Simple Model for the Phase Coexistence and Electrical Conductivity of Alkali Fluids

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We report the first theoretical model for the alkali fluids which yields a liquid-vapor phase coexistence with the experimentally observed features and electrical conductivity estimates which are also in accord with observations. We have carried out a Monte Carlo simulation for a lattice gas model which allows an integrated study of the structural, thermodynamic, and electronic properties of metal-atom fluids. Although such a technique is applicable to both metallic and nonmetallic fluids, nonadditive interactions due to valence electron delocalization are a crucial feature of the present model.

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Until recently little has been known regarding metal-atom fluids near the high temperatures and pressures characteristic of their liquid-vapor critical points. However, such knowledge is not only of considerable scientific interest but is also required for potential technological applications near those conditions. The electronic and thermodynamic properties of such fluids are intimately related, and knowledge of these properties is essential in determining the right material for a given application. Such considerations have motivated experimental studies of those materials with the lowest critical temperatures: Hg (1751 K), Cs (1924 K), and Rb (2017 K) [1], with data on K (2178 K) now being available [2]. The data have become precise and reliable in the last decade and span thermodynamic and electrical measurements under the same conditions. Such data show that the liquid-vapor coexistence curve of metal-atom fluids are different from those of Lennard-Jones-like ones [2,3]. For example, the liquid and vapor branches of the coexistence curves are strongly asymmetric and the rectilinear diameter law breaks down over a large temperature range, not only very close to the critical points. These materials also undergo a metal-nonmetal (M-NM) transition. This body of data, however, still seeks microscopic theoretical foundations [4]. This paper presents a simple model which appears to contain the basic ideas required to reproduce, in a unified manner, the peculiar characteristics observed in the alkali fluids.

The goal of the present work—understanding the structural, thermodynamic, and electronic properties of metal-atom fluids—poses a considerable scientific challenge. Its various aspects are coupled since it is the electrons which determine interatomic interactions and thus the structure and thermodynamic data. The ionic structure, in turn, determines the electronic properties. In the study of metal-atom fluids it is difficult to impose a structure, since it is so intimately related to electronic effects and there is no long-range symmetry to simplify the problem. Also, because in such materials the interactions are not pairwise for intermediate densities due to electron delocalization over some regions, the problem is more complicated than that for fluids in which the interactions are not state dependent. Similarly, as these materials also undergo a M-NM transition, the traditional techniques used to study free-electron-like fluids are not applicable over many of the conditions of interest. The microscopic theory required for these materials should seek to explain the essential interdependence of thermodynamic, structural, and electronic properties. Previous theoretical efforts to comprehensively explain the available experimental data on metal-atom fluids have been sparse. The points of view taken were usually based on the limiting cases of either a metallic dense liquid or solid, or alternatively of a nonmetallic dilute vapor. Attempts were then made to describe the fluid, or some of its properties, in a limited density and temperature range [5–7]. General arguments based on electron correlation effects (Hubbard model) and/or disorder induced localization (Anderson model) [8] are useful to study the M-NM transition in systems with frozen ionic structure but probably not in metal-atom fluids.

A first step towards a comprehensive theoretical treatment attempted the extension of concepts and techniques of plasma physics to treat both liquid and vapor phases, and then tried to introduce the required neutral atoms and small clusters [9]. We also proposed such an approach [10,11] and showed that a toy model gives a liquid-vapor coexistence and a critical point with some correct features, but we were far from reproducing the peculiar coexistence curve of alkali fluids. In recent work [12], we followed this approach including a quantitatively good description of the plasma: a standard description of liquid metals near their triple point [13]. Extension of this treatment to high temperature and low density gave a plasma liquid-vapor coexistence with a very high critical temperature (around 4 times the experimental value) and a very different shape for the coexistence curve than that observed. We then extended the model to allow for chemical coexistence

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of neutral atoms with the plasma. Virial ion-atom interactions were used, instead of being neglected as in the previous toy model. However, reasonable values of the parameters did not improve the previous plasma results. We have concluded that a mean-field theory is not capable of reproducing the structure or phase diagram of the alkali fluids [12].

