Unified treatment of the metal–non-metal and liquid–vapour transitions in monovalent-atom fluids

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Abstract. A unified framework is presented with which to treat the metal–non-metal and liquid–vapour transitions of simple metal-atom fluids. The basic element consists of allowing the electrons in the system a choice between delocalized conducting states and localized atomic valence states. Thermal equilibrium between such states, at fixed total density, leads to the metal–non-metal transition. Replacing this constraint by the equal total pressure and chemical potential one yields the liquid–vapour transition. Both phase transitions, with their unifying and differentiating aspects, are obtainable. The spectrum of experimental observations in the alkali-atom fluids can be qualitatively reproduced, even with extremely simplified assumptions.

The metal–non-metal (MNM) and liquid–vapour (LV) transitions in fluids, such as those of the alkali atoms, have been closely linked through a body of experimental data that has become quite precise and reliable in the last decade and that spans thermodynamic and electrical measurements under the same conditions [1]. This body of data still seeks a microscopic theoretical foundation, as noted in the recent review by Stratt [2]. Previous theoretical efforts to explain the data coherently have been sparse. The points of view usually taken begin with the limiting cases of a metallic dense liquid or solid, or a non-metallic dilute vapour, and then attempt to describe the fluid over a limited density and temperature range [3–5]. This situation is unsatisfactory for unifying the transitions while differentiating between them. We present an alternative that is satisfactory in this respect.

In this paper we discuss a general framework and then, as an example, an extremely simple model, which yields in qualitative terms the electronic and thermodynamic features observed experimentally in the alkali-atom fluids: a liquid–vapour transition that hides a metal–non-metal one; also, an LV coexistence with a critical point whose temperature is a weak function of the vacuum ionization potential of the atoms in the material, but whose density and pressure are increasing functions of that potential. This simple model, though unrealistic for the alkali-atom fluids, shows that our general framework can achieve the above results, and it is generalizable to realistic interactions.

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The crucial simplifying aspect of the framework presented is the assumption that the fluid of interest can be described as an interacting mixture of neutral ground-state atoms, monopositive ions and neutralizing delocalized conduction electrons. Thus the electrons are being given a variational choice between delocalized conduction states and ground-state atomic valence states that are localized, mainly due to exchange and correlation effects, on the ions to make up neutral atoms. This mixture provides sufficient flexibility with which to describe both a liquid and a vapour, as well as a metallic or non-metallic fluid (dominantly atomic, with thermally activated conduction electrons). We shall show that this proposal can lead to unified but distinct MNM and LV transitions with characteristics typical of those observed experimentally. Such a unification has been unavailable up to now, though a similar approach was investigated by Gitterman and Steinberg [6].

Charge neutrality constrains the system to equal ionic and conduction-electron densities; the above mixture thus has two-components. Requiring thermodynamic equilibrium between these two species constrains the difference of their chemical potentials. That is, the cycle in which an atom is removed from the system, is ionized in a vacuum, and then the ion and conduction electron pair is reintroduced into the system, must cost no net energy. The procedure we shall follow has two steps. We first require equilibrium of the mixture at fixed total density; we then remove that constraint and require, instead, equal total pressure and chemical potential. We shall give a simple model as an example, in which the first step causes a first-order phase transition at which the conduction electron density jumps: this we consider to be the MNM transition; the second step results in the LV transition. The critical points are distinct.

We begin with the general framework for the mixture. We then treat the simplified model which, though it is unrealistic, yields the type of features we seek. After discussing the results, we point out how to set up a more realistic model, which will maintain the general type of results obtained in the previous simplification.

The Helmholtz free energy of the two-component mixture, per unit volume, is written by explicitly separating atom and ion ideal-gas terms (with no further loss in generality):

$$f \equiv k_B T[\rho_a(\ln(\rho_a \Lambda^3/2) - 1) + \rho_i(\ln(\rho_i \Lambda^3) - 1)] + f_e(\rho_i, \rho_a, T) \quad (1)$$

where Λ is the atomic de Broglie thermal wavelength and $\rho_{a(i)}$ is the atomic (ionic) density; we assume two spin states for the atoms (a single valence electron) and one for the ions. The thermal energy is $k_B T$. As we wish to demand thermodynamic equilibrium between the components, we first construct the grand potential Ω and then extremize it with respect to $\delta \equiv \rho_a - \rho_i$, at fixed total density, $\rho_T \equiv \rho_a + \rho_i$. By definition

$$\Omega = f - \mu_a \rho_a - \mu_i \rho_i = (f - E\delta/2) - [(\mu_a + \mu_i)/2]\rho_T. \quad (2)$$

