] is justified and adequate. Our conclusion that the system becomes metallic or not according mainly to the self-consistent percolation of the site occupation is based on the one-electron approximation. Since we assumed a paramagnetic system and did not include Hubbard-type interactions, we cannot speculate on the effects of Mott–Hubbard interactions on the metal–non-metal transition. Such effects will be investigated in future work.

The model is a very simplified representation of a metal–atom fluid, as only the electronic band energy contributes to the system’s cohesion. Nevertheless, the results obtained show that the model contains the basic ingredients to allow qualitative reproduction of the peculiar behaviour observed in the alkali fluids. These peculiarities include the metal–non-metal and

liquid–vapour transitions, the general shape of the coexistence curve, and the connection between the ionic and electronic structures. The self-consistency of the electronic and ionic structures is the feature which allows the model to give a unified treatment of a wide spectrum of the system properties and to qualitatively describe observations for the alkali fluids.

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