



**HAL**  
open science

# Screened activity expansion for the pressure of a quantum multi-component plasma and consistency with the local charge neutrality

A. Alastuey, V. Ballenegger, D. Wendland

► **To cite this version:**

A. Alastuey, V. Ballenegger, D. Wendland. Screened activity expansion for the pressure of a quantum multi-component plasma and consistency with the local charge neutrality. *Physical Review E* , 2020, 10.1103/PhysRevE.102.023203 . hal-02637957v1

**HAL Id: hal-02637957**

**<https://hal.science/hal-02637957v1>**

Submitted on 13 Dec 2019 (v1), last revised 28 May 2020 (v2)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Screened activity expansion for the pressure of a quantum multi-component plasma and consistency with the local charge neutrality

A. Alastuey<sup>1</sup>, V. Ballenegger<sup>2</sup> and D. Wendland<sup>1,2</sup>

<sup>1</sup>Laboratoire de Physique, ENS Lyon, UMR CNRS 5672  
46 allée d'Italie, 69364 Lyon Cedex 07, France

<sup>2</sup>Institut UTINAM, Université de Bourgogne-Franche-Comté, UMR CNRS 6213  
16, route de Gray, 25030 Besançon Cedex, France

(Dated: December 13, 2019)

## Abstract

We consider a quantum multi-component plasma made of point charged particles interacting *via* the two-body Coulomb potential. Within the Feynman-Kac path integral representation of the system in terms of a classical gas of loops, we derive screened activity series for the pressure in the grand-canonical ensemble. The method is based on the Abe-Meeron summations which remove all long-range Coulomb divergences. Moreover, we show that the particle densities can be inferred from the diagrammatic series for the pressure, through partial differentiations with respect to suitable effective activities, consistently with the local charge neutrality. We briefly argue how these results can be used for including, in the equation of state at moderately low densities, the contributions of recombined entities made with three or more particles.

PACS numbers: 05.30.-d, 05.70.Ce, 52.25.Kn

## I. INTRODUCTION

Mayer diagrams have been introduced while ago in order to derive low-density expansions of equilibrium quantities for classical systems with short-range pair interactions. For charged fluids, every Mayer diagram diverges because of the long-range of Coulomb interactions. Abe and Meeron showed that such divergences can be removed *via* systematic summations of convolution chains built with the Coulomb interaction. The whole Mayer series is then exactly transformed into a series of so-called prototype graphs, with the same topological structure as the Mayer diagrams, but with effective bonds built with the familiar Debye potential in place of the bare Coulomb interaction. The contribution of each prototype graph is finite thanks to the screening collective effects embedded in the Debye potential.

For a quantum Coulomb system, it turns out that Mayer-like diagrammatic series can be also introduced within its path integral representation in terms of an equivalent classical gas of loops [1–3]. Hence, the Abe-Meeron strategy can be extended to the gas of loops which interact via pairwise Coulomb-like interactions. However, the corresponding summations are carried out in the activity series which, contrarily to the case of classical point particles, cannot be transformed into particle-density series through the principle of topological reduction. The method was applied to the derivation of low-activity series for the one-body and two-body particle distribution functions in a first step, while term-by-term inversion of these series combined with thermodynamic identities provide particle-density expansions of the pressure in a second step. The corresponding equation of state has been calculated up to order  $\rho^{5/2}$  [4], and is fully consistent [5] with results obtained independently using different formalisms, like the pioneering work of Ebeling [6, 7] based on the effective-potential method, charge-expansions within the standard many-body perturbation theory [8] or field-theory calculations [9].

In this paper, we derive the screened activity-series for the pressure of a quantum multi-component plasma within the loop gas mapping. These series would provide a direct access to the equation of state, once the activities are eliminated in favor of the densities. However, such elimination requires to avoid the pitfalls related to the

local charge neutrality. As proved by Lieb and Lebowitz [10], the particle densities calculated in the grand-canonical ensemble always satisfy the local charge neutrality, whatever the activities are. This remarkable property is exploited for reducing the number of prototype graphs which contribute to the pressure at a given order in the small activities. At the same time, the particle densities determined through suitable differentiations of this pressure, do satisfy the local charge neutrality. We briefly argue how the corresponding scheme would allow one to improve previous results for the equation of state, on the analytical and/or numerical side.

The paper is organized as follows. In Section II, we recall the main results proved by Lieb and Lebowitz for a quantum Coulomb system made with  $\mathcal{S}$  components. As a consequence of the neutrality property in the grand-canonical ensemble, we infer that the pressure depends on  $(\mathcal{S} - 1)$  independent combinations of the  $\mathcal{S}$  activities  $\{z_\alpha\}$ . This leads to the introduction of a set of  $(\mathcal{S} - 1)$  effective activities  $\{y_i\}$  defined by suitable transformations of the usual activities  $\{z_\alpha\}$ . The pressure  $P$  then only depends on the set  $\{y_i\}$  and on the temperature, while the particle densities obtained by suitable partial differentiations with respect to the  $y_i$ 's do satisfy local charge neutrality. The screened activity series for  $P(T; \{z_\alpha\})$  is derived in Section III. The Abe-Meeron summations are applied to the Mayer diagrams for the equivalent gas of classical loops. The pressure is then expressed as a series of prototype graphs where the usual points are replaced by loops, which are connected by screened bonds and carry dressed statistical weights. Within the degeneracy property exposed in Section II, we introduce a pseudo-neutrality prescription for the set  $\{z_\alpha\}$  which allows us to determine the small- $y$  expansion of  $P(T; \{y_i\})$  at a given order by keeping a finite number of prototype graphs. As illustrated in Section IV for the simple cases  $\mathcal{S} = 2$  and  $\mathcal{S} = 3$ , such expansion of  $P(T; \{y_i\})$  gives access to the corresponding expansion of particle densities, which is consistent order by order with the charge neutrality. Concluding comments are given in Section V.

