Binary ionic mixtures and a solvable model

by B. JANCOVICI

Laboratoire de Physique Théorique et Hautes Energies†,
Université Paris-Sud, 91405 Orsay, France

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The theory of solutions of McMillan and Mayer is applied to the jellium model of a binary ionic mixture: two species of charged particles, with charges $e$ and $Ze$, immersed in a neutralizing background. The density $p_1$ of the particles of charge $Ze$ is considered as small, and is used as an expansion parameter. The free energy, the pair distribution functions, the internal energy, and the pressure of the mixture are expressed as power series in $p_1$; the coefficients are integrals of correlation functions defined in the system at $\rho = 0$ (the reference system). Explicit expressions are obtained in the two-dimensional case, at a special temperature, since in that case the reference system (the two-dimensional, one-component plasma) is a solvable model.

1. INTRODUCTION

A systematic approach to the equilibrium statistical mechanics of solutions was given many years ago in a classic paper by McMillan and Mayer [1]. In this approach, the pure solvent is considered as a reference system, and the thermodynamical functions and correlation functions of the solution are expanded in power series of the activities or of the concentrations of the solutes; the coefficients of these expansions can be systematically expressed in terms of quantities pertaining to the reference system, such as the correlation functions for $n$ solute molecules in the solution at vanishing concentrations of the solutes. However, for real solutions, the above mentioned theory cannot be applied in practice without approximations, because the necessary ingredients, i.e. for instance correlation functions of arbitrary order in the pure solvent limit, are not exactly known.

Recently, an exactly solvable model of a fluid has been developed: the two-dimensional, one-component plasma (also called jellium), at a special value of the temperature [2, 3]. Starting from this model, a system of point particles of charge $e$ immersed in an inert uniform neutralizing background, and adding as a solute other particles of charge $Ze$, it is possible to carry out explicitly the programme of McMillan and Mayer, at least for a few leading terms in the expansions. This is the subject of the present paper. This exercise, in addition to providing an illustration of the general formalism, gives results on which approximate theories could be tested in view of their application to more realistic cases.

† Laboratoire associé au Centre National de la Recherche Scientifique.
For electrolyte solutions considered as solutions of ions in a neutral solvent, it is well known that specific difficulties arise because the potentials of average force between the ions are long ranged, and the cluster integrals which appear as coefficients in a simple power series of the ionic concentrations are divergent; in fact, the quantities of interest, as functions of the concentrations, are non-analytic at zero concentrations, and it is necessary to perform delicate resumptions \cite{4, 5}. These difficulties will not appear for the binary ionic systems which will be considered here, because the 'solvent' which is used as the reference system is a one-component plasma, i.e., a Coulomb system with the characteristic feature of screening: the potentials of average force between the solute charges \( Ze \) are short ranged, and the quantities of interest can be expanded in simple power series of the concentration of these charges.

In \( \S \; 2 \) we review the McMillan–Mayer formalism, adapting it to the case of a jellium model of a binary ionic mixture, going as far as possible in the general case, with no restrictions about the dimensionality (which could be 3 for instance!) and with an arbitrary ratio \( Z \) between the ionic charges. We discuss the specific features of the grand-canonical formalism for such a Coulomb system, and show how the free energy, the pair distribution functions, the internal energy, and the pressure can, in principle, be computed. When \( Z \) is an integer (and more especially when \( Z = 2 \)), simplifications occur. In \( \S \; 3 \), we consider, as a special case, the two-dimensional system, when the coupling constant for the 'solvent' has the special value \( \Gamma = 2 \); more explicit results are then obtained.

2. Binary Ionic Mixture

In this section, we adapt the McMillan–Mayer formalism to the case of a model of a binary ionic mixture: particles of charge \( e \) and particles of charge \( Ze \) in a neutralizing background. For the time being, \( Z \) is not necessarily an integer, and the dimensionality \( d \) may have any value larger than 1; the Coulomb potential is the \( d \)-dimensional one.

2.1. Grand-canonical formalism

The system will be considered in a grand-canonical ensemble defined for a fixed background. The box of volume \( V \) in which the system is contained and the background density is fixed, while the numbers, \( N \) particles of charge \( e \) and \( M \) particles of charge \( Ze \), may vary. The grand partition function is

\[
\Xi = \sum_{N,M} \frac{z^{N+M}}{N!M!} Q(N, M),
\]

where \( Q(N, M) \) is the configuration integral for numbers \( N \) and \( M \). The fugacities of each species of particles are \( z \) and \( t \) respectively.

