

# On the stability of a classical plasma

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## ARTICLE INFO

### Article history:

Received 14 September 2018  
 Received in revised form 20 November 2018  
 Accepted 15 March 2019  
 Available online 20 March 2019  
 Communicated by F. Porcelli

### Keywords:

Classical plasma  
 Debye-Huckel screening  
 Variational approach  
 Solid phase  
 Condensed phases

## ABSTRACT

A linearized self-consistent variational approach is employed to investigate the (thermodynamic) stability of a classical plasma (electrons and positive ions). It is shown, by using this approach, that a classical plasma, which consists of ions “dressed” with electrons, has a well-defined thermodynamics. In the strong-coupling regime the “plasma” is a solid, while, on passing to the weak-coupling regime, it becomes gradually a liquid, a non-ideal gas, and, finally, in the weak-coupling limit, it behaves as an ideal classical gas. A van der Waals-type equation is established for the plasma non-ideal gas.

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## 1. Introduction

There is a long-standing interest regarding the relation between a classical ensemble of neutral atoms, molecules (a gas) and its ionized (plasma) state. This problem may be termed the thermodynamic stability (instability) of a classical plasma, in the sense of the existence of a finite lower bound to the energy of the plasma (distinct from the ensemble of neutral atoms, molecules). As it is well known, a classical ensemble of Coulomb interacting pointlike charges would be unstable, the stability being achieved by resorting to the quantum-mechanical behaviour of the electrons in atoms and the exclusion principle [1–4]. The problem is still debated at present [5–10]. We show in this Note, by means of a linearized self-consistent variational approach, that the classical plasma, which may be viewed as a collection of ions “dressed” with electrons, has a well-defined thermodynamics. In the strong-coupling regime [11,12] the “plasma” is a solid, while, on passing to the weak-coupling regime, it becomes gradually a liquid, a non-ideal gas, and, finally, in the weak-coupling limit, an ideal classical gas. A van der Waals-type equation is established here for the plasma non-ideal gas. Probably the first authors who suggested the existence of an ionic lattice as the “ground-state” of a plasma at (very) high densities were Kirzhnits [13] and Abrikosov [14,15]. Long-range ordered phases have been reported recently in cold, strongly-coupled plasmas by computer simulations [16,

17]. Coulomb crystals of jellium and one-component plasmas are known since long [18,19].

The thermodynamics of classical plasmas has been extensively investigated by using the so-called Colulomb systems [20,21]. A Coulomb system is an ensemble of electrical charges like ions and electrons (and, sometimes, neutral atoms) with Coulomb interaction, where the electrons are given well-defined positions, *i.e.* the electrons are viewed as pointlike particles. Such approaches encounter difficulties, related not only to the long-range character of the Coulomb interaction (which may be removed by screening), but also to the singularities arising from the Coulomb interaction at short distances. These short-range singularities may be effective at high densities, where the electron positions may be close to the ion positions. It is well known, for instance, that a consistent classical treatment of the Coulomb systems requires an effective repulsion of charges of different signs, or the presence of a compensating background (like in the jellium model). Usually, such difficulties are solved by making use of various model hypotheses, though, naturally, they are cured by the quantum-mechanical behaviour of the electrons. For instance, relatively reasonable results are obtained by postulating that a strongly-coupled plasma has a quasi-crystalline structure [22–24]. A thorough critical analysis of the statistical mechanics of the Coulomb systems was made by Norman and Starostin [25] (see also Refs. [26,27]).

The novelty of the present paper consists in assuming that the electrons in a classical plasma are distributed with a statistical (Boltzmann) density. This assumption leads straightforwardly to “dressed” ions, interacting through (screened) potentials which exhibit equilibrium positions. The main new result of the present

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paper is included in equations (18) and (25), which give these potentials. Having equilibrium positions (minima points), the ion-ion potentials may lead to a solid phase of the classical plasma, which occurs naturally (there is no need to be postulated). The “dressed” ions can then be treated statistically, and their thermodynamics can be derived. Also, by making use of the ion-ion potentials, an excluded volume is identified and a van der Waals-type equation is derived, which indicates a precursory liquid phase.