## II. OVERALL NEUTRALITY IN THE GRAND-CANONICAL ENSEMBLE

### A. Quantum multi-component Coulomb system and the thermodynamic limit

We consider a quantum multi-component plasma made of  $\mathcal{S}$  species of charged point particles enclosed in a box with volume  $\Lambda$ . The species index is denoted  $\alpha$ ,  $\{\alpha = 1, \dots, \mathcal{S}\}$ . Each particle of species  $\alpha$  has a mass  $m_\alpha$ , while it carries a charge  $e_\alpha$  and a spin  $s_\alpha$ . Each of them obeys to either Bose or Fermi statistics, according to the integer or half-integer value of  $s_\alpha$  respectively. In order to ensure thermodynamic stability, at least one species needs to be fermions [10] and there are both positively and negatively charged species. The species  $\alpha = 1, \dots, \mathcal{S}$  and the position  $\mathbf{x}$  of a given particle is denoted by the single notation  $\mathbf{x} = (\alpha, \mathbf{x})$ . The total interaction potential  $U(\mathbf{x}_1, \dots, \mathbf{x}_N)$  of  $N$  particles is the sum of pairwise pure Coulomb interactions,

$$U(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{i < j} V_C(\mathbf{x}_i, \mathbf{x}_j) \quad (\text{II.1})$$

with

$$V_C(\mathbf{x}_i, \mathbf{x}_j) = e_{\alpha_i} e_{\alpha_j} v_C(|\mathbf{x}_i - \mathbf{x}_j|) \quad (\text{II.2})$$

and  $v_C(r) = 1/r$ . The corresponding non-relativistic Coulomb Hamiltonian reads

$$H_N = - \sum_{i=1}^N \frac{\hbar^2}{2m_{\alpha_i}} \Delta_i + U(\mathbf{x}_1, \dots, \mathbf{x}_N) \quad (\text{II.3})$$

where  $\Delta_i$  is the Laplacian with respect to position  $\mathbf{x}_i$ . The nucleo-electronic plasma is an example of such multi-component system, where the negative point charge are electrons, while all positive point charges are nuclei.

As proved by Lieb and Lebowitz, the present quantum multi-component plasma has a well-behaved thermodynamic limit (TL), and all statistical ensembles become equivalent in this limit. In the grand-canonical ensemble the TL is defined by fixing the chemical potentials  $\mu_\alpha$  of each species as well as the inverse temperature  $\beta = 1/(k_B T)$ , and letting  $\Lambda \rightarrow \infty$ . The grand-partition function  $\Xi_\Lambda$  of the finite system reads

$$\Xi_\Lambda = \text{Tr} \exp[-\beta(H - \sum_{\alpha=1}^{\mathcal{S}} \mu_\alpha N_\alpha)], \quad (\text{II.4})$$

where the trace runs on all particle numbers, not only on neutral configurations. The grand canonical pressure

$$P_\Lambda(T, \{\mu_\alpha\}) = \frac{k_B T \ln \Xi_\Lambda}{|\Lambda|} \quad (\text{II.5})$$

has a well-defined TL

$$P(T; \{\mu_\alpha\}) = k_B T \lim_{\text{TL}} \frac{\ln \Xi_\Lambda}{\Lambda}, \quad (\text{II.6})$$

which is a function of the chemical potentials and of the temperature.

It turns out that the non-neutral configurations associated with  $\sum_{\alpha=1}^S e_\alpha N_\alpha \neq 0$ , have such large positive Coulomb energies that they eventually do not contribute to the trace (II.4) in the TL. As a consequence the system maintains charge neutrality in the bulk

$$\sum_{\alpha=1}^S e_\alpha \rho_\alpha = 0 \quad (\text{II.7})$$

where  $\rho_\alpha$  is the particle density of species  $\alpha$ . Thanks to the thermodynamic identity

$$\rho_\alpha = \frac{\partial P}{\partial \mu_\alpha}(T; \{\mu_\gamma\}), \quad (\text{II.8})$$

charge neutrality (II.7) can be recast as

$$\sum_{\alpha=1}^S e_\alpha \frac{\partial P}{\partial \mu_\alpha}(T; \{\mu_\gamma\}) = 0. \quad (\text{II.9})$$

## B. Consequence of the Lieb-Lebowitz theorem

The identity (II.9) is valid for any set  $\{\mu_\gamma\}$ . This means that the pressure depends in fact on  $(S - 1)$  independent combinations of the chemical potentials, while there exist one combination which is irrelevant. This remarkable property can be easily understood by first considering the simplest case of a two-component system with  $S = 2$  and  $e_1 e_2 < 0$ . Let us express both  $N_1$  and  $N_2$  in terms of the total particle number  $N = N_1 + N_2$  and of the total charge  $Q = e_1 N_1 + e_2 N_2$ . A straightforward calculation provides

$$\begin{aligned} N_1 &= -\frac{e_2}{(e_1 - e_2)} N + \frac{Q}{(e_1 - e_2)} \\ N_2 &= \frac{e_1}{(e_1 - e_2)} N - \frac{Q}{(e_1 - e_2)}. \end{aligned} \quad (\text{II.10})$$