It should be noted at once that, for any Coulomb system, the grand-canonical formalism has a rather special behaviour: for an \( n \)-component system, only \( n-1 \) fugacity variables are relevant for determining the state of the system, because there is a neutrality constraint. This can be seen here as follows. The canonical free energy \( F(N, M) \) is defined by

\[
\beta F(N, M) = -\ln \frac{Q(N, M)}{N!M!\lambda_N^{eN}\lambda_Z^{eM}},
\]

(2.2)
where $\beta = 1/kT$ is the inverse temperature, $\lambda_1$ and $\lambda_2$ the thermal wavelengths. In the thermodynamic limit, the electrostatic forces make the free energy density $F/V$ infinite [6] for systems that are not neutral in that limit (i.e., when the particle charge densities do not cancel the background charge density), and the corresponding configuration integrals $Q$ become negligible. Thus, the only relevant contributions to (2.1) are for

$$N + ZM = N^*, \quad (2.3)$$

where $N^* e$ is the background charge, and (2.1) can also be written as

$$\Xi = \sum_{\mathcal{M}} z^{N^* - ZM} \frac{\mathcal{M}!}{(N^* - ZM)!M!} Q(N^* - ZM, M). \quad (2.4)$$

The usual way of relating the fugacities to the densities is to write that $\Xi$ is dominated by its maximum term. However, here $Q$ has a sharp crest along the line (2.3) and looking for the maximum term of (2.4) (or equivalently of (2.1)) gives only one relation:

$$\ln (t\lambda_2 e) - Z \ln (z\lambda_1 e) = \frac{d}{dM} \beta F(N^* - ZM, M). \quad (2.5)$$

In other words, only the combination of $z$ and $t$ of (2.5) will be relevant for determining the particle numbers (constrained by (2.3)).

This maximum-term method gives the familiar relation

$$\ln \Xi = N \ln (z\lambda_1 e) + M \ln (t\lambda_2 e) - \beta F(N^* - ZM, M), \quad (2.6)$$

or, using (2.3) and (2.5),

$$\ln \Xi = N^* \ln (z\lambda_1 e) + M \frac{d}{dM} \beta F(N^* - ZM, M) - \beta F(N^* - ZM, M). \quad (2.7)$$

Therefore, after (2.5) has been used, $\ln \Xi$ still depends upon the additional variable $z$, and $(\beta V)^{-1} \ln \Xi$ is certainly not a bulk physical quantity; it cannot be the pressure (several different pressures have been defined for jellium models [7, 8], here we mean the usual one $- \partial F/\partial V$ with the derivative taken for constant values of the particle numbers and of the background total charge in such a way that the system remains neutral). This special feature of the jellium models, that $(\beta V)^{-1} \ln \Xi$ is not the pressure $- \partial F/\partial V$, does not prevent us however from using (2.6) for computing the free energy.

2.2. Free energy

We now proceed to using the McMillan-Mayer method, formally manipulating the double sum (2.1), but keeping in mind the above remarks. The aim is to expand the free energy of the mixture in powers of the density $\rho_2$ of the particles of charge Ze.

Let us first consider, as a reference system, the one with $t = 0$, i.e., with only particles of charge $e$ in a background of fixed charge density $-e\rho^*$. The grand partition function (2.1) becomes

$$\Xi^* = \sum_{N} \frac{z^N}{N!} Q(N, 0). \quad (2.8)$$

† For an ordinary multicomponent plasma (without a fixed background) the same reasoning as the one used here shows that $(\beta V)^{-1} \ln \Xi$ is the pressure, and only meaningful combinations of the fugacities appear in it.
In the thermodynamic limit, the only relevant term of (2.8) is for \( N = N^* = V \rho^* \), whatever the value of \( z \) may be, and the number density \( \rho_1 \) of the particles is equal to \( \rho^* \):

\[
\rho_1 = z \frac{\partial}{\partial z} \frac{1}{\nu} \ln \Xi^* = \rho^*. \tag{2.9}
\]

For non-zero values of \( t \), expansions in powers of \( t \) should be built. Let \( \rho^{(p)}_{z \geq 0}(r_1, r_2, \ldots, r_p) \) be the \( p \)-body density of particles of charge \( z \epsilon \), depending upon \( p \) particle coordinates \( r_1, r_2, \ldots, r_p \); the one-body density is \( \rho^*(r_1) = \rho_1 \). From the usual grand-canonical definition of \( \rho^{(p)}_{z \geq 0} \), one obtains

\[
\rho^{(p)}_{z \geq 0}(r_1, r_2, \ldots, r_p) \, \text{d}r_1 \, \text{d}r_2 \ldots \text{d}r_p = \frac{1}{\Xi^{2N}} \sum_{M \geq p} \frac{2^N \nu^M}{N! \gamma^M} Q(N, M). \tag{2.10}
\]

Let \( g^{(p)}_{z \geq 0} \) be the limit of the \( p \)-body distribution function of particles of charge \( z \epsilon \) when \( t \) (and thus when the density \( \rho_2 \) of these particles) go to zero, while \( z \) keeps a fixed value,

\[
g^{(p)}_{z \geq 0}(r_1, r_2, \ldots, r_p) = \lim_{t, \rho_2 \to 0} \frac{1}{\rho_2} \rho^{(p)}_{z \geq 0}(r_1, r_2, \ldots, r_p), \tag{2.11}
\]

and let \( \gamma \) be the limit

\[
\gamma = \lim_{t, \rho_2 \to 0} \frac{t}{\rho_2}. \tag{2.12}
\]

