

A note on plasma

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Plasma is an ensemble of positive and negative ions and neutral atoms (molecules), usually electrically neutral; sometimes, it may include ionized small particles (dusty plasmas). The negative "ions" may be electrons. A typical example of plasma is the electrolyte, consisting usually of a species of positive ions, a species of negative ions, in equal numbers, arising from the dissociation of a species of molecules, and neutral (undissociated) molecules. If the dissociation is weak, the electrolyte is called a weak electrolyte; if the dissociation is extended, the electrolyte is called a strong electrolyte; an extreme case is the ionic crystal. Another typical examples are the ionized gas and the electrons in a metal. Although similar in many respects, there exists an important difference between a plasma consisting only of ions (electrolyte) and a plasma which includes electrons.

First, we should note that plasmas exist at finite temperatures; at zero temperature, the entropy should be zero, and the most ordered state is an insulating, probably covalent, or ionic, solid; the spectrum of a metal is continuous and it is difficult to define its zero-temperature limit.[1]

Second, in defining a plasma the problem of the degree of dissociation or ionization appears. If the plasma is at equilibrium, *i.e.* if it has the same temperature for all species of particles, then for gases and, to some extent also, for liquids, the degree of dissociation or ionization is given by Saha equation.[2] Strong electrolytes may exist at room temperature, while for a reasonable degree of ionization high temperatures are necessary. The assumption of equilibrium is usually fulfilled for electrolytes, but it is difficult to have it fulfilled for plasma with electrons, though it may be fulfilled also in this case over some limited range of parameters. This is so because of the great disparity between the electron mass and ion mass; as a consequence, the electrons take more energy and have, usually, a much higher temperature than the ions; this is called a non-thermal plasma.

The main problem for a plasma is to derive its cohesion, stability and thermodynamics. This problem is complicated because of the presence of the Coulomb interaction. In ideal gases there is no interaction and their thermodynamics is solved by the principle of statistical equilibrium. Corrections to thermodynamics arising from interaction are solved by the van der Waals equation for non-ideal gases; in particular, the van de Waals equation indicates a transition to the liquid state. Such corrections are obtained, in general, by the so-called virial expansion, *i.e.* the expansion of the thermodynamic potentials in series of powers of the density. A thermodynamics of liquids, where the interaction is important, is described in Ref. [3]. The cohesion and the thermodynamics of metals is given in Ref. [4]. In order to establish the thermodynamics of an interacting ensemble we need first to solve the problem of the interaction, for knowing the stability, the cohesion, the possible phases and the corresponding elementary excitations. Solving the problem of interaction

looks like we should treat the ensemble at zero temperature. But this is an unphysical case, so we need, in fact, to solve the problem of interaction at finite temperatures, which is an interesting special case; *e.g.*, this happens for superconductivity.

The key for solving the problem of the Coulomb interaction in plasma was given by Debye and Huckel.[5] The long range of the Coulomb interaction gives rise to divergencies in the virial coefficients, such that a direct virial expansion is not appropriate. Debye and Huckel[5] noticed that there exists a self-consistency relation between the electrostatic potential generated by charges and the charge density, which leads to a screened Coulomb potential; the screening length is governed by the charge density and the temperature. A similar self-consistency relation exists for a Fermi gas of electrons in metals, governed by the electron density and the quantum effects; it was used in Ref. [4]. Moreover, in Refs. [4] and [6] a screened ion-ion interaction potential has been derived, which acts between the same species of ions; this was achieved by applying consistently the Debye-Huckel approach. These potentials exhibit equilibrium minima, which indicate a plasma solid phase and a precursory liquid phase. These condensed plasma phases and the corresponding transitions are of considerable interest, especially in plasmas with electrons, where they may be attained by high pressure. The weak electrolytes are far from these transitions, and their thermodynamics is mainly that of a non-ideal plasma gas, where the original solution given by Debye and Huckel,[5] and Onsager,[7] may suffice. The strong electrolytes or the extreme case of ionic solids may exhibit such liquid and solid plasma phases. The Madelung method of estimating the cohesion energy of an ionic solid is appropriate, but the liquid phase of strong electrolytes needs further investigations.