Accordingly, we obtain

$$\mu_1 N_1 + \mu_2 N_2 = \left[ -\frac{e_2}{(e_1 - e_2)} \mu_1 + \frac{e_1}{(e_1 - e_2)} \mu_2 \right] N + (\mu_1 - \mu_2) \frac{Q}{(e_1 - e_2)}. \quad (\text{II.11})$$

After inserting this decomposition into the trace (II.4), we see that the combination  $\mu = (e_1 \mu_2 - e_2 \mu_1)/(e_1 - e_2)$  determines the total particle density  $\rho = \lim_{TL} \langle N \rangle_{GC} / \Lambda$  in the thermodynamic limit, while the combination  $\nu = \mu_1 - \mu_2$  becomes irrelevant in the TL since the charge density  $\lim_{TL} Q / \Lambda$  always vanishes. Hence the pressure  $P(T; \{\mu_\gamma\})$  reduces to a function of only two variables instead of three, namely  $P(T; \mu_1, \mu_2) = P(T; \mu)$ . The particle densities are then expressed as

$$\begin{aligned} \rho_1 &= \frac{\partial P}{\partial \mu}(T; \mu) \frac{\partial \mu}{\partial \mu_1}(\mu_1, \mu_2) = -\frac{e_2}{(e_1 - e_2)} \frac{\partial P}{\partial \mu}(T; \mu) \\ \rho_2 &= \frac{\partial P}{\partial \mu}(T; \mu) \frac{\partial \mu}{\partial \mu_2}(\mu_1, \mu_2) = \frac{e_1}{(e_1 - e_2)} \frac{\partial P}{\partial \mu}(T; \mu). \end{aligned} \quad (\text{II.12})$$

Note that the expressions (II.12) do satisfy the neutrality property (II.7), whatever the function  $P(T; \mu)$  is. Moreover, the total particle density becomes

$$\rho = \rho_1 + \rho_2 = \frac{\partial P}{\partial \mu}(T; \mu), \quad (\text{II.13})$$

in agreement with the above interpretation of  $\mu$ .

For multi-component systems with three or more components, we can determine in a similar way the irrelevant combination of the chemical potentials by noting that

$$\sum_{\alpha=1}^{\mathcal{S}} \mu_\alpha N_\alpha = \boldsymbol{\mu} \cdot \mathbf{N} \quad (\text{II.14})$$

where  $\boldsymbol{\mu}$  and  $\mathbf{N}$  are vectors in a  $\mathcal{S}$ -dimensional space with respective components  $\mu_\alpha$  and  $N_\alpha$ . Let  $\mathbf{e}$  be the  $\mathcal{S}$ -dimensional vector with components  $e_\alpha$ . If we decompose  $\boldsymbol{\mu}$  as

$$\boldsymbol{\mu} = \boldsymbol{\mu}_\perp + \frac{\boldsymbol{\mu} \cdot \mathbf{e}}{e^2} \mathbf{e} \quad (\text{II.15})$$

where  $\boldsymbol{\mu}_\perp$  is orthogonal to  $\mathbf{e}$ , we find that the scalar product (II.14) reduces to

$$\sum_{\alpha=1}^{\mathcal{S}} \mu_\alpha N_\alpha = \boldsymbol{\mu}_\perp \cdot \mathbf{N} + \frac{\boldsymbol{\mu} \cdot \mathbf{e}}{|\mathbf{e}|^2} Q. \quad (\text{II.16})$$

This implies that the linear combination  $\sum_\alpha e_\alpha \mu_\alpha / |\mathbf{e}|$  is not relevant. A relevant combination can be built by forming the scalar product  $\boldsymbol{\mu} \cdot \mathbf{e}_\perp$  where  $\mathbf{e}_\perp$  is orthogonal

to  $\mathbf{e}$ . For  $\mathcal{S} = 2$ , there are two opposite vectors  $\mathbf{e}_\perp$  with components  $\pm(-e_2, e_1)$ , so there is a single generic relevant combination, namely  $(-e_2\mu_1 + e_1\mu_2)$ . Note that the multiplication of this generic combination by  $1/(e_1 - e_2)$  does provide the chemical potential  $\mu = (-e_2\mu_1 + e_1\mu_2)/(e_1 - e_2)$  which controls the total number of particles, as shown above. For  $\mathcal{S} \geq 3$ , there are  $(\mathcal{S} - 1)$  independent vectors  $\{\mathbf{e}_\perp^{(1)}, \mathbf{e}_\perp^{(2)}, \dots, \mathbf{e}_\perp^{(\mathcal{S}-1)}\}$  which form a basis of the  $(\mathcal{S} - 1)$ -dimensional plane orthogonal to  $\mathbf{e}$ . They generate  $(\mathcal{S} - 1)$  independent linear combinations of the chemical potentials which are relevant. Of course the choice of the basis  $\{\mathbf{e}_\perp^{(1)}, \mathbf{e}_\perp^{(2)}, \dots, \mathbf{e}_\perp^{(\mathcal{S}-1)}\}$  remains arbitrary, as well as that of the  $(\mathcal{S} - 1)$  relevant combinations of the  $\mu_\alpha$ 's.