From these definitions, one readily sees that (2.1) can be rewritten as

\[
\frac{\Xi}{\Xi^*} = 1 + \frac{t}{\gamma} V + \sum_{M \geq 2} \left( \frac{t}{\gamma} \right)^M \frac{1}{M!} \int g^{(M)}_{z \geq 0}(r_1, r_2, \ldots, r_M) \, \text{d}r_1 \, \text{d}r_2 \ldots \text{d}r_M. \tag{2.13}
\]

This is the essence of the McMillan–Mayer rearrangement. Equation (2.13) has the same structure as the grand partition function of a one-component system of particles of charge \( z \epsilon \). The presence of the solvent of particles of charge \( \epsilon \) is taken into account by the replacement of the fugacity \( t \) by the activity \( t/\gamma \), and by the replacement of the configuration integral for \( M \) particles by the integral of the distribution function \( g^{(M)}_{z \geq 0} \) of \( M \) particles immersed in the solvent at infinite dilution of these particles.

From (2.13), one proceeds in the same way as for a one-component system. One goes from \( \Xi/\Xi^* \) to its logarithm by replacing the distribution functions by their connected parts:

\[
\frac{1}{\nu} \ln \frac{\Xi}{\Xi^*} = \frac{t}{\gamma} + \sum_{M \geq 2} b_M \left( \frac{t}{\gamma} \right)^M, \tag{2.14}
\]

where

\[
b_M = \frac{1}{M! \nu} \int (g^{(M)}_{z \geq 0})(r_1, r_2, \ldots, r_M) \, \text{d}r_1 \, \text{d}r_2 \ldots \text{d}r_M. \tag{2.15}
\]

Involves an integral upon the truncated \( M \)-body distribution function \( g^{(M)}_{z \geq 0} \) defined from the \( g^{(M)} \) as usual:

\[
\begin{aligned}
g^{(2)}_{z \geq 0}(r_1, r_2) &= g^{(2)}(r_1, r_2) + 1, \\
g^{(3)}_{z \geq 0}(r_1, r_2, r_3) &= g^{(3)}(r_1, r_2, r_3) + g^{(2)}(r_1, r_2) + g^{(2)}(r_1, r_3) + g^{(2)}(r_2, r_3) + 1, \\ & \quad + g^{(2)}(r_1, r_3) + g^{(2)}(r_2, r_3) + g^{(2)}(r_3, r_1) + 1, \ldots.
\end{aligned} \tag{2.16}
\]

† For simplicity, we shall not explicitly indicate the thermodynamic limit in our notation.
The coefficients $b_M$ which appear now are finite in the thermodynamic limit if the distribution functions have good cluster properties. Let us stress again that the truncated distribution function $g^{(M)}_{12...2T}$ in (2.15) is for $M$ impurities of charge $Ze$ in an otherwise pure solvent made of particles of charge $e$, and the density of the solvent particles must be taken as $\rho_1 = \rho^s$ for evaluating the integrals (2.15); $-e\rho^s$ is the unchanged background charge density.

For finite values of $t$, the density $\rho_2$ of the particles of charge $Ze$ is

$$
\rho_2 = t \frac{1}{V} \ln \Xi = \frac{t}{\gamma} + \sum_{M \geq 2} \frac{Mb_M}{M} \left( \frac{t}{\gamma} \right)^M. \tag{2.17}
$$

From (2.14) and (2.17), one obtains in the usual way the inverse formulas

$$
\ln \frac{t}{\gamma} = \ln \rho_2 + \sum_{M \geq 2} \frac{M}{M-1} B_M \rho_2^{M-1}, \tag{2.18}
$$

and

$$
\frac{1}{V} \ln \frac{\Xi}{\Xi^2} = \rho_2 + \sum_{M \geq 2} B_M \rho_2^M, \tag{2.19}
$$

where the 'virial' coefficients $B_M$ are related to the cluster integrals $b_M$ in the same way as for an imperfect gas†:

$$
B_2 = -b_2, \quad B_3 = -2b_2 + 4b_2^2, \quad B_4 = -3b_4 + 18b_2b_2 - 20b_2b_2, \ldots. \tag{2.20}
$$