The chemical potentials ($\mu_{a(i)}$) are defined as $\partial f/\partial \rho_{a(i)}$. The first term in round brackets in (2) is the free energy of the equivalent one-component system, and the term in square brackets its chemical potential. We have used an exact, previously noted, equilibrium requirement: replacing $\mu_a - \mu_i$ by E, the atomic vacuum ionization potential. Extremizing (2), at fixed total density, relates the atomic and ionic densities:

$$\rho_a = 2\rho_i \exp[(\mu_e + E)/k_B T] \quad (3)$$

with $\mu_e \equiv \partial f_e / \partial \rho_i - \partial f_e / \partial \rho_a$. This relation, when inserted into (2), yields the extremized grand potential; the system will choose the absolute minimum. A first-order phase transition may result, which we would interpret as an MNM one (at zero temperature the conduction electron density would jump from one per nucleus to zero). An LV coexistence curve may now be obtained, on lifting the constant total density requirement and requiring equal total pressures and chemical potentials. For any temperature, the total density at which the MNM transition takes place, if it does, must lie in the interval between the corresponding vapour and liquid values. This fact may be appreciated by constructing isotherms of extremized grand potential against total density and examining the conditions for the phase transitions described. The only approximation introduced thus far is limiting the variational basis.

Figure 1 shows two isotherms of the atomic against ionic density that (3) could yield; note that E is a constant, depending on the material, while μ_e depends on ρ_i, ρ_a and T. A fixed total-density example is presented in this figure; it has to be a straight line of slope -1. The intersection(s) of this line and those of (3) correspond to grand-potential extrema. A single crossing is a minimum, while a triple crossing corresponds to local minima with a maximum in between. In this latter case, the system will choose the lower of the two minima, with the first-order phase transition occurring when the minima are degenerate. As the temperature is raised and the triple crossing degenerates to a single ionic density, the critical point for this transition has been reached. This critical point can be described by the conditions that the crossing must take place at a point at which the first derivative of ρ_a with ρ_i is -1, while the second derivative vanishes.

We provide a specific example in which the above pair of phase transitions takes place, by caricaturing f_e to be merely due to electronic kinetic energy and exchange in the jellium model (the electronic Hartree–Fock solution to the jellium problem). An effective attractive interaction is being introduced, as well as terms of the ideal-gas type. The model is physically unrealistic for the alkali fluids, but it is instructive. In a further approximation, we shall use the familiar $T = 0$ result [7], fully realizing we are thereby neglecting a physical effect (the full ionization of atoms at sufficiently low densities due to entropy considerations). In this case, using atomic units, we have

$$f_e(\rho_i) = (3k_F^2/10 - 3k_F/4\pi)(k_F^3/3\pi^2) \qquad k_F^3 = 3\pi^2\rho_i. \qquad (4)$$

Thus, $\mu_e(k_F)$ is a parabola ($k_F^2/2 - k_F/\pi$). The above function can now be used in (3) to yield the equilibrium atomic density for each ionic density, temperature and material (specified by E). For any $E < 1.38$ eV (the maximum value of $-\mu_e$), there will be a first-order MNM transition. The values of ρ_T, as a function of temperature, at which the minima of Ω become degenerate specify the phase-transition line. In figure 1 the value of $E = 1$ eV was used to give examples of (3). The 1800 K example shows the magnitude of the jump of ρ_i at the phase transition. The phase separation line is shown in figure 2, as the short-dash broken curve, for $E = 1$ eV. For any E, the critical point of this transition is described by the ionic density and temperature, which self-consistently satisfy ((3) with a first derivative of ρ_a with $\rho_i = -1$, while the second derivative vanishes):

$$(k_BT)^{-1} = -\mu_e''/\mu_e'^2 - 2/\rho_i\mu_e' \qquad -(\mu_e + E)/k_BT = \ln[2(1 + \rho_i\mu_e''/\mu_e')] \qquad (5)$$