For further purposes, it is useful to translate the previous considerations in terms of the particle activities

$$z_\alpha = (2s_\alpha + 1) \frac{e^{\beta\mu_\alpha}}{(2\pi\lambda_\alpha^2)^{3/2}}, \quad (\text{II.17})$$

where  $\lambda_\alpha = (\beta\hbar^2/m_\alpha)^{1/2}$  is the de Broglie thermal wavelength of the particles of species  $\alpha$ . The  $(\mathcal{S} - 1)$  relevant linear combinations  $\{\mu \cdot \mathbf{e}_\perp^{(1)}, \mu \cdot \mathbf{e}_\perp^{(2)}, \dots, \mu \cdot \mathbf{e}_\perp^{(\mathcal{S}-1)}\}$  provide the corresponding  $(\mathcal{S} - 1)$  independent combination of the particle activities,

$$y_i = K_i(\{z_\alpha\}) \quad \text{with} \quad i = 1, \dots, \mathcal{S} - 1. \quad (\text{II.18})$$

Each function  $K_i(\{z_\alpha\})$  is a monomial in the  $z_\alpha$ 's,

$$K_i(\{z_\alpha\}) = \prod_{\alpha=1, \dots, \mathcal{S}} z_\alpha^{\omega_\alpha^{(i)}}, \quad (\text{II.19})$$

where the respective dimensionless powers  $\omega_\alpha^{(i)}$  are proportional to the components  $e_{\perp, \alpha}^{(i)}$  of the vector  $\mathbf{e}_\perp^{(i)}$ . The corresponding proportionality constant  $C_i$ , which is the same for all species  $\alpha$  and a given  $i$ , can be always chosen such that

$$\sum_{\alpha=1, \dots, \mathcal{S}} \omega_\alpha^{(i)} = 1. \quad (\text{II.20})$$

This ensures that the new variables  $y_i$  have all the dimension of an activity, *i.e.* a density. Accordingly, the pressure is a function of the temperature and of the  $(\mathcal{S} - 1)$  effective activities  $y_i$ , *i.e.*  $P(T; \{\mu_\alpha\}) = P(T; \{z_\alpha\}) = P(T; \{y_i\})$ . The thermodynamical identity (II.8) which provides the particle densities is then rewritten as

$$\rho_\alpha = z_\alpha \sum_{i=1}^{\mathcal{S}-1} \frac{\partial \beta P}{\partial y_i}(T; \{y_j\}) \frac{\partial K_i}{\partial z_\alpha}(T; \{z_\gamma\}). \quad (\text{II.21})$$



The total local charge density then reads

$$\sum_{\alpha} e_{\alpha} \rho_{\alpha} = \sum_{i=1}^{S-1} \frac{\partial \beta P}{\partial y_i}(T; \{y_j\}) \sum_{\alpha} e_{\alpha} z_{\alpha} \frac{\partial K_i}{\partial z_{\alpha}}(T; \{z_{\gamma}\}), \quad (\text{II.22})$$

and it indeed vanishes as it should since

$$\begin{aligned} \sum_{\alpha} e_{\alpha} z_{\alpha} \frac{\partial K_i}{\partial z_{\alpha}}(T; \{z_{\gamma}\}) &= C_i K_i(T; \{z_{\gamma}\}) \sum_{\alpha} e_{\alpha} e_{\perp, \alpha}^{(i)} \\ &= C_i K_i(T; \{z_{\gamma}\}) \mathbf{e} \cdot \mathbf{e}_{\perp}^{(i)} = 0. \end{aligned} \quad (\text{II.23})$$

### III. ACTIVITY EXPANSION OF THE PRESSURE

#### A. The equivalent classical gas of loops

The trace (II.4) defining  $\Xi_{\Lambda}$  can be expressed in the position and spin space, where the corresponding states have to be symmetrized according to Bose or Fermi statistics. The corresponding sum involves both diagonal and off-diagonal matrix elements of  $\exp(-\beta H_N)$  in position space. Diagonal matrix elements account for Maxwell-Boltzmann statistics, while off-diagonal matrix elements describe exchange contributions. Within the Feynman-Kac representation, all the matrix elements of  $\exp(-\beta H_N)$  in position space can be rewritten as functional integrals over paths followed by the particles. The off-diagonal matrix elements generate open paths. However all the open paths followed by the particles exchanged in a given cyclic permutation, can be collected into a close filamentous object, namely a loop  $\mathcal{L}$ , also sometimes called polymer in the literature. Each contribution of a given spatial matrix element of  $\exp(-\beta H_N)$  for a given set of particles, can be related to that of a classical Boltzmann factor for a given set of loops. The last non-trivial step consists in showing that the sum of all these contributions, namely  $\Xi_{\Lambda}$ , can be exactly recast as the grand-partition function of a classical gas of loops, namely [1–3]

$$\Xi_{\Lambda} = \Xi_{\Lambda, \text{Loop}} = \sum_{k=0}^{\infty} \frac{1}{N!} \left[ \prod_{i=1}^N \int_{\Lambda} D(\mathcal{L}_i) z(\mathcal{L}_i) \right] e^{-\beta U(\mathcal{L}_1, \mathcal{L}_2, \dots, \mathcal{L}_N)}, \quad (\text{III.1})$$

where loop phase-space measure  $D(\mathcal{L})$ , loop fugacity  $z(\mathcal{L})$ , and total interaction potential  $U(\mathcal{L}_1, \mathcal{L}_2, \dots, \mathcal{L}_N)$  are defined as follows.

