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The phase diagram and fluid structure from a simple model of the alkalis

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Abstract. We present a lattice-gas model with attractive interactions arising from valence electron delocalization from single-site orbitals. Such effects cannot be described by a pair-interaction potential and produce a strongly asymmetric phase diagram for a nonmetallic molecular vapour coexisting with a liquid metal. Although the model is extremely simplified, it reproduces features of the alkali fluids which contrast with those of simple fluids. A unified treatment of the ionic and electronic structures allows obtaining the electrical conductivity at chosen thermodynamic conditions. We have found that the metal–nonmetal transition in this model is driven by the break in the percolation of the ionic structure, which takes place in the vapour phase close to the critical temperature, rather than by electronic localization induced by other effects of disorder.

Simple liquids are described as systems of classical particles with isotropic, pair-additive interactions. The alkali fluids show strong deviations from these requirements, with fully delocalized valence electrons in the dense liquid metal and electrons which are localized around each ion (making neutral atoms) or small clusters in the rarefied vapour. A large body of experimental data has been obtained for the alkali fluids at high temperatures [1], and the vapour–liquid phase diagrams of these systems, with temperatures and densities scaled to their critical values, clearly show a law of corresponding states, but one which is different from that for simple atomic and molecular fluids.

Theoretical studies of the dense liquid metal phase [2] use electron–ion pseudopotentials and standard perturbation theories which begin with a jellium model for the valence electrons and a reference simple fluid for the ions. These approaches provide fairly good descriptions of the thermodynamics and structure of the dense liquid metals. However, they start failing near the critical region of the fluids, as the system approaches the transition to a nonmetallic molecular vapour, with a qualitatively different structure for the valence electrons [3]. We have recently presented a study of the alkali fluids which combines the perturbation approach for the dense liquid metal with a molecular description of the low-density vapour, through a variational principle [4]. The internal energy for each ion is taken as the lower of the atomic ground state and that of a plasma, described by the perturbation theory, with an effective density ($\hat{\rho}$) which describes the local environment of the ion. When this effective density is taken to be the macroscopic one (ρ), the theory becomes a variational mean-field approximation which gives a gross overestimate of the critical temperature (by about

a factor of 3.5) and a very bad description of the vapour–liquid coexistence curve. In computer simulations for both lattice-gas [4] and continuous [5] fluids, when we use an *ad hoc* description of $\hat{\rho}$ in terms of the coordination of each ion, we obtain both a good estimate of the critical temperature and a qualitatively correct shape for the vapour–liquid coexistence curve.

However, the above description is far from being fully satisfactory. First, because of the purely *ad hoc* character of the energy map in terms of the local environment and second, because, although it provides fairly accurate thermodynamic properties, it does not give a self-consistent description of the electronic structure. Such a description is required to understand the nature of the transition from metal to nonmetal. In our previous work [4], we claimed that this transition was essentially driven by percolation of the ionic structure; this view was supported by our results for the electric conductivity along the critical isotherm, calculated with a ‘classical’ description of a network of unit resistors between ions at the nearest-neighbour distance. Now, we present a simplified model which allows for a self-consistent treatment of the ionic and electronic structures. Our aim is not a quantitative description of the alkali fluids, but rather, the simplest model sharing with them the basic qualitative features of their thermodynamics and electronic structure.

As a first simplification, we use a lattice-gas description of the ions; this approach was already taken in some of our previous work [4]. Thus, the ions partially occupy a BCC lattice, so at high density (dense liquid) each ion has eight nearest neighbours. The electronic structure is described by a tight-binding model, with one orbital localized at each occupied lattice site. The electronic hopping matrix element is restricted to nearest-neighbour ions and has a fixed value t . For a given ionic configuration of the lattice gas with N monovalent ions, the electronic states and energy are obtained from occupying the N lowest one-electron eigenstates (including the twofold spin degeneracy) of the tight-binding Hamiltonian. Isolated ions contribute with the ‘atomic energy’, ϵ_a , which will be taken as our zero of energy. In the dense fluid, the electronic states are extended over the entire system and their energies form a continuous band from $-8t$ to $8t$. In its ground state, the lower half of the energy band is occupied. The typical description of a metal results, with a cohesive energy of about $2t$ per ion. In the critical region, we expect large clusters with complex connectivity, the electronic states would reflect the topological disorder of the tight-binding Hamiltonian, and the internal energy of the system would result from occupation of the N lowest eigenstates. The model could be related to the electronic structure in disordered systems, but in our case: the topological disorder of the ions is obtained self-consistently, with the electronic band energy, through Monte Carlo simulation in a finite lattice. The hopping element t is the only parameter and it sets the scale of energy and temperature. In this tight-binding model the nonadditive character of the interactions is clear, e.g. the ratio of the cohesive energy per ion of an isolated dimer to that of a dense liquid is approximately 2; in the equivalent model for simple fluids (a lattice gas with additive, nearest-neighbour, pair interactions), the above ratio would be the coordination number (8). The experimental values for that ratio in the alkali fluids are about 3, so our model gives a qualitatively correct, but somewhat exaggerated, description of this crucial aspect.