For arbitrary values of $z$ and $t$, $\rho_1$ and $\rho_2$ must always satisfy the neutrality requirement

$$
\rho_1 + Z\rho_2 = \rho^s. \tag{2.21}
$$

The validity of (2.21) can be checked by using the screening properties of the distribution functions. By performing upon (2.1) manipulations similar to the ones leading to (2.14) or (2.17), one finds [1]

$$
\rho_1 = -z \frac{1}{\gamma V} \ln \Xi = \rho^s \left[ 1 + \sum_{M \geq 1} b_{1,M} \left( \frac{t}{\gamma} \right)^M \right], \tag{2.22}
$$

where

$$
b_{1,M} = \frac{1}{M!V} \int g^{(M+1)}_{12...2T}(r_1, r_2, \ldots, r_M) \, dr_1 \, dr_2 \, \ldots \, dr_M. \tag{2.23}
$$

and $g^{(M+1)}_{12...2T}$ is the truncated distribution function for 1 particle of charge $e$ at $r$ and $M$ impurities of charge $Ze$ at $r_1, r_2, \ldots, r_M$ in the otherwise pure solvent. The general condition that these impurities must be perfectly screened [10] can be readily written as

$$
\rho^s \int g^{(M+1)}_{12...2T}(r_1, r_2, \ldots, r_M) \, dr = -ZMg^{(M)}_{12...2T}(r_1, r_2, \ldots, r_M). \tag{2.24}
$$

Thus

$$
\rho^s b_{1,M} = -ZMb_M \quad \text{(with } b_1 = 1), \tag{2.25}
$$

and (2.17) and (2.22) do satisfy (2.21).

From $\Xi$, one obtains the free energy $F(N^* - ZM, M)$ by

$$
\frac{BF}{V} = -\frac{1}{V} \ln \Xi + \rho_1 \ln (z\lambda^d) + \rho_2 \ln (t\lambda^d). \tag{2.26}
$$

† Our definition of $B_M$ follows the now standard one [9] for imperfect gases and differs from the original one [1] by a factor $1 - M$. 
Similarly, the free energy \( F^* = F(N^*, 0) \) of the reference system is given by
\[
\frac{\beta F^*}{V} = -\frac{1}{V} \ln Z^* + \rho^* \ln (\zeta \lambda_d^4). \tag{2.27}
\]
Subtracting the perfect gas contributions, and using (2.18), (2.19) and (2.21), one finally obtains from (2.26) and (2.27) the excess free energy difference as an expansion in powers of the density \( \rho_2 \):
\[
\frac{\beta (F_{\text{exc}} - F_{\text{exc}}^*)}{V} = \beta (\mu_2^{\text{exc}} - Z\mu_1^{\text{exc}})\rho_2 - (\rho^* - Z\rho_2) \ln \frac{\rho^*}{\rho^*} - Z\rho_2 + \sum_{M=2}^{\infty} \frac{1}{M-1} B_{MP}\rho^M, \tag{2.28}
\]
where
\[
\mu_1^{\text{exc}} = \frac{1}{\beta} \ln \frac{\zeta}{\rho^*}, \tag{2.29}
\]
and
\[
\mu_2^{\text{exc}} = \frac{1}{\beta} \ln \gamma = \lim_{t, \rho_2 \to 0} \frac{1}{\beta} \ln \frac{t}{\rho_2}, \tag{2.30}
\]
are the excess chemical potentials of a charge \( e \) and an impurity \( Z \), respectively, in the otherwise pure solvent. By expanding the logarithm in (2.28), one obtains the equivalent expression
\[
\frac{\beta (F_{\text{exc}} - F_{\text{exc}}^*)}{V} = \beta (\mu_2^{\text{exc}} - Z\mu_1^{\text{exc}})\rho_2 + \sum_{M=2}^{\infty} \frac{1}{M-1} \left( B_M - \frac{Z^M}{M\rho_M^{M-1}} \right) \rho^M. \tag{2.31}
\]
The interpretation of \( \mu_1^{\text{exc}} \) and \( \mu_2^{\text{exc}} \) as excess chemical potentials is possible, notwithstanding the arbitrariness in the choice of \( z \) and \( t \) separately, because only the neutrality-preserving combination \( \mu_2^{\text{exc}} - Z\mu_1^{\text{exc}} \) appears in (2.28) or (2.31). By (2.5), this quantity has the well-defined meaning
\[
\mu_2^{\text{exc}} - Z\mu_1^{\text{exc}} = \frac{d}{dM} F_{\text{exc}}(N^* - ZM, M) \bigg|_{M=0} = F_{\text{exc}}(N^* - Z, 1) - F_{\text{exc}}(N^*, 0), \tag{2.32}
\]
where the derivative \( dF_{\text{exc}}/dM \) has to be taken at constant background charge. It is however convenient to define separately \( \mu_1^{\text{exc}} \) and \( \mu_2^{\text{exc}} \) by
\[
\mu_1^{\text{exc}} = F_{\text{exc}}(N^* + 1, 0) - F_{\text{exc}}(N^*, 0), \tag{2.33}
\]
\[
\mu_2^{\text{exc}} = F_{\text{exc}}(N^*, 1) - F_{\text{exc}}(N^*, 0), \tag{2.34}
\]
where now each excess free energy is defined for a background which is varied in a way which keeps the system neutral (thus \( F_{\text{exc}}(N^* + 1, 0) \) is defined for a background charge \(- (N^* + 1)e\), etc. . . ); obviously, the background charge variations cancel one another in the combination (2.32).