A loop  $\mathcal{L}$  located at  $\mathbf{x}$  containing  $q$  particles of species  $\alpha$ , is a closed path  $X(s) = \mathbf{x} + \lambda_\alpha \boldsymbol{\mathcal{X}}(s)$ , parametrized by an imaginary time  $s$  running from 0 to  $q$  where  $\boldsymbol{\mathcal{X}}(s)$ , the shape of the loop, is a Brownian bridge subjected to the constraints  $\boldsymbol{\mathcal{X}}(0) = \boldsymbol{\mathcal{X}}(q) = \mathbf{0}$ . The state of a loop, collectively noted  $\mathcal{L} = \{\mathbf{x}, \chi\}$ , is defined by its position  $\mathbf{x}$  together with an internal degree of freedom  $\chi = \{\alpha, q, \boldsymbol{\mathcal{X}}\}$ , which includes its shape  $\boldsymbol{\mathcal{X}}$  as well as the number  $q$  of exchanged particles of species  $\alpha$ . The loop phase-space measure  $D(\mathcal{L})$  means summation over all these degrees of freedom,

$$\int_{\Lambda} D(\mathcal{L}) \cdots = \sum_{\alpha=1}^S \sum_{q=1}^{\infty} \int_{\Lambda} d\mathbf{x} \int D_q(\boldsymbol{\mathcal{X}}) \cdots . \quad (\text{III.2})$$

The functional integration over the loop shape  $D_q(\boldsymbol{\mathcal{X}})$  is the normalized Gaussian measure for the Brownian bridge  $\boldsymbol{\mathcal{X}}(s)$  entirely defined by its covariance

$$\int D_q(\boldsymbol{\mathcal{X}}) \boldsymbol{\mathcal{X}}_{\mu}(s_1) \boldsymbol{\mathcal{X}}_{\nu}(s_2) = q \delta_{\mu\nu} \left[ \min \left( \frac{s_1}{q}, \frac{s_2}{q} \right) - \frac{s_1 s_2}{q^2} \right]. \quad (\text{III.3})$$

The loop activity reads

$$z(\mathcal{L}) = (2s_\alpha + 1) \frac{\eta_\alpha^{q-1}}{q} \frac{e^{\beta \mu_\alpha q}}{(2\pi q \lambda_\alpha^2)^{3/2}} e^{-\beta U_{\text{self}}(\mathcal{L})}, \quad (\text{III.4})$$

where the factor  $\eta_\alpha$  is related to the genuine symmetrization or anti-symmetrization of the position and spin states, namely  $\eta_\alpha = 1$  for bosons and  $\eta_\alpha = -1$  for fermions. Moreover,  $U_{\text{self}}(\mathcal{L})$  is the self-energy of the loop which is generated by the interactions between the exchanged particles,

$$U_{\text{self}}(\mathcal{L}) = \frac{e_\alpha^2}{2} \int_0^q ds \int_0^q ds' (1 - \delta_{[s][s']}) \tilde{\delta}(s - s') v_C(\lambda_\alpha \boldsymbol{\mathcal{X}}(s) - \lambda_\alpha \boldsymbol{\mathcal{X}}(s')), \quad (\text{III.5})$$

with the Dirac comb

$$\tilde{\delta}(s - s') = \sum_{n=-\infty}^{\infty} \delta(s - s' - n) = \sum_{n=-\infty}^{\infty} e^{2i\pi n(s-s')} = \delta(\tilde{s} - \tilde{s}'). \quad (\text{III.6})$$

The Dirac comb ensures that particles only interact at equal times  $s$  along their paths, as required by the Feynman-Kac formula, while the term  $(1 - \delta_{[s][s']})$  removes the contributions of self-interactions.

Eventually, the total interaction potential  $U(\mathcal{L}_1, \mathcal{L}_2, \dots, \mathcal{L}_N)$  is a sum of pairwise interactions,

$$U(\mathcal{L}_1, \mathcal{L}_2, \dots, \mathcal{L}_N) = \frac{1}{2} \sum_{i \neq j} V(\mathcal{L}_i, \mathcal{L}_j) \quad (\text{III.7})$$

with

$$V(\mathcal{L}_i, \mathcal{L}_j) = e_{\alpha_i} e_{\alpha_j} \int_0^{q_i} ds_i \int_0^{q_j} ds_j \tilde{\delta}(s_i - s_j) v_C(\mathbf{x}_i + \lambda_{\alpha_i} \boldsymbol{\mathcal{X}}_i(s_i) - \mathbf{x}_j - \lambda_{\alpha_j} \boldsymbol{\mathcal{X}}_j(s_j)) . \quad (\text{III.8})$$

The loop-loop interaction  $V(\mathcal{L}_i, \mathcal{L}_j)$  is generated by the interactions between any particle inside  $\mathcal{L}_i$  and any particle inside  $\mathcal{L}_j$ . Like in formula (III.5), the Dirac comb (III.6) guarantees that interactions are taken at equal times along particle paths.

The introduction of the gas of loops is particularly useful at low densities, because the standard Mayer diagrammatic expansions, valid for classical systems with pairwise interactions, can be straightforwardly applied by merely replacing points by loops. However, as in the case of classical Coulomb systems, the Mayer-like diagrams for the loop gas are plagued with divergences arising from the large-distance behavior

$$V(\mathcal{L}_i, \mathcal{L}_j) \sim \frac{q_i e_{\alpha_i} q_j e_{\alpha_j}}{|\mathbf{x}_i - \mathbf{x}_j|} \quad \text{when } |\mathbf{x}_i - \mathbf{x}_j| \rightarrow \infty . \quad (\text{III.9})$$

Note that such behavior is nothing but the Coulomb interaction between point charges, because the finite spatial extensions of both loops  $\mathcal{L}_i$  and  $\mathcal{L}_j$  can be neglected with respect to their relative large distance  $|\mathbf{x}_i - \mathbf{x}_j|$ . It has been shown that all these long-range divergences can be removed within a suitable extension of the Abe-Meeron summation process introduced long ago for classical Coulomb fluids. The method has been applied for both the one- and two-body distribution functions [2, 11]. In the next Section, we derive the corresponding Abe-Meeron series for the pressure.