An unanswered question, in the above approach, is: Why do some fraction of the valence electrons choose to be bound in atoms while others are delocalized, at fixed temperature and density? The answer must lie in a hitherto ignored underlying structure. An important clue is that clustering effects are strongly enhanced for metal-atom systems, compared to nonmetallic ones, due to their high cohesion which arises from the valence electron delocalization over the cluster. Such cohesion is known in rather small alkali-atom clusters; they have interionic separation typical of normal liquids. In contrast, to retain its valence electron an atom should have no near neighbors (in the above scale) to which that electron can be favorably delocalized; in the language of metals, weak screening results in atom formation. We present here a simple lattice gas model which includes such considerations and yields results showing the observed peculiarities of the alkali fluids.

In our model, we allow the ions to partially occupy the sites of a body centered cubic (bcc) lattice, which has the same maximum number of nearest neighbors as do real metals. The lattice parameter is determined by the condition that the maximum density ρ_0 be equal to that of the liquid metal at its triple point. The energy, in a mean-field treatment of the model, is obtained from the energy per ion $u(\rho)$ in a normal treatment for a liquid metal with mean density ρ [13]. That is, using a jellium reference system for the delocalized valence electrons yields kinetic, exchange, and correlation energy contributions, and a linear response function. Also, a hard-sphere reference for the ions gives a pair distribution function. Finally, a pseudopotential is associated with the ions (Ashcroft, empty core, fitted to the liquid metal conductivity or packing fraction at the melting point) and the screened ion-electron and ion-ion interactions (minus reference system effects) are treated by perturbation theory. This is a Gibbs-Bogoliubov variational approximation. The electronic effects are treated at zero temperature since no appreciable changes result from including the temperature effects in the kinetic and exchange energies. The results with the mean-field lattice model (Table I) are very close to those of the previous, continuous, plasma model [12].

TABLE I. Comparison of the calculated critical conditions, using lattice gas mean-field and the present theory, with the experimental results of Refs. [2] and [3]. The temperature T is in kelvin, the pressure P in bar, and the density ρ in $\mathrm{g\,cm^{-3}}$.

	Cesium			Potassium		
	T_c	ρ_c	P_c	T_c	ρ_c	P_c
Mean field	6760	0.03	9.8	7890	0.018	19
Our theory	3640	0.59	140	3750	0.25	200
Experiment	1924	0.38	92.5	2178	0.18	148

The crucial point, however, is to calculate the energy of the system not in mean field but by taking into account the strong inhomogeneities due to clustering and atom formation. We carried out exact diagonalizations of tight-binding calculations on a finite bcc lattice with a single orbital per site. The samples have a few hundred monovalent atoms (site energy $-E$, of the order of the alkali ionization potential) and the remaining sites empty (site energy 0), at fixed density but with randomly disordered lattice site occupations (the hopping matrix element is a constant). The ensemble yielded an electronic structure which strongly depends on the specific realization. However, the total electronic energy throughout the ensemble could be well fitted by a single function which only depended on how many occupied sites had n occupied nearest neighbors. Based on such results but desiring adequate energies, we proceed as follows. We now propose to get the energy per ion with an interpolation scheme for the disordered system, using the mean-field energy $u(\hat{\rho})$ which is to be evaluated at a local average density $\hat{\rho}$. This density takes into account the ion and its environment, through the occupation of its nearest-neighbor lattice sites. Such an averaging length scale is typical of both the screening length at high densities and of atom formation, as shown below. Thus, $\hat{\rho} = (n + 1)\rho_0/9$ and n is the number of occupied nearest-neighbor sites; it takes values from 0 to 8. For ions without any nearest neighbors ($n = 0$), this energy, calculated as in a plasma, is suspect due to the long screening length, so it is compared with that of a free atom (i.e., minus the ionization energy) and in a variational spirit the lower value is chosen. Although the energy difference is small, the atomic state is lower for all the alkalis. This approach thus includes the structurally based possibility of valence electron localization, to form atoms, or some degree of delocalization. We will test this scheme on various alkalis and a spectrum of properties. For cesium we take common values of $\rho_0 = 1.84\ \mathrm{g/cm^3}$, a hard sphere diameter of 8.81 a.u., a pseudopotential core radius of 2.62 a.u., and obtain the following energies per ion (in eV):

n	0	1	2	3	4	5	6	7	8
u	−3.89	−4.20	−4.43	−4.59	−4.73	−4.85	−4.95	−5.04	−5.12

This simple model for the configuration energy contains a basic difference with the pairwise interactions of usual lattice models: nonadditive interactions with neighboring ions due to valence electron delocalization. Also, such interactions are misrepresented in a mean-field treatment of a metal-atom fluid if the density fluctuations become important.