## 2. Screening

We consider a classical plasma consisting of a large (macroscopic) number  $N$  of identical ions with electric charge  $q$  ( $q > 0$ ) and an equal number  $N$  of electrons with charge  $-q$ , confined to a large (macroscopic) volume  $V$  and interacting by Coulomb forces. For simplicity we consider one type of singly-ionized atoms, though the procedure described below is valid for  $N_\alpha$  ions,  $\alpha = 1, 2, \dots$ , with charge  $z_\alpha q$  and  $N = \sum_\alpha z_\alpha N_\alpha$  electrons (where  $z_\alpha$  is a positive integer). The ions are viewed as point particles, while the electrons are viewed as a fluid with density  $n(\mathbf{r})$ , where  $\mathbf{r}$  is the position vector. We leave aside for the moment the thermal motion of the ions and give the ions parametric positions  $\mathbf{R}_i$ ,  $i = 1, 2, \dots, N$ . We may expect such an ensemble to be unstable, as will be shown below, in the sense that the ions get “dressed” with electrons. We shall show here that the “dressed” ions exhibit thermodynamically stable phases.

We denote by  $a$  the mean separation distance between ions (electrons) and write the concentration as  $n = N/V = 1/a^3$ . We assume  $T \gg \hbar^2/ma^2$ , where  $T$  is the temperature of the electrons; this is the condition of classical thermodynamics of the electrons with mass  $m$ ; also, we assume  $a \gg a_H = \hbar^2/mq^2$ , where  $a_H$  is the Bohr radius and  $\hbar$  is Planck’s constant. We neglect any energy loss which may appear in plasma.

The potential  $\Phi(\mathbf{r})$  generated by the electric charges in plasma satisfies the Poisson equation

$$\Delta \Phi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi q n(\mathbf{r}). \tag{1}$$

The solution of this equation can be written as

$$\Phi(\mathbf{r}) = q \sum_i \frac{1}{|\mathbf{r} - \mathbf{R}_i|} - q \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + f(\mathbf{r}), \tag{2}$$

where the function  $f(\mathbf{r})$  is a solution of the Laplace equation  $\Delta f = 0$ . If we identify the interaction Coulomb potential  $\Psi$  through  $\Phi = \Psi + f$ , the potential energy of the plasma is given by

$$E_p = \frac{1}{2}q^2 \sum_{i \neq j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} - \frac{1}{2}q^2 \int d\mathbf{r} n(\mathbf{r}) \Psi(\mathbf{r}) - \frac{1}{2}q^2 \sum_i \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_i|} + q \sum_i f(\mathbf{R}_i) - q \int d\mathbf{r} n(\mathbf{r}) f(\mathbf{r}), \tag{3}$$

or

$$E_p = \frac{1}{2}q^2 \sum_{i \neq j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} - q^2 \sum_i \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_i|} + \frac{1}{2}q^2 \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + q \sum_i f(\mathbf{R}_i) - q \int d\mathbf{r} n(\mathbf{r}) f(\mathbf{r}), \tag{4}$$

where we recognize the ion-ion and electron-electron Coulomb repulsion and the ion-electron Coulomb attraction. The function  $f(\mathbf{r})$  plays the role of an external potential, whose effect in energy disappears for  $f = const$ , as expected. For a uniform density of ions and electrons the potential  $\Phi$  (equation (1)) and the potential energy given by equation (4) are vanishing. For pointlike electrons placed at  $\mathbf{r}_j$  an infinite attraction may arise for  $\mathbf{r}_j = \mathbf{R}_i$  (we assume that all  $\mathbf{R}_i$  are distinct and, separately, all  $\mathbf{r}_j$  are distinct), with an infinite negative energy, which would mean the collapse of

the plasma. Such a “catastrophic” situation may be avoided by the quantum-mechanical behaviour of the electrons inside the atoms.

The electron density is given by Gibbs distribution

$$n(\mathbf{r}) = C n e^{\beta q \Phi(\mathbf{r})}, \tag{5}$$

where  $C$  is a normalization constant and  $\beta = 1/T$  is the reciprocal of the temperature  $T$ . The normalization constant  $C$  is obtained from

$$C n \int d\mathbf{r} e^{\beta q \Phi(\mathbf{r})} = N. \tag{6}$$

For a quasi-uniform potential  $\Phi$  we may use the representation

$$e^{\beta q \Phi} = 1 + \beta q \Phi + \frac{1}{2!} \beta^2 q^2 \Phi^2 + \frac{1}{3!} \beta^3 q^3 \Phi^3 + \dots \simeq 1 + \beta q \Phi \left( 1 + \frac{1}{2!} \beta q \bar{\Phi} + \frac{1}{3!} \beta^2 q^2 \bar{\Phi}^2 + \dots \right), \tag{7}$$