## B. Abe-Meeron like summations for the pressure

Here, we will not detail the various counting processes which are identical to those arising in the classical case. Note that simplified presentations of the summation process are extensively described in Refs. [2] and [11]. The key starting point is the decomposition of the Mayer bond

$$b_M(\mathcal{L}_k, \mathcal{L}_l) = \exp(-\beta V(\mathcal{L}_k, \mathcal{L}_l)) - 1 , \quad (\text{III.10})$$

into

$$b_M(\mathcal{L}_k, \mathcal{L}_l) = b_T(\mathcal{L}_k, \mathcal{L}_l) + b_I(\mathcal{L}_k, \mathcal{L}_l) , \quad (\text{III.11})$$

with the interaction bond

$$b_I(\mathcal{L}_k, \mathcal{L}_l) = -\beta V(\mathcal{L}_k, \mathcal{L}_l) \quad (\text{III.12})$$

and the truncated bond

$$b_T(\mathcal{L}_k, \mathcal{L}_l) = \exp(-\beta V(\mathcal{L}_k, \mathcal{L}_l)) - 1 + \beta V(\mathcal{L}_k, \mathcal{L}_l) . \quad (\text{III.13})$$

A loop  $\mathcal{L}_l$  which is singly connected to an articulation loop  $\mathcal{L}_k$  is called an ending loop. Then, the corresponding Mayer bond  $b_M(\mathcal{L}_k, \mathcal{L}_l)$  is decomposed as

$$b_M(\mathcal{L}_k, \mathcal{L}_l) = b_{TE}(\mathcal{L}_k, \mathcal{L}_l) + b_I(\mathcal{L}_k, \mathcal{L}_l) + [b_I(\mathcal{L}_k, \mathcal{L}_l)]^2/2 , \quad (\text{III.14})$$

with the truncated ending bond

$$b_{TE}(\mathcal{L}_k, \mathcal{L}_l) = \exp(-\beta V(\mathcal{L}_k, \mathcal{L}_l)) - 1 + \beta V(\mathcal{L}_k, \mathcal{L}_l) - (\beta V(\mathcal{L}_k, \mathcal{L}_l))^2/2 . \quad (\text{III.15})$$

Then, after inserting the decompositions (III.11) and (III.14) in every diagram of the Mayer series for the pressure  $P$ , we proceed to systematic summations of chain convolutions  $b_I * b_I * \dots * b_I * b_I$  made with arbitrary numbers  $p$  of interaction bonds  $b_I$ . The sum of  $p = 1, 2, \dots, \infty$  single convolution chains between two fixed loops  $\mathcal{L}_i$  and  $\mathcal{L}_j$  generate the quantum analogue  $\phi(\mathcal{L}_i, \mathcal{L}_j)$  of the Debye potential, which reads [?

$$\phi(\mathcal{L}_i, \mathcal{L}_j) = \int_0^{q_i} ds_i \int_0^{q_j} ds_j \psi_{\text{loop}}(\mathbf{x}_j + \lambda_{\alpha_j} \boldsymbol{\mathcal{X}}_j(s_j) - \mathbf{x}_i - \lambda_{\alpha_i} \boldsymbol{\mathcal{X}}_i(s_i), s_i - s_j) , \quad (\text{III.16})$$

with

$$\psi_{\text{loop}}(\mathbf{r}, s) = \sum_{n=-\infty}^{\infty} \exp(2i\pi ns) \tilde{\psi}_{\text{loop}}(\mathbf{r}, n) \quad (\text{III.17})$$

and

$$\tilde{\psi}_{\text{loop}}(\mathbf{r}, n) = \int \frac{d\mathbf{k}}{(2\pi)^3} \exp(i\mathbf{k} \cdot \mathbf{r}) \frac{4\pi}{k^2 + \kappa^2(k, n)} . \quad (\text{III.18})$$

Note that  $\tilde{\psi}_{\text{loop}}(\mathbf{r}, n)$  has a structure analogous to the classical Debye form, except that an infinite number of frequency dependent screening factors  $\kappa^2(k, n)$  occur,

$$\kappa^2(k, n) = 4\pi\beta \sum_{\alpha} \sum_{q=1}^{\infty} qe_{\alpha}^2 \int_0^q ds \exp(2i\pi ns) \int D_q(\boldsymbol{\mathcal{X}}) \exp(i\mathbf{k} \cdot \lambda_{\alpha} \boldsymbol{\mathcal{X}}(s)) z(\chi) . \quad (\text{III.19})$$

The collective effects are embedded in these screening factors  $\kappa^2(k, n)$ , while the frequencies  $2\pi n$  are the analogues of the familiar Matsubara frequencies in the standard many-body perturbative series.