We present the results of grand canonical Monte Carlo simulations for this model, applied to cesium and potassium. We have carried out simulations within a cube with twelve bcc cells on each side (3456 sites). Some results have been checked using a larger cube (8192 sites), without appreciable changes in the results. The simulations, carried out at fixed temperature and chemical potential, give the equilibrium density and internal energy of the system. The pressure is obtained by thermodynamic integration. Structural features such as a nearly linear decrease in the average coordination of ions in the expanded coexisting liquid result from this calculation; that feature agrees with what has been deduced from analysis of neutron scattering data [14]. In Fig. 1, we show the coexistence curves, in critical reduced units, obtained for cesium along with the experimental result. Using the present method, the shape of the coexistence curve is in good agreement with experiments, recovering the strong liquid-vapor asymmetry. Although the size of our simulation box prevents a closer approach to the critical point than about 1%, our results clearly show a nonclassical critical behavior, in agreement with experiment and previous theoretical predictions [15,16]. Near the critical point, the diameter $\rho_d = (\rho_L + \rho_V)/2\rho_C$ is indicated in the figure and clearly shows the nonlinear behavior $\rho_d - 1 \propto |(T_C - T)/T_C|^{1-\alpha}$. Our estimate for $1 - \alpha$, 0.8 ± 0.1, is compatible with the experimental value [3] of 0.87 ± 0.03. We have also calculated the phase diagram for potassium (hard sphere diameter of 7.51 a.u. and pseudopotential core radius of 2.12 a.u.); in reduced critical units it is very similar to that of cesium. In agreement with experiments, our results for different alkali fluids give similar reduced phase diagrams.

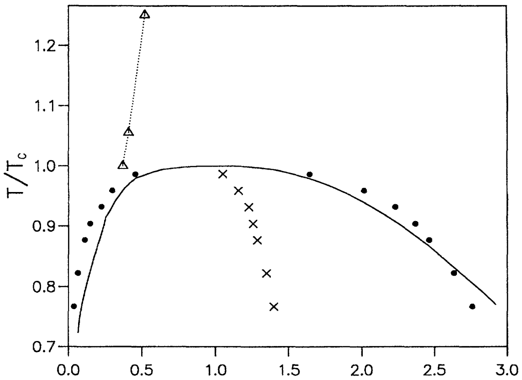

FIG. 1. Liquid-vapor coexistence curve of cesium. Filled circles: present MC simulation; full line: fit to the experimental results of Ref. [3]. The MC simulation diameter function ρ_d is also plotted (crosses). The triangles show our metal-nonmetal transition (i.e., the percolation line); the dotted line is a guide to the eye.

The critical temperatures in our model are higher than those of the real fluids, as one would expect from a lattice gas treatment of the configurational entropy. However, the results in Table I show that the correlation effects included in the present model produce a very large decrease of the critical temperature compared with the previously mentioned mean-field approach. Also, the critical densities and pressures are brought into reasonable agreement with experiments. Moreover, the critical parameters of cesium and potassium, in our model, show the experimental systematics.

We have next explored electronic properties related to structure. The experimental signature of a M-NM transition in these systems is a decrease of several orders of magnitude in the conductivity of the expanded fluid metal. In our model, such behavior is driven by the percolation of the ionic cluster structure, rather than by considerations such as those of Mott or Anderson. From typical configurations of our Monte Carlo simulation for cesium, we have obtained the cluster structure at different temperatures and pressures. The conductivity was estimated following the Kirchoff's law model proposed by Nield *et al.* [17], with arbitrary units fitting the experimental conductivity at the maximum density. The results in Fig. 2 show the conductivity estimated in this manner along the critical isotherm versus the pressure, in excellent agreement with experiment [1]. The figure also shows the calculated conductivity versus density at the critical temperature, and that arising from a random filling of the lattice. The difference clearly shows the effects of clustering. The percolation density (at which the conductivity goes to zero) at T_c is less than half that obtained with random occupation.