As a check of (2.31), using the screening property (2.24), one easily verifies that (2.31) vanishes for \( Z = 1 \), as it should.
2.3. Pair distribution functions

By similar manipulations [1, 11] it is also possible to expand the pair distribution functions of the mixture in powers of the density $\rho_0$ of the particles of charge $Ze$. We only quote the results at first order in $\rho_0$. Let $g_{\alpha\beta}(t)\mid r_1 - r_2 \rangle; \rho_0)$ be the pair distribution function at density $\rho_0$ for two particles of species $\alpha$ and $\beta$ at $r_1$ and $r_2$; the species index $\alpha$ or $\beta$ is 1 if the particle charge is $e$ and 2 if the particle charge is $Ze$. One then finds

$$g_{\alpha\beta}(t)\mid r_1 - r_2 \rangle; \rho_0) = g_{\alpha\beta}^{(1)}(r_1 - r_2) + \rho_0 \int g_{\alpha\beta}(t)\mid r_1 - r_2 \rangle; \rho_0) \, dr_3 - \int g_{\alpha\beta}(t)\mid r_1 - r_2 \rangle; \rho_0) \, dr - \ldots,$$

where the distribution functions in the right-hand side of (2.35) are to be taken in the limit $\rho_0 \to 0$.

If $\alpha = 1$ or $\beta = 1$, a simplification occurs in (2.35), since

$$\rho_0 \int g_{12}(t)\mid r \rangle; \rho_0) \, dr = -Ze,$$

a special case of the screening rule (2.24).

2.4. Internal energy and pressure

The internal energy of the mixture can be obtained by differentiating the free energy (2.31) with respect to the temperature, provided one knows the temperature dependence of the “virial” coefficients $B_{\alpha\beta}$, i.e. the temperature dependence of the cluster integrals (2.15) defined in the reference system. Alternatively, one can express the excess internal energy $U_{\text{exc}}$ in terms of the pair distribution functions by

$$\frac{U_{\text{exc}}}{V} = \frac{1}{2} \rho_0^2 \int g_{11}(t)\mid r \rangle; \rho_0) \, dr + \rho_0 \rho_1 Z \int g_{12}(t)\mid r \rangle; \rho_0) \, dr$$

$$+ \frac{1}{2} \rho_0^2 Z^2 \int g_{22}(t)\mid r \rangle; \rho_0) \, dr,$$

(2.37)

(where $v(r)$ is the Coulomb interaction between two particles of charge $e$) and use the expansion (2.35) for the pair distribution functions.

For a three-dimensional system, the excess pressure is related to the excess internal energy by a scaling relation [9], which can be easily extended to the case of a $d$-dimensional system ($d > 2$)

$$P_{\text{exc}} = \frac{d-2}{d} \frac{U_{\text{exc}}}{V}.$$

(2.38)

However, this relation is not valid in two dimensions. In that latter case, scaling gives for the excess pressure the explicit expression

$$P_{\text{exc}} = -\frac{\epsilon a}{4} \rho_1 - \frac{(Ze)^2}{4 \rho_0},$$

(2.39)

a simple generalization of the equation of state for a one-component, two-dimensional system [12].
2.5. What should be known

The results of §§ 2.2, 2.3, 2.4, are that the free energy, the pair distribution functions, and the internal energy of the mixture can be expressed in terms of quantities defined in the one-component plasma used as a reference system. Some of these quantities involve the completely pure, one-component plasma: its excess free energy \( F_{\text{ex}} \), its excess chemical potential \( \mu_{\text{ex}} \), its distribution functions. Other required quantities are distribution functions involving an arbitrary but finite number of impurities of charge \( Z \) in the otherwise pure, one-component plasma; the excess chemical potential \( \mu_{Z} \) of one impurity, which is also needed, can be expressed in terms of such a distribution function by the coupling parameter technique [13] as

\[
\mu_{Z} = \rho Z \int_{0}^{Z} dZ' \int [g_{12}^{(2)}(r|Z') - 1] \psi(r) \, dr,
\]

(2.40)

where \( g_{10}^{(2)}(r|Z') \) is the pair distribution function for an impurity of charge \( Z \) and a particle of charge \( e \).