Similarly to the case of the Mayer diagrams for the one-body loop density, the summation of all convolution chains in the Mayer diagrams for the pressure can be expressed in terms of  $\phi$ , except in the single ring diagrams built with arbitrary numbers  $p \geq 2$  of interaction bonds  $b_I$ . In such diagrams made with  $p$  black points (loops), the symmetry factor is  $1/(2p)$ , while in the single chain diagram connecting two different loops with  $p$  intermediate black points and  $(p + 1)$  interaction bonds  $b_I$ , the symmetry factor is 1 for any  $p$ . After replacing each bare interaction  $V$  by its decomposition over Matsubara frequencies, we find that the contribution to the pressure of a single ring made with  $p$  black loops and  $p$  bonds  $b_I = -\beta V$  reduces to

$$\frac{1}{2} \sum_{n=-\infty}^{\infty} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{1}{p} \left[ \frac{-\kappa^2(k, n)}{k^2} \right]^p. \quad (\text{III.20})$$

The calculation is similar to that involved in the convolution chain and gives again raise to the screening factors  $\kappa^2(k, n)$ . Now, the summation over  $p$  of all ring contributions leads to a logarithmic function instead of the rational fraction  $1/[k^2 + \kappa^2(k, n)]$  for the chain contributions, namely

$$\beta P_R = \frac{1}{2} \sum_{n=-\infty}^{\infty} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[ \frac{\kappa^2(k, n)}{k^2} - \ln \left( 1 + \frac{\kappa^2(k, n)}{k^2} \right) \right]. \quad (\text{III.21})$$

The summations for all the remaining diagrams are carried out as for the one-body density (??). They generate the same screened bonds and the same dressed activities. The summations of single convolution chains between two fixed loops  $\mathcal{L}_i$  and  $\mathcal{L}_j$  made with arbitrary numbers of intermediate loops and bonds  $b_I$  provides the Debye-like bond

$$b_D(\mathcal{L}_i, \mathcal{L}_j) = -\beta e_{\alpha_i} e_{\alpha_j} \phi(\mathcal{L}_i, \mathcal{L}_j). \quad (\text{III.22})$$

The so-called Abe-Meeron bond,

$$b_{AM}(\mathcal{L}_i, \mathcal{L}_j) = \exp(b_D(\mathcal{L}_i, \mathcal{L}_j)) - 1 - b_D(\mathcal{L}_i, \mathcal{L}_j). \quad (\text{III.23})$$

is obtained by summing more complex structures connecting the fixed pair  $\mathcal{L}_i$  and  $\mathcal{L}_j$  which may involve one bond  $b_T(\mathcal{L}_i, \mathcal{L}_j)$ , one bond  $b_I(\mathcal{L}_i, \mathcal{L}_j)$  and one or more

convolution chains made with arbitrary numbers  $p \geq 2$  of interaction bonds  $b_I$ . If  $\mathcal{L}_i$  is an ending loop, such summation provides the Abe-Meeron ending bond

$$b_{\text{AME}}(\mathcal{L}_i, \mathcal{L}_j) = \exp(b_{\text{D}}(\mathcal{L}_i, \mathcal{L}_j)) - 1 - b_{\text{D}}(\mathcal{L}_i, \mathcal{L}_j) - [b_{\text{D}}(\mathcal{L}_i, \mathcal{L}_j)]^2/2. \quad (\text{III.24})$$

A first kind of dressed activity is obtained by summing all rings made with arbitrary numbers  $p \geq 1$  of loops and  $(p + 1)$  bonds  $b_I$  which can be attached to a given loop  $\mathcal{L}_i$ . Inside each of these rings, the symmetry factor is now  $1/2$  because of the particular role of the given attaching loop  $\mathcal{L}_i$ . The summation over  $p$  for single rings provides the ring sum

$$I_{\text{R}}(\mathcal{L}_i) = \frac{1}{2} [b_{\text{D}}(\mathcal{L}_i, \mathcal{L}_i) - b_{\text{I}}(\mathcal{L}_i, \mathcal{L}_i)]. \quad (\text{III.25})$$

Adding to the bare activity  $z(\mathcal{L}_i)$  the contributions of an arbitrary number of rings attached to  $\mathcal{L}_i$ , we find the dressed ring activity

$$z_{\text{R}}(\mathcal{L}_i) = z(\mathcal{L}_i) \exp(I_{\text{R}}(\mathcal{L}_i)). \quad (\text{III.26})$$

Finally, the truncated dressed activity

$$z_{\text{RT}}(\mathcal{L}_j) = z(\mathcal{L}_j) (\exp(I_{\text{R}}(\mathcal{L}_j)) - 1). \quad (\text{III.27})$$

also emerges for loops  $\mathcal{L}_i$  connected to the rest of the diagram by two bonds  $b_I$  and to which are attached one or more rings.

The final screened Mayer series of the pressure reads

$$\beta P = \beta P_{\text{R}} + \int D(\mathcal{L}) z(\mathcal{L}) [e^{I_{\text{R}}(\mathcal{L})} - I_{\text{R}}(\mathcal{L})] + \sum_{\mathcal{P}} \frac{1}{S(\mathcal{P})} \int [\prod D(\mathcal{L}) z^*(\mathcal{L})] [\prod b^*]_{\mathcal{P}}. \quad (\text{III.28})$$

In this expression, the term next to the ring pressure  $\beta P_{\text{R}}$  is the contribution of the prototype graph made with a single black loop, and the sum in the second line is carried over all prototype graphs  $\mathcal{P}$  made with  $N \geq 2$  black points. Thanks to translation invariance, once the integration over  $(N - 1)$  black loops have been performed in  $\mathcal{P}$ , the result no longer depends on the position of the remaining black loop. The  $1/\Lambda$  factor in the definition (II.5) of the pressure of the finite