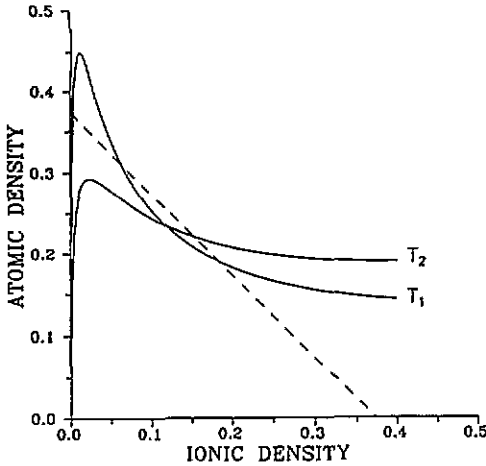where the primes indicate derivatives with ρ_i.

Figure 1. Possible isotherms $(T_2 > T_1)$ representing (3), in arbitrary units; the straight line is a constant total density; its intercepts with the isotherms are the extrema of (2). The curves are obtained (see text after (4)) using $E = 1$ eV, $T_1 = 1800$ K, $T_2 = 2150$ K; the straight line is for the phase transition at T_1, $T_c = 2087$ K, and the density units are 10^{-3} au.
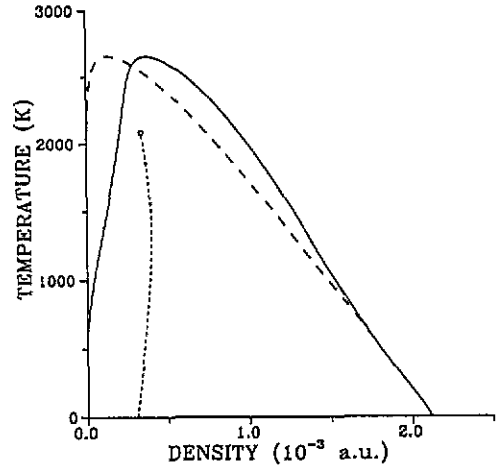
Figure 2. Phase diagrams for the simplified model ($E = 1$ eV). The short-dash broken curve is the MNM transition. The long-dash broken curve is the plasma (no atoms) coexistence curve to which the atomic densities (from (3)) are added to obtain the full curve, which is the LV coexistence curve. Note that at low temperatures the vapour has negligible ionic density and the liquid has negligible atomic density.

In this example the atomic ideal-gas assumption decouples the atoms and simplifies the analysis of the LV transition. Requiring that the plasma (ion ideal gas plus the $T = 0$ jellium) yield an LV coexistence can be demanded from equal pressures and chemical potentials, whose values for the plasma are well known. The plasma coexistence is shown as the long-dash broken curve in figure 2. Its critical-point parameters are obtainable analytically (from requiring vanishing first and second derivatives of pressure with density at the critical point):

$$\rho_{ic} = \mu_e'/\mu_e'' \qquad k_B T_c = \mu_e'^2/\mu_e'' \qquad P_{ic} = -f_e + \rho_{ic}(k_B T_c + \mu_e). \qquad (6)$$

Using (4) in (6) yields $\rho_{ic} = (24\pi^5)^{-1}$, $k_B T_c = (12\pi^2)^{-1}$, $P_{ic} = (2880\pi^7)^{-1}$; in common units these values are respectively: 0.918×10^{21} cm^{-3}, 2662 K (for the critical temperature) and 33.8 bar. These results are independent of E. As the interaction is unrealistically weak ($\mu_{e,\min} = -1.38$ eV), a small enough E is needed (in (5)) to allow an MNM transition. Its critical point depends on E but both its temperature and ionic density are always lower than those of the plasma critical point. If E were chosen to be too large (>1.38 eV, for this example) there would always be more atoms than ions and no MNM phase transition; instead, there would only be a weakly ionized plasma. Finally, the total LV coexistence curve (now including the atoms) is shifted from that of the plasma by the appropriate equilibrium density of atoms at each temperature (3). This shift cannot change the critical temperature and it maintains equal pressures at coexistence. The stepwise procedure described gives identical results to one proceeding from extremized Ω. For the $E = 1$ eV example, the total LV coexistence curve is also shown in figure 2. Note that in this simplified model the critical temperature coincides with that of the plasma, and thus is

independent of E, while the total critical density and pressure are increasing functions of E: the plasma values given above plus the ideal-gas contribution of the atoms (ρ_a from (3) and $P_a = \rho_a k_B T$). The plasma transition (like the MNM one) is not a direct experimental observable, being an intermediate calculational step. Naturally, in such a mean-field calculation, the LV critical exponents are classical (as the critical point is approached, an analytic free energy leads to a symmetric coexistence curve—in contrast to experiment).