or

$$e^{\beta q \Phi} \simeq 1 + \gamma \beta q \Phi, \tag{8}$$

where

$$\gamma = 1 + \frac{1}{2!} \beta q \bar{\Phi} + \frac{1}{3!} \beta^2 q^2 \bar{\Phi}^2 + \dots \tag{9}$$

and

$$\bar{\Phi}^n = \frac{1}{V} \int d\mathbf{r} \Phi^n(\mathbf{r}), \quad n = 1, 2, 3, \dots \tag{10}$$

Moreover, for a quasi-uniform potential  $\Phi$  the correlations involved in  $\bar{\Phi}^n$ , for any integer  $n$  in equation (10), can be left aside; we may replace  $\bar{\Phi}^n$  by  $\bar{\Phi}^n$  and write

$$\gamma = \frac{e^{\beta q \bar{\Phi}} - 1}{\beta q \bar{\Phi}}. \tag{11}$$

The energy associated to the mean potential  $\bar{\Phi}$  plays the role of the chemical potential; the mean potential  $\bar{\Phi}$  is viewed here as a variational parameter for minimizing the energy.

Making use of this variational approach, we get from equations (5) and (6) the electron density

$$n(\mathbf{r}) = C n (1 + \gamma \beta q \Phi), \quad C = \frac{1}{1 + \gamma \beta q \bar{\Phi}} = e^{-\beta q \bar{\Phi}}, \tag{12}$$

where  $n(\mathbf{r})$  is a linear functional of the potential  $\Phi$  (hence the denomination “linearized variational approach”).

Inserting the density  $n(\mathbf{r})$  given by equation (12) in equation (1), we get

$$\Delta \Phi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi C n q + 4\pi C \gamma n \beta q^2 \Phi. \tag{13}$$

We note that the neutrality of the plasma implies  $C = 1$  and  $\bar{\Phi} = 0$ ,  $\gamma = 1$ , a result which will be obtained below. Also, from equation (2) we expect  $\bar{\Phi} \geq 0$ , due to the contributions of the regions where  $\mathbf{r}$  is close to  $\mathbf{R}_i$ . We write the potential  $\Phi$  in equation (13) as  $\Phi = \Psi - 1/\gamma \beta q$  and identify the function  $f(\mathbf{r})$  in equation (2) as the constant  $f(\mathbf{r}) = -1/\gamma \beta q$ ; being a constant,  $f(\mathbf{r})$  does not contribute to the potential energy. Equation (13) becomes

$$\Delta \Psi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi C \gamma n \beta q^2 \Psi, \tag{14}$$

whose solution is the well-known Debye-Huckel screened potential [28]

$$\Psi(\mathbf{r}) = q \sum_i \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}; \quad (15)$$

the screening parameter is  $\kappa = (4\pi C\gamma n\beta q^2)^{1/2}$ . Making use of the potential  $\Psi$  in equation (12), we can express the electron density as

$$n(\mathbf{r}) = C\gamma n\beta q\Psi(\mathbf{r}); \quad (16)$$

the potential energy given by equation (3) becomes

$$E_p = \frac{1}{2}q^2 \sum_{i \neq j} \frac{1}{R_{ij}} - \frac{\kappa^2 q}{8\pi} \int d\mathbf{r} \Psi^2(\mathbf{r}) - \frac{\kappa^2 q}{8\pi} \sum_i \int d\mathbf{r} \frac{\Psi(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|}, \quad (17)$$

where  $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ . The integrals in equation (17) can be effected immediately (they are two-centre integrals [29]); we get the potential energy

$$E_p = -\frac{1}{4}q^2\kappa \left[ 3N + \sum_{i \neq j} \left( 1 - \frac{2}{\kappa R_{ij}} \right) e^{-\kappa R_{ij}} \right]. \quad (18)$$

From equations (15) and (16) we can see that each ion is surrounded by an electron cloud extending, approximately, over distances of the order  $\kappa^{-1}$ . Also, from equation (18) we can see that these “dressed” ions have a self-energy  $-(3q^2\kappa N/4)$  (the first term on the right in equation (18)) and interact with the screened effective (pseudo-) potential  $\sim -(1 - 2/\kappa R_{ij})e^{-\kappa R_{ij}}$ ; this potential has a zero at  $R_{ij} = 2/\kappa$  and a minimum at  $R_{ij} = (\sqrt{3} + 1)/\kappa$ . As it is well-known, the electrons “dress” the ions and screen the original Coulomb interaction. The electron-ion attraction and the electron-electron repulsion contribute to the ion self-energy. The repulsive part of the interaction potential is due to the ion-ion Coulomb repulsion. The same form of the ion-ion interaction potential has been derived in Ref. [30] for a solid-state (quantum) plasma.