The model has been studied in two steps. We generate random configurations of lattice occupation, over the whole range of mean density ρ . For each configuration, the tight-binding problem is solved exactly and the band energy is obtained. As a first step, we can fit these values to a single function $u(\rho)$, giving the mean energy per ion, and this function can be used to get the mean-field-approximation phase diagram for the model. Alternatively, the same electronic configurations may be used to fit a map of the energy to the local environment of each ion, so that the total energy is given by $U = \sum u_k N_k$,

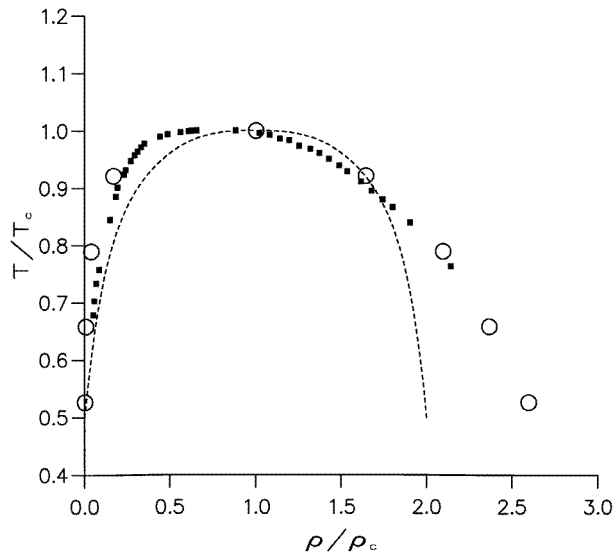


Figure 1. Liquid–vapour coexistence curves in reduced critical units, T/T_c and ρ/ρ_c . Open circles are the results of the Monte Carlo simulations for the present model. The full squares are experimental data for caesium. The broken line presents the symmetric phase diagram of the BCC lattice gas with additive, nearest-neighbour, pair interactions, from a Monte Carlo simulation.

where the N_k are the number of ions in each configuration which have k (1 to 8) occupied nearest-neighbour sites. The coefficients u_k are free parameters used to fit the whole set of U for the various N_k in the configurations generated previously. This energy has the same form as the *ad hoc* map we had used previously [4] and also that in the ‘glue models’ [6] used to describe the properties of metals in another context, but now it is a parametric function used to fit the results of an ensemble of microscopic electronic calculations. The good accuracy of the fit (always within 2%) gives support to this map of the energy in terms of the local environment of each ion and allows us to use it in a larger series of Monte Carlo simulations to generate the thermodynamics and phase coexistence of the model. The critical point, at a fractional lattice occupation of $\rho_c = 0.29$, has $k_B T_c = 0.38t$, which is quite different from the mean-field results of $\rho_c = 0.13$ and $k_B T_c^{mfa} = 0.64t$. This large discrepancy was already noted in our previous work and seems to indicate that the clustering effects are much more important in alkali fluids than in simple fluids. The results for the vapour–liquid coexistence are presented in figure 1, in reduced critical units. The shape of the curve obtained is compared to that for the lattice-gas model with pair interactions and, also, with the experimental results for caesium. It is clear that our simple model provides a good qualitative description of the asymmetry in the experimental coexistence curve. The asymmetry results from the nonadditive character of the interactions.

The metal–nonmetal transition can be studied within the model, using the electronic structures of equilibrium statistical configurations at any chosen thermodynamic conditions. The model will recover the limits of the metallic dense liquid and the nonmetallic molecular vapour. We can follow the transition with a Kubo–Greenwood approximation for the electrical conductivity. We have obtained results showing that in the statistical average, the transition from metal to nonmetal in the model is mainly driven by the lack of percolation in

the ionic structures. The results with the Kubo–Greenwood approximation are very similar to those obtained with a network of classical resistors [4].

We are working on the extension of the model to include thermal effects on the electronic structure and the main effects of the electron–electron interaction. This would allow us to check the possibility of a Mott-type metal–nonmetal transition and also to calculate the paramagnetic susceptibility for comparison with experimental data.

Acknowledgments

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