system can then be absorbed in the TL by restricting the spatial integrations to the positions of  $(N - 1)$  loops in all graphs  $\mathcal{P}$  and keeping one of them fixed. For instance, in the contribution of the simplest graph with one black loop  $\mathcal{L}$ , it is understood that the integration  $D(\mathcal{L})$  is carried out over all the internal degrees of freedom of loop  $\mathcal{L}$  except its position. The prototype diagrams  $\mathcal{P}$  have the same topological structure as the genuine Mayer diagrams. They are simply connected and may contain articulation loops. Two loops can be connected by at most one bond  $b^*$  and each loop carries a statistical weight  $z^*$ . There exist three possible bonds  $b^* = b_D, b_{AM}, b_{AME}$  and three possible activities  $z^* = z, z_R, z_{RT}$ . Their occurrence is determined by the specific rules listed below which avoid double counting. The sum in diagrammatic series (III.28) is carried out over all unlabeled prototype graphs with different topological structures: the contribution of a given  $\mathcal{P}$  is calculated by labeling the  $N$  field loops once for all. The symmetry factors  $S(\mathcal{P})$  are defined as usual, namely they are given by the number of permutations of those labeled field loops which leave the product of bonds and weights unchanged.

The activity  $z^*(\mathcal{L}_i)$  of a given field loop  $\mathcal{L}_i$  depends on the number of loops which are connected to it and on the corresponding bonds  $b^*$ , as follows :

- Ending field loop  $\mathcal{L}_i$  connected to a single loop  $\mathcal{L}_j$ , which can be either a field or a root loop

$$\begin{aligned} z^*(\mathcal{L}_i) &= z(\mathcal{L}_i) \quad \text{for } b^*(\mathcal{L}_i, \mathcal{L}_j) = b_D(\mathcal{L}_i, \mathcal{L}_j), b_{AME}(\mathcal{L}_i, \mathcal{L}_j) \\ z^*(\mathcal{L}_i) &= z_{RT}(\mathcal{L}_i) \quad \text{for } b^*(\mathcal{L}_i, \mathcal{L}_j) = b_D(\mathcal{L}_i, \mathcal{L}_j), b_{AM}(\mathcal{L}_i, \mathcal{L}_j) \end{aligned} \quad (\text{III.29})$$

- Intermediate field loop  $\mathcal{L}_i$  in a convolution of two bonds  $b^*(\mathcal{L}_k, \mathcal{L}_i)$  and  $b^*(\mathcal{L}_i, \mathcal{L}_l)$  which connect  $\mathcal{L}_i$  to two loops  $\mathcal{L}_k$  and  $\mathcal{L}_l$ , which can be either field or root loops

$$\begin{aligned} z^*(\mathcal{L}_i) &= z_{RT}(\mathcal{L}_i) \quad \text{for } b^*(\mathcal{L}_k, \mathcal{L}_i) = b_D(\mathcal{L}_k, \mathcal{L}_i), b^*(\mathcal{L}_i, \mathcal{L}_l) = b_D(\mathcal{L}_i, \mathcal{L}_l) \\ z^*(\mathcal{L}_i) &= z_R(\mathcal{L}_i) \quad \text{for } (b^*(\mathcal{L}_k, \mathcal{L}_i), b^*(\mathcal{L}_i, \mathcal{L}_l)) \neq (b_D(\mathcal{L}_k, \mathcal{L}_i), b_D(\mathcal{L}_i, \mathcal{L}_l)) \end{aligned} \quad (\text{III.30})$$

- Field loop  $\mathcal{L}_i$  connected at least to three loops which can be either field or root loops

$$z^*(\mathcal{L}_i) = z_R(\mathcal{L}_i) \quad \text{for all } b^* \quad (\text{III.31})$$

The central quantity is the Debye bond  $b_D(\mathcal{L}_i, \mathcal{L}_j) = -\beta e_{\alpha_i} e_{\alpha_j} \phi(\mathcal{L}_i, \mathcal{L}_j)$ . As shown in Ref. [12],  $\phi$  decays as  $1/r^3$  at large distances  $r$  between two loops. Thus bonds  $b_{AM}$  and  $b_{AME}$  decay respectively as  $1/r^6$  and  $1/r^9$ , and they are integrable. The bond  $b_D$  decays as  $\phi$  itself, *i.e.* as  $1/r^3$ , which is at the border line for integrability. Accordingly, the graphs with ending loops connected to the rest of the diagram by bonds  $b_D$  have to be dealt with some care. In fact, since the corresponding weights of the ending loops,  $z$  or  $z_{RT}$  are even functions of the loop shapes  $\mathcal{X}(s)$ , if we proceed first to functional integrations over such shapes, then the  $1/r^3$ -algebraic tails vanish since their amplitudes are odd functions of  $\mathcal{X}(s)$  [12]. Within this recipe, every prototype graph provides a finite contribution, as expected.

### C. Relation to the activity expansion of the species densities

The screened activity expansion of the loop density can be readily inferred from the corresponding expansion (III.28) of the pressure by using

$$\rho(\mathcal{L}_a) = z(\mathcal{L}_a) \frac{\delta \beta P}{\delta z(\mathcal{L}_a)}. \quad (\text{III.32})$$

The functional derivative of each prototype diagram  $\mathcal{P}$  is calculated by either whitening a black loop  $\mathcal{L}$  with weight  $z(\mathcal{L})$  into the root loop  $\mathcal{L}_a$  with weight  $z(\mathcal{L}_a)$  or by taking the functional derivative with respect to  $z(\mathcal{L}_a)$  of  $\beta P_R$  and  $b_D(\mathcal{L}_i, \mathcal{L}_j)$ , namely

$$z(\mathcal{L}_a) \frac{\delta \beta P_R}{\delta z(\mathcal{L}_a)} = z(\mathcal{L}_a) I_R(\mathcal{L}_a) \quad (\text{III