### 3. Solid phase

The equilibrium is achieved for well-defined values of the parameters  $\kappa R_{ij}$ , which ensure the minimum of the potential energy (interacting part) given by equation (18). The global minimum of the potential energy requires also the maximum value of the parameter  $\kappa = (4\pi C\gamma n\beta q^2)^{1/2}$ , i.e. the maximum value of the product

$$C\gamma = \frac{\gamma}{1 + \gamma\beta q\bar{\Phi}} = \frac{1 - e^{-\beta q\bar{\Phi}}}{\beta q\bar{\Phi}} \quad (19)$$

(according to equations (11) and (12)). It is easy to see that the maximum value of this parameter is reached for  $\bar{\Phi} = 0$ ,  $C = \gamma = 1$  (as expected from neutrality). For  $C = \gamma = 1$  the screening parameter  $\kappa$  becomes  $\kappa_D = 1/\lambda_D = (4\pi n\beta q^2)^{1/2}$ , where  $\lambda_D = a(aT/4\pi q^2)^{1/2}$  is the well-known Debye length. Henceforth, we use  $\kappa_D$  for  $\kappa$  and  $\lambda_D$  for  $\lambda = 1/\kappa$  and remove the suffix  $D$ .

The equilibrium mean value of the parameters  $\kappa R_{ij}$  is given approximately by  $\kappa \bar{R}_{ij} \simeq \sqrt{3} + 1$ ; making use of this value, the potential energy given by equation (18) can be written as

$$E_p \simeq -\frac{1}{4}q^2(4\pi n\beta q^2)^{1/2} \left[ 3 + \frac{\sqrt{3}-1}{\sqrt{3}+1} e^{-(\sqrt{3}+1)z} \right] N \simeq -\frac{3q^2}{4\lambda} N, \quad (20)$$

where  $z$  is the mean number of nearest-neighbours; we can see that the interaction energy brings a small contribution in comparison with the self-energy of the “dressed” ions. The equilibrium configuration of  $N = 23$  ions, resulting from numerical calculation (gradient method), is shown in Fig. 1. In quantum-mechanical terms this solid phase of the “plasma” may be viewed as its

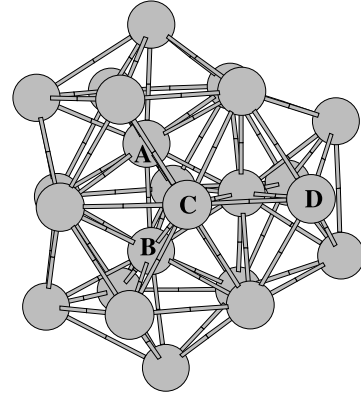


Fig. 1. Equilibrium configuration (solid state) of  $N = 23$  ions, according to equation (18); configuration parameters  $x_{ij} = \kappa R_{ij}$  are of the order  $x_{AB} = 2.04$ ,  $x_{BC} = 2.4$ ,  $x_{CD} = 2.27$ , and bond angles are of the order  $(ABC) = 64.83$ ,  $(ACD) = (BCD) = 103.57$  (degrees); the interaction energy is  $-1.2(q^2/\lambda)$ .

“ground-state”, though it is at a finite temperature. The frequency of oscillation  $\omega_0$  of an ion in the potential well generated by its nearest-neighbours can be estimated from the potential given by equation (18); it is of the order  $\omega_0 \simeq (zq^2/M\lambda^3)^{1/2}$ , where  $M$  is the ion mass. For a highly-compressed plasma the existence of an ionic lattice ground-state was suggested long ago [13–15].