An important simplification occurs if \( Z \) is an integer, i.e. if the impurities have a charge \( Z \) which is a multiple of the charge \( e \) of a particle of the reference system. In that case, the distribution functions involving impurities can be expressed in terms of distribution functions involving only particles of charge \( e \). This is achieved by considering an impurity of charge \( Z \) as built from \( Z \) particles of charge \( e \), the mutual Coulomb repulsion of which has been turned off. For instance, if \( Z = 2 \), the pair distribution function for two impurities in the otherwise pure reference system is

\[
g_{22}^{(2)}(r_1, r_2) \rightarrow \lim_{|r_1 - r_2| \rightarrow 0} \frac{g_{1111}^{(4)}(r_1, r_2, r_3, r_4)}{g_{11}^{(2)}(r_1 - r_2)g_{11}^{(2)}(r_3 - r_4)}
\]

(2.41)

where the distribution functions in the right-hand side are for particles of charge \( e \); similarly,

\[
g_{22}^{(2)}(r_1, r_2, r_3) = \lim_{|r_1 - r_2| \rightarrow 0} \frac{g_{11111}^{(6)}(r_1, r_2, r_3, r_4, r_5, r_6)}{g_{11}^{(2)}(r_1 - r_2)g_{11}^{(2)}(r_3 - r_4)g_{11}^{(2)}(r_5 - r_6)},
\]

(2.42)

\[
g_{12}^{(2)}(r_1 - r_2) = \lim_{|r_1 - r_2| \rightarrow 0} \frac{g_{111}^{(3)}(r_1, r_2, r_3)}{g_{11}^{(2)}(r_1 - r_2)},
\]

(2.43)

etc. Furthermore, if \( Z = 2 \), the free energy difference (2.32) is related to the short-range behaviour of the pair distribution function \( g_{11}^{(2)} \) in such a way [14] that

\[
\beta (\mu_{Z} - 2\mu_{1}) = -\ln \lim_{r \rightarrow 0} \{ \exp [\beta \psi(r)]g_{11}^{(2)}(r) \}.
\]

(2.44)

this latter relation can be easily generalized to higher integer values of \( Z \).
3. Solvable two-dimensional model

As an illustration of the formalism of the previous section, we consider the two-dimensional case. The Coulomb potential between two particles of charge $e$ is

$$\Phi(r) = -\frac{e^2}{r},$$  \hspace{1cm} (3.1)

where $L$ is a length scale. The dimensionless coupling constant is $\Gamma = \frac{\beta e^2}{\rho^*}$. When $\Gamma = 2$, the one-component plasma is an exactly solvable model [2, 3], in which it is possible to compute explicitly a few coefficients in the expansions in powers of $\rho_2$.

In the distribution functions of this section, all distances are expressed in units of $(\pi \rho^*)^{-1/2}$.

3.1. The reference system

The reference system is the pure, one-component plasma at $\Gamma = 2$, made of particles of charge $e$ in a background. The particle density is $\rho^*$. In the thermodynamic limit, the excess free energy per unit volume (area) is such that [2]

$$\frac{\beta F_{\text{exc}}^*}{V} = -\frac{1}{2} \rho^* \ln (\pi \rho^* L^2) + \rho^* [1 - \frac{1}{2} \ln (2\pi)]^2,$$ \hspace{1cm} (3.2)

the truncated pair distribution function is [3, 15]

$$\hat{g}_{12}^{(0)}(r) = -\exp(-r^2),$$ \hspace{1cm} (3.3)

the $n$-body distribution function is

$$g^{(n)}_{12\ldots n}(r_1, r_2, \ldots, r_n) = \exp \left[ - (r_1^2 + r_2^2 + \ldots + r_n^2) \right] \times \text{Det} \left[ \exp \left( \hat{z}_i z_j \right) \right]_{i,j=1,2,\ldots,n}$$ \hspace{1cm} (3.4)

(where $z_i$ is the complex number which represents the position of the $i$th particle in the plane and $\hat{z}_i$ its complex conjugate), the excess internal energy per unit volume (area) is such that

$$\frac{\beta U_{\text{exc}}^*}{V} = -\frac{1}{2} \rho^* \ln (\pi \rho^* L^2) - \frac{1}{2} \rho^* C$$ \hspace{1cm} (3.5)

(where $C = 0.5772\ldots$ is Euler’s constant).

3.2. Impurities of arbitrary charge

For arbitrary (in general non-integer) values of $Z$, it is possible to obtain explicit expressions for the distribution functions in the reference system when they involve at most one impurity. One considers the reference system in a circular background, adding now an impurity of charge $Ze$ fixed at the centre (which is taken as the origin), and one computes the density $\rho(r|Z)$ of the particles of charge $e$ in presence of that impurity, by a straightforward extension of the method which gave the results of § 3.1. In the thermodynamic limit, the pair distribution function for two particles of charge $Ze$ and $e$ respectively is found to be, at $\rho_2 = 0$,

$$\hat{g}_{12}^{(0)}(r) = \frac{\rho(r|Z)}{\rho^*} = \exp \left( -r^2 \right) \sum_{n=0}^{\infty} \frac{\rho^{2(n+1)}}{\Gamma(Z+n+1)} \left( \frac{r^2}{\Gamma(Z)} \right)^n$$ \hspace{1cm} (3.6)
where $\Gamma(Z)$ is the gamma function and