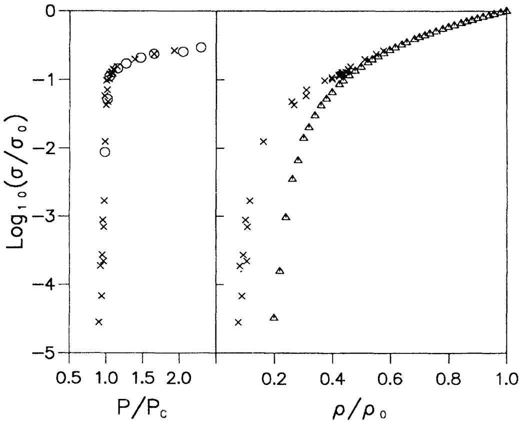

FIG. 2. On the left we show the electrical conductivity σ versus the reduced pressure along the critical isotherm: crosses—our model; open circles—experimental values of Ref. [1], both normalized to the conductivity σ_0 at our highest density ρ_0. On the right we show our calculated electrical conductivity but now versus the fractional occupation of the lattice; crosses are our results for $T = T_c$ and triangles for the random filling of the lattice.

We have presented a model allowing a unified study of the structural, thermodynamic, and electronic properties of metal-atom fluids. The model takes into account nonadditive interactions, due to valence electron delocalization, and it is studied with a Monte Carlo simulation which goes beyond mean field, as is required. Although the model is a very simplified representation of a metal-atom fluid, comparisons with a range of experimental results show that it contains the basic ingredients to allow reproduction of the peculiar behavior observed in these systems. These peculiarities include the metal-nonmetal and liquid-vapor transitions and the connection between ionic and electronic structures. Our results for the critical temperatures are still too high, though the densities and pressures are acceptable. It is reasonable to expect that, with a more realistic description of the fluid entropy, a similar model (though more cumbersome to study) would also give a quantitatively good result for the critical temperatures. Our simplified model appears to allow a unified understanding of the peculiar characteristics of the alkali fluids.

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[1] F. Hensel, in *Physics and Chemistry of Electrons and Ions in Condensed Matter,* edited by J. V. Acrivos, N. F. Mott, and A. D. Yoffee (Dordrecht, Reidel, 1984), p. 401; F. Hensel, S. Jungst, F. Noll, and R. Winter, in *Localization and Insulator-Metal Transitions,* edited by D. Adler and H. Fritzche (Plenum, New York, 1985), p. 109; F. Hensel and H. Uchtmann, Annu. Rev. Phys. Chem. **40**, 61 (1989).

[2] G. Hohl, Ph.D. thesis, Marburg, 1992 (unpublished).

[3] S. Jüngst, B. Knuth, and F. Hensel, Phys. Rev. Lett. **55**, 2164 (1985).

[4] R. M. Stratt, Annu. Rev. Phys. Chem. **41**, 175 (1990).

[5] J. Hafner, *From Hamiltonians to Phase Transitions*, Springer Series in Solid-State Sciences (Springer-Verlag, Heidelberg, 1987), p. 70.

[6] P. Minchin, M. Watanabe, and W. H. Young, J. Phys. F **7**, 563 (1977).

[7] J. P. Hernandez, Phys. Rev. Lett. **57**, 3183 (1986).

[8] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[9] See W. Kraeft, D. Kremp, W. Ebeling, and G. Ropke, *Quantum Statistics of Charged Particle Systems* (Plenum, New York, 1986); R. Redmer and G. Ropke, Physica (Amsterdam) **130A**, 523 (1985); Contrib. Plasma Phys. **29**, 343 (1989); R. Redmer and W. W. Warren, Jr., Phys. Rev. B **48**, 14 892 (1993).

[10] E. Chacón, J. P. Hernandez, and P. Tarazona, J. Phys. Condens. Matter **5**, 1753 (1993).

[11] J. P. Hernandez, Z. Phys. Chem. (to be published).

[12] P. Tarazona, J. P. Hernandez, and E. Chacón (unpublished). A brief report of part of this work was presented at the VII International Workshop on the Physics of Nonideal Plasmas (Rostock, 1993); see P. Tarazona, E. Chacon, and J. P. Hernandez, Contrib. Plasma Phys. **33**, 370 (1993).

[13] M. Shimoji, *Liquid Metals* (Academic, New York, 1977), p. 28; N. W. Ashcroft and D. Stroud, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1978), Vol. 33, p. 1; and Ref. [5].

[14] R. Winter, C. Pilgrim, F. Hensel, C. Morkel, and W. Glaser, J. Non-Cryst. Solids **156-158**, 9 (1993).

[15] R. E. Goldstein and N. W. Ashcroft, Phys. Rev. Lett. **55**, 2164 (1985).

[16] R. E. Goldstein, A. Parola, and A. P. Smith, J. Chem. Phys. **91**, 1853 (1989).

[17] V. M. Nield, M. A. Howe, and R. L. McGreevy, J. Phys. Condens. Matter **3**, 7519 (1991).