The solid phase of the “plasma” exists for  $\bar{R}_{ij} \simeq (\sqrt{3} + 1)\lambda < a$ , i.e. for  $a < 1.68(q^2/T)$ . It is convenient to introduce the length  $a_0 = q^2/T$  and the notation  $a_s = 1.68a_0$ ; the ratio  $a/a_0 = aT/q^2$  may be taken as the coupling parameter of the plasma. We can see that in the strong-coupling regime  $a \ll a_0$  the “plasma” is a solid. For  $a \simeq a_s$  the vibration energy of an ion is comparable with the depth of the potential well and its vibration amplitude is comparable with the mean inter-ionic distance. If we compare the electron localization energy  $\hbar^2/m\lambda^2$  with the temperature  $T$ , we find that the quantum-mechanical solid appears for  $T < \sqrt{4\pi(\hbar^2/ma^2)}(q^2/a)$  (which is, usually, smaller than the Coulomb energy  $q^2/a$ ). For  $a = a_s$  this condition becomes  $a_H > 0.38a_0$ . For  $T < 0.38(q^2/a_H)$  we may view the “plasma” solid as a classical solid. This classical solid-phase is a distinct type of a classical solid; it may be termed a “plasmonic” solid, produced by inter-ionic (pseudo-) potentials which depend on temperature and density (equation (15)); in this solid phase the electrons behave classically. On passing to the weak-coupling regime, the “plasma” becomes gradually a liquid, a non-ideal gas, and, finally, in the weak-coupling limit  $a/a_0 \gg 1$ , the plasma behaves as an ideal gas. This is the well-known condition of the existence of a (genuine) plasma [31–34]. A numerical example of the parameter  $a_0$  is  $a_0 \simeq 10^{-7}$  cm for  $T = 10^4$  K (electron charge  $-q = 4.8 \times 10^{-10}$  esu). The parameter  $a_0^2$  may be taken as the electron-electron collision cross-section in the weak-coupling limit of the plasma gas. (A similar, usually much larger, parameter exists for ions).

The above estimations are valid as long as the potential  $\Psi$  (equation (15)) is quasi-uniform, i.e. it differs little from its mean value  $\bar{\Psi} = 1/\beta q$  ( $\bar{\Phi} = 0$ ). This condition is not fulfilled in small regions surrounding the ion positions, so we may estimate the error by comparing

$$\frac{1}{V_i} \int_{V_i} d\mathbf{r} \frac{qe^{-\kappa r}}{r} \quad (21)$$

with  $\bar{\Psi} = 1/\beta q$ , where  $V_i$  is a volume of the order  $\lambda^3$ ; we get the relative error  $\simeq (a/\lambda)^3$ , which is very small for  $\lambda \gg a$  (weak-coupling regime). In the solid phase, when  $a$  is comparable with

$\lambda$  (strong-coupling regime), we can get a more accurate estimation of the error by computing the self-energy

$$E_s = -\frac{1}{2}q \int_{V_i} d\mathbf{r} n(\mathbf{r}) \Psi(\mathbf{r}) - \frac{1}{2}q^2 \int_{V_i} d\mathbf{r} \frac{n(\mathbf{r})}{r} \quad (22)$$

associated with the volume  $V_i$  per ion (equation (3)); we get  $E_s = -(q^2/4\lambda)[3 - (1 + 2e)/e^2]$ , which should be compared with  $-(3q^2/4\lambda)$  given by equation (20). We get a relative error  $\simeq 0.28$  and we can see that equation (20) provides a lower bound to the binding energy.

#### 4. Liquid phase. van der Waals equation

According to equation (18), the potential energy of the plasma may be written as

$$E_p = N\Phi_0 + \frac{1}{2}N\Phi_i, \quad (23)$$

where

$$\Phi_0 = -\frac{3}{4}q^2\kappa = -\frac{3q^2}{4\lambda} \quad (24)$$

is the self-energy and

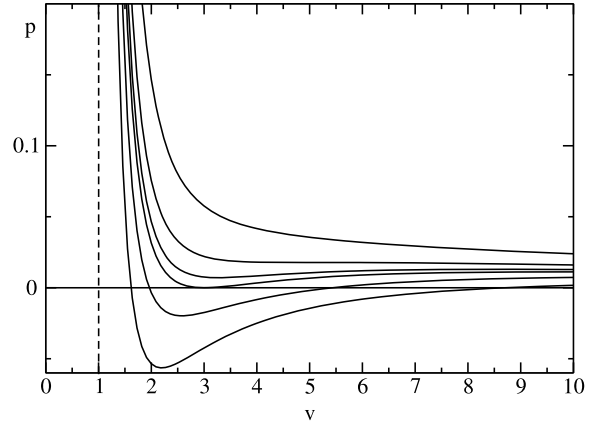
$$\Phi_i = \sum_j' U_{ij}, \quad U_{ij} = -\frac{1}{2}q^2\kappa \left(1 - \frac{2}{\kappa R_{ij}}\right) e^{-\kappa R_{ij}} \quad (25)$$