$$\gamma(Z, x) = \int_0^{\infty} \exp(-t) t^{Z-1} dt$$

is the incomplete gamma function; the last equality in (3.6) expresses a relation [16] between $\gamma$ and a degenerate hypergeometric function. Similarly, the three-body distribution function for one impurity of charge $Ze$ and two particles of charge $e$ is found to be, at $\rho_e = 0$,

$$g_{31}(0, r_1, r_2) = \frac{1}{[\Gamma(Z)]^2} \left[ \gamma(Z, r_1) \gamma(Z, r_2) - \exp(-|r_1 - r_2|^2) \gamma(Z, \bar{z}_1 \bar{z}_2) \right].$$

From (3.6) and (3.1) one obtains

$$\beta \rho^* \int (g_{31}(r | Z') - 1) \psi(r) dr = Z' \left[ \frac{d}{dZ'} \ln \Gamma(Z' + 1) - 1 - \ln \left(\pi \rho^* L^2 \right) \right].$$

(3.9)

Thus, from (2.40)

$$\beta \mu_{31 \text{ exc}}^* = \int_0^{Z} dZ' Z' \frac{d}{dZ'} \ln \Gamma(Z' + 1) - \frac{1}{2} Z^2 \ln(1 + \ln(\pi \rho^* L^2)).$$

(3.10)

Either from (3.10) for $Z = 1$, or from (2.33) and (3.2),

$$\beta \mu_{1 \text{ exc}}^* = \frac{1}{2} \left[ 1 - \ln(2\pi) - \ln(\pi \rho^* L^2) \right].$$

(3.11)

Therefore, using (3.2), (3.10), (3.11) in (2.31), we know explicitly the expansion of the excess free energy up to the first order in $\rho_e$.

In principle, (2.35) and (2.37) allow to expand also the pair distribution function $g_{31}(r; \rho_e)$ and the excess internal energy $U_{\text{exc}}$ up to first order in $\rho_e$. However, these expansions involve integrals of the three-body distribution function (3.8), and we have not been able to perform these integrals explicitly.

### 3.3. Impurities of integer charge $Z = 2$

The calculations can be carried on further for integer values of $Z$. Here, we consider the simplest case, $Z = 2$.

Either from (2.44), or from (3.10) and (3.11), one finds

$$\beta \mu_{2 \text{ exc}}^* - 2 \mu_{1 \text{ exc}}^* = -\ln(\pi \rho^* L^2).$$

(3.12)

Using (3.4) in (2.41), one finds, at $\rho_e = 0$,

$$g_{222}^{(a)}(r) = -(2 + r^2) [1 + \psi(r)] + \exp(-2 \psi(r)).$$

(3.13)

Similarly, using (3.4) in (2.42), one finds after a very tedious calculation a rather complicated expression for $g_{2222}^{(a)}$. Let $z_1, z_2, z_3$ be the complex numbers associated to the positions $r_1, r_2, r_3$ of these particles of charge $2e$, let us define $s_1 = z_1 - z_3, s_2 = z_2 - z_1, s_3 = z_1 - z_2, s_4 = z_1 - z_2$, and let $A$ be the area of the triangle formed
by the three particles. Then, at $\rho_2 = 0$,

$$
\begin{align*}
\mathcal{E}_{1222}^{(3)}(r_1, r_2, r_3) &= \left[-|s_1s_2s_3|^2 - 16A^2 + 2 + 2 \cos(4A)\right] \exp \left(-|s_1|^2 - |s_2|^2 - |s_3|^2\right) \\
&+ \left[-2|s_1^2s_3^3| + |s_1|^4 + |s_2|^4 + |s_3|^4 + 4\right] \cos(2A) \\
&+ 4(|s_1|^2 + |s_2|^2 + |s_3|^2)^2 \sin(2A) \exp \left[-\frac{1}{2}(|s_1|^2 + |s_2|^2 + |s_3|^2)\right] \\
&+ \left[|s_1^2s_2s_3|^2 + |s_1|^2 + |s_2|^2 - 2|s_2s_3|^2 + 2\right] \exp \left(-|s_1|^2 - |s_2|^2\right) \\
&- [2 + (s_1s_2)^2] \exp \left(-2|s_2|^2 + s_1s_2\right) \\
&- [2 + (s_2s_3)^2] \exp \left(-2|s_3|^2 + s_2s_3\right) + \ldots + \ldots, \tag{3.14}
\end{align*}
$$

where the dots stand for two more terms obtained by circular permutations of the indices $1, 2, 3$ in the last curly bracket.