For plasmas with electrons the high-density zone, where the liquid and solid phases occur, is of interest. The current approaches, besides assuming a thermal plasma, treat the electrons as pointlike particles (though the Debye-Huckel screened potentials are derived by assuming the electrons statistically distributed with the Boltzmann density). The Coulomb potential exhibit another difficulty, besides the long-range divergence (this latter divergence is solved by the screened potentials). This additional difficulty arises from the short-range singularity of the Coulomb potentials, which may appear when the electron positions are close to the ion positions, a situation which may be present in the high-density range. Usually, this difficulty is removed by resorting to quantum effects, or model-based hypotheses (ions as rigid spheres, or postulating a solid, for instance). In such treatments it is necessary to make connection with the low-density region. At first sight, it may appear that such calculations could be carried out by successive virial-type corrections. Unfortunately, such an approach is not possible, since the inter-ionic potentials are, in fact, pseudo-potentials, which depend on temperature and density, and their range varies widely with density. At low densities the repulsive part of these potentials includes many ions, such that the pairwise-type virial coefficients have little relevance. In addition, on one side the assumption of pointlike electrons is not warranted at finite temperatures and, on the other side, there is no need for this assumption because a careful analysis of the inter-ionic potentials indicates an excluded volume at high densities, related to the screening length, which opens the way toward a van der Waals equation of state. At high densities the screening length of the inter-ionic pseudo-potentials is sufficiently small to provide an excluded volume for ions, where the bare highly-repulsive Coulomb potential acts. This van der Waals equation for a plasma is derived in Ref. [6], where the transitions gas-liquid-solid are identified. Over this whole range of densities and temperatures the plasma behaves classically. Moreover, it is shown in Ref. [6] that the gas-liquid transition does not occur for a thermal plasma and a perturbation series for the non-ideal gas would converge slowly to the non-analytical behavior of the van der Waals equation in the vicinity of the liquid and solid phases.

The theory of the classical plasma given in Ref. [6] gives parametric positions to the ions, while

treating the electrons as distributed with a classical (Boltzmann) density; after solving the problem of interaction, the ions, dressed by electrons, are treated statistically, with their own temperature or with the same temperature as the electrons. It arises naturally the question whether the electrolytes can be treated in a similar way. The answer is positive. We may view one species of ions as "ions" with definite positions and the other species of ions as "electrons" endowed with a density. The results are independent of which species of ions is chosen as "ions" and which is chosen as "electrons". The reason for such a theoretical basis originates in the long-range character of the Coulomb potential, which is effective over large spatial regions, and over large spatial regions, which include many particles, we may always define a density of particles. With the notations of Ref. [6] the equilibrium positions of the "ions" are given by $\bar{R}_{ij} \simeq 2.73\lambda$ ($a_s \simeq 1.68a_0$, $a_0 = q^2/T$) (and the excluded volume of the liquid is given by $a = 2\lambda$ ($a_l = \pi a_0$)), while the "electrons" are distributed over a distance $a \simeq \lambda$, *i.e.* $a = 4\pi a_0$ about the "ions"; we may write

$$a = 4\pi a_0 = \frac{4\pi}{1.68} a_s = \frac{4\pi\sqrt{2}}{1.68} \cdot \frac{a_s}{\sqrt{2}} \simeq 10.5 \cdot \frac{a_s}{\sqrt{2}} , \quad (1)$$

which is close to an *fcc* lattice with 12 nearest neighbours, or

$$a = 4\pi a_0 = \frac{4\pi}{1.68} a_s = \frac{4\pi}{1.68} \cdot \frac{2}{\sqrt{3}} \cdot \frac{a_s\sqrt{3}}{2} \simeq 8.6 \cdot \frac{a_s\sqrt{3}}{2} , \quad (2)$$

which is very close to a *bcc* lattice with 8 nearest neighbours. We may say that this theory predicts that the very strong electrolytes in their extreme (ionic-crystal) limit crystalize in a *bcc* lattice (the same is true for ionic crystals). In the above notations λ is the screening length, a is the mean separation distance between the ions of the same species, q is the ion charge and T is the temperature.

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