The general features resulting from this example are in striking qualitative accord with those measured (Cs and Rb) [8] or extrapolated (other alkalis) [9] for the LV transition of such simple fluids (the experimental E ranges from 3.89 eV for Cs to 5.39 eV for Li): a critical temperature that varies weakly with material (1924 K for Cs to ~ 3000 K for Li), and more strongly varying critical densities and pressures that increase with E (1.71×10^{21} cm^{-3}, 92 bar for Cs to $\sim 3.4 \times 10^{21}$ cm^{-3}, ~ 500 bar for Li). Model results and observations are also of a smoothly changing electron concentration throughout the single-phase region [1].

Having shown that a simplified mixture model can yield the general features observed experimentally, we suggest a more realistic treatment method for $f_e(\rho_i, \rho_a, T)$, which allows using the experimental E values, extending the normal one used for simple liquid metals [3, 10]. A jellium model is first treated, in which the ions are smeared out to form a uniform positive background whose effect is to cancel the Hartree interactions among the electrons. A hard-sphere reference system is then introduced for the ions, along with an electron–ion pseudopotential and an electron response function. The electron–ion interactions modify the jellium results via perturbation theory and the ion–ion interactions are modified, now being controlled by the hard-sphere pair correlation function and the screening due to the electron response function. The model contains effects of hard spheres, pseudopotentials, a temperature-dependent exchange [11], and approximate conduction-electron correlation and response functions. The introduction of the atoms into the above scheme can be accomplished using the device of treating the system as a mixture; the interactions of the atoms with each other and with the other system components must be included.

We note that if in such a procedure the atoms are approximated as a hard-sphere system (assumed dominance of the interactions among charges) then the resulting critical temperatures are too high. Such an approximation appears to overemphasize the charged-particle interactions. It seems that the effect of interactions with the atoms will result in an attempt by the atoms to surround each ion; such an effect would be similar to the positive molecular ions that were suggested previously [5]. Preliminary calculational results are of the type described by the very simplified model discussed previously. A full account of the work with the detailed model will be published elsewhere [12]. A similar approach could be investigated for application to divalent-atom systems (Hg, for example). In that case a thermal equilibrium mixture of atoms, monopositive and dipositive ions (and of course electrons) needs to be considered. The caricature that has been given for f_e would be even more unrealistic for such a case, since the cancelling Hartree term does not allow differentiation between monopositive and dipositive ions in the interactions. Detailed consideration of such systems must await improved treatment methods such as that described above. The central simplifying assumption in the theoretical framework presented limits the electrons to a variational choice between delocalized conduction states and the free-atom ground valence state. It is probable that this assumption leads to the first-order

nature of the MNM transition, and strongly determines its critical point. A more flexible variational basis might be needed for quantitative work. However, there is little point in detailed arguments about a transition that cannot be experimentally observable. The only reasonable argument is on the effects in the vapour, liquid or gas that enhancing the basis might yield. A more flexible basis may be incorporated into the present framework by changing from a two-component to a multi-component mixture; some of the components might be multi-atom ones.

In the type of framework discussed, treatment of the purely electronic properties, such as electrical conductivity, are phenomenologically straightforward (the conduction-electron density is calculated and mean-free paths, for instance, could be estimated), though clearly we have not yet delved into the difficult problems of localization through disorder or the details of electronic correlations (other than in the crude but essential manner leading to electron localization to form atoms). Also, the description has concentrated on the thermodynamic coexistence conditions, but this is merely from choice; there is no problem in attempting to find equations of state, for instance.

In summary, a powerful but conceptually simple framework has been presented to show that the metal–non-metal and liquid–vapour transitions of simple metal-atom fluids can be unified and differentiated, with the electronic and thermodynamic properties being on an equal footing. A mixture framework is sufficient to unify the effects observed experimentally. A simplified, though unrealistic, model has been treated in some detail to exemplify the previous assertions and to show the minimal conditions required to obtain the qualitative features observed in experimental measurements of these materials. A more realistic treatment has been briefly noted and such calculations are underway.

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