is the interaction energy of the  $i$ -th ion, generated by the two-particle interaction  $U_{ij}$ ; the prime on the summation means  $j \neq i$ . We note that  $U_{ij}$  is positive for  $R_{ij} < 2\lambda$  and negative for  $R_{ij} > 2\lambda$ . Two distinct regimes of interaction can be identified in the ensemble of ions “dressed” with electrons, depending on the relation between the mean separation distance  $a$  and the length  $2\lambda$  (the third regime of interaction, which leads to the solid phase, is identified above by  $\bar{R}_{ij} = (\sqrt{3} + 1)\lambda = a$ ). If  $a \ll 2\lambda$ , i.e.  $a \gg \pi a_0$  (weak-coupling regime), the positive part of the screened interaction inside the sphere with radius  $2\lambda$  (which may be called the Debye sphere) is cancelled out by the negative part of the interaction generated by the ions lying outside this sphere. Indeed, from equation (25) we may write

$$\Phi_i = -\frac{Nq^2\kappa}{2V} \int d\mathbf{R} \left(1 - \frac{2}{\kappa R}\right) e^{-\kappa R} = 0. \quad (26)$$

In these conditions the ions are practically free (with a small self-energy) and, since the Debye length  $\lambda$  is very large, the electrons may also be viewed as being free; in this weak-coupling regime, we have a genuine plasma, which behaves very much as an ideal gas. As long as  $2\lambda$  decreases and become comparable with  $a$ , the situation changes. For  $a \lesssim 2\lambda$  the Coulomb repulsion dominates, and the ensemble of ions behaves as if it would have an excluded volume. It follows that the condition  $2\lambda = a$  provides the excluded-volume parameter of a van der Waals-type equation; the solution, denoted  $a_l$ , of the equation  $2\lambda = a$  is  $a_l = \pi a_0$ . It should be compared with the solution, denoted  $a_s$  above, of the equation  $\bar{R}_{ij} \simeq (\sqrt{3} + 1)\lambda = a$ , which is the condition of occurrence of the solid phase; we get  $a_s = 4\pi a_0 / (2.73)^2 \simeq 0.5a_l$  (smaller than  $a_l$ ). If we compare the electron localization energy  $\hbar^2/m\lambda^2$  with the temperature  $T$  for  $a = a_l$ , we get that the liquid phase may be viewed as a classical liquid (where electrons behave classically) for  $T < 2.46(q^2/a_H)$ .

The change in the free energy brought about by the interaction is given by



**Fig. 2.** van der Waals isotherms  $p(v) = T_i/(v-1) - 1/v^{3/2}$  (equation (29)) for reduced pressure  $p$  and volume  $v = V/N$ ; from top to bottom the temperatures are  $T_i = 0.5, 0.429, 0.4, 0.385, 0.35, 0.3$ .

$$\Delta\mathcal{F} = -T_i \ln \left( \frac{1}{V^N} \int' e^{-\beta_i E_p} d\mathbf{r}_1 \dots d\mathbf{r}_N \right), \quad (27)$$

where  $T_i$  is the ion temperature ( $\beta_i = 1/T_i$ ) and the prime means integration over the whole volume minus the excluded volume  $b = \frac{1}{2} \cdot 4\pi a_l^3/3$  (the factor 1/2 arises from counting twice this volume in the integration over the independent variables  $\mathbf{r}_i$ ,  $i = 1, 2, \dots, N$ , in equation (27)). Making use of equations (23)-(26), we get

$$\Delta\mathcal{F} = -NT_i \ln \left(1 - \frac{Nb}{V}\right) + N\Phi_0 \quad (28)$$

and the van der Waals-type equation

$$\left[ p + \alpha(N/V)^{3/2} \right] (V - Nb) = NT_i, \quad (29)$$

where  $p$  is the pressure and the notation  $\alpha = \frac{3}{4}q^2 \sqrt{\pi a_0}$  is introduced ( $b = 2\pi^4 a_0^3/3$ ). Equation (29) can be viewed as the equation of state of a classical plasma. It differs from the equation of state of a classical plasma with continuously-distributed ions [35].