From (3.13) and (3.14) respectively, one obtains the cluster integrals (2.15)

$$\rho^*b_2 = \frac{3}{2}, \quad \rho^*b_3 = \frac{1555}{324}, \tag{3.15}$$

and the 'virial' coefficients (2.20)

$$\rho^*B_2 = \frac{3}{2}, \quad \rho^*B_3 = \frac{859}{324}. \tag{3.16}$$

Therefore the excess free energy expansion is

$$
\begin{align*}
\frac{\beta F_{\text{exp}}}{V} &= -\frac{1}{2} \rho^* \ln(\pi \rho^* L^2) + \rho^*[1 - \frac{1}{2} \ln(2\pi)] \\
&- \frac{\ln(\pi \rho^* L^2)}{4\rho^*} \rho^2 - \frac{5}{648\rho^*} \rho^2 + \ldots \tag{3.17}
\end{align*}
$$

A remarkable feature of this expansion is the smallness of the last coefficient which has been computed, $5/648$. This indicates for a fast convergence might be considered as supporting the validity of a theory [17] which was built, in the three-dimensional case, on the basis of expansions of the free energy truncated at the first order in $\rho_2^*$.

Using either (3.8) or relations analogous to (2.41-43), one finds, at $\rho_2 = 0$,

$$
\mathcal{E}_{2112}^{(3)}(0, r_1, r_2)
$$

and

$$
\mathcal{E}_{1122}^{(3)}(0, r_1, r_2)
$$

where

$$
\begin{align*}
\mathcal{E}_{1222}^{(3)}(0, r_1, r_2) &= (r_1 - r_2)^2 \exp \left(-r_1^2 - r_2^2\right) + (1 + \bar{s}_1s_2) \exp \left(-r_1^2 - r_2^2 + \bar{s}_1s_2\right) \\
&+ (1 + \bar{s}_2s_3) \exp \left(-r_1^2 - r_2^2 + \bar{s}_2s_3\right) \tag{3.18}
\end{align*}
$$

and

$$
\begin{align*}
\mathcal{E}_{1222}^{(3)}(0, r_1, r_2) &= [(r_1 - r_2)^2(r_2^2 - 1) + r_2^2 + 1] \exp \left[-(r_1 - r_2)^2 - r_2^2\right] \\
&+ [(r_1 - r_2)^2(r_1^2 - 1) + r_1^2 + 1] \exp \left[-(r_1 - r_2)^2 - r_1^2\right] \\
&+ [(r_1 - r_2)^2(-\bar{s}_1s_2 + 1) + \bar{s}_1s_2 + 1] \exp \left[-(r_1 - r_2)^2 - \bar{s}_1s_2\right] \\
&+ [(r_1 - r_2)^2(-\bar{s}_2s_3 + 1) + \bar{s}_2s_3 + 1] \exp \left[-(r_1 - r_2)^2 - \bar{s}_2s_3\right] \\
&- (\bar{s}_1s_2 + 1) \exp \left[-2(r_1 - r_2)^2 - \bar{s}_1s_2\right] \\
&- (\bar{s}_2s_3 + 1) \exp \left[-2(r_1 - r_2)^2 - \bar{s}_2s_3\right]. \tag{3.19}
\end{align*}
$$
Using these distribution functions at $\rho_e = 0$, one finds from (2.35) the pair distribution function expansions

\[ g_{111}^{(2)}(r; \rho_e) = -\exp(-r^2) + \frac{\rho_e}{\rho_0} \frac{r^2}{2} \exp\left(-\frac{r^2}{2}\right) + \ldots , \quad (3.20) \]

\[ g_{122}^{(3)}(r; \rho_e) = -(1 + r^2) \exp(-r^2) + \frac{\rho_e}{\rho_0} \left[ -\frac{1}{2}(1 + r^2) \exp(-r^2) \right. \]

\[ + \left. (1 + \frac{1}{2}r^2 + \frac{1}{3}r^4) \exp\left(-\frac{r^2}{2}\right) \right] + \ldots , \quad (3.21) \]

and

\[ g_{222}^{(3)}(r; \rho_e) = -(2 + r^2) \exp(-r^2) + \exp(-2r^2) \]

\[ + \frac{\rho_e}{\rho_0} \left[ (1 + \frac{3}{2}r^2 + \frac{1}{2}r^4) \exp\left(-\frac{r^2}{2}\right) - (2 + r^2) \exp(-r^2) \right. \]

\[ + \left. (1 - \frac{3}{2}r^2 - \frac{1}{2}r^4) \exp\left(-\frac{r^2}{2}\right) \right] + \ldots . \quad (3.22) \]

Finally, the excess internal energy expansion is obtained from (2.37) as

\[ \frac{\beta U_{\text{ex}}}{V} = -\frac{1}{2} \rho^* \ln(\pi \rho^* L^2) - \frac{1}{2} \rho^* C + \rho_e [-\ln(2\pi \rho^* L^2) - C + 1] + \ldots . \quad (3.23) \]

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References