The  $(N/V)^{3/2}$ -term in equation (29) is well-known. It was derived in Ref. [28] for electrolytes (with a different numerical coefficient; it is related to the correlation energy [36]). A possible phase transition indicated by this term was first discussed by Norman and Starostin [37]. Experimental results which may be interpreted as confirming such a transition are discussed in Ref. [38].

The van de Waals equation for plasma (29) differs from the standard van de Waals equation (for gases with short-range interaction) by the power  $(N/V)^{3/2}$  in the internal pressure (arising from the ionic self-energy) instead of  $(N/V)^2$ . Formally, this may not look as a qualitative difference. However, a qualitative difference appears from the relation between the parameters  $\alpha$  and  $T_i b$ . While in the standard van der Waals equation this relation prevents, usually, the pressure to acquire negative values, in plasmas such a circumstance may appear; this is due to the long-range character of the Coulomb forces. The pressure given by equation (29) has an asymptote at the excluded volume  $V = Nb$ , two extrema and one inflexion point (the pressure is positive for  $T_i > 2\alpha/3\sqrt{3}b = T/(2\pi)^{3/2}$ ), depending on the temperature  $T_i$ . A few van der Waals isotherms given by equation (29) are shown in Fig. 2. The inflexion point occurs at the critical values  $V_c = 5Nb$ ,  $T_{ic} = 24\alpha/25\sqrt{5}b^{1/2}$  and  $p_c = \alpha/25\sqrt{5}b^{3/2}$ . It is worth noting that the critical temperature can be written as

$$T_{ic} = \frac{18}{25\pi} \sqrt{\frac{3}{10\pi}} \frac{q^2}{a_0} = \frac{18}{25\pi} \sqrt{\frac{3}{10\pi}} T \simeq 7 \times 10^{-2} T. \quad (30)$$



In the region near the asymptote the repulsive Coulomb part of the interaction dominates, while the unstable region with negative pressure is caused by an excess of self-energy. The two extrema of the function  $p(V)$  given by equation (29) correspond to liquid-gas mixed phases of the “plasma”; for  $V$  close to the excluded volume  $Nb$ , *i.e.* for  $a$  close to  $a_l$ , the “plasma” is a liquid. In the narrow region between  $a_l$  and  $a_s$  ( $a_s \simeq 0.5a_l$ ) the “plasma” is in a solid-liquid mixed phase; and for  $a$  smaller than  $a_s$  the “plasma” is a solid. All these regions correspond to the strong-coupling regime. It is worth noting that in the strong-coupling regime the electrons are strongly correlated with the ions and their temperature  $T$  is only a parameter. The thermodynamics of the ensemble (“dressed” ions) is controlled by the ion temperature  $T_i \ll T$ . We can see from equations (29) and (30) that there is no critical point for  $T = T_i$ . Moreover, for  $T = T_i$  equation (28) gives the correlation energy  $E = -T^2 \frac{\partial}{\partial T} (\Delta\mathcal{F}/T)$ .

## 5. Conclusion

In conclusion, we may say that the classical plasma investigated here by means of a linearized self-consistent variational approach consists of ions “dressed” by electrons, which interact by a screened (pseudo-) potential. This potential exhibits minima which may accommodate the ions in a solid phase. In the strong-coupling regime the ensemble is in a solid-state phase, while, on passing to the weak-coupling regime, the ensemble becomes gradually a liquid, a non-ideal gas, and, finally, an ideal gas. We may say that a classical plasma, *i.e.* an ensemble of electrons and positive ions, has a consistent thermodynamics. The solid, liquid and non-ideal gas phases of the classical plasma are identified here. The method used in this paper is provided by a linearized self-consistent variational approach where the electrons are described by their statistical (Boltzmann) distribution (density).

## Acknowledgements

The authors are indebted to the members of the Laboratory of Theoretical Physics at Magurele-Bucharest for many fruitful discussions. This work has been supported by the Scientific Research Agency of the Romanian Government through Grants 04-ELI / 2016 (Program 5/5.1/ELI-RO), PN 16 42 01 01 / 2016, PN (ELI) 16 42 01 05 / 2016 and PN 19 09 01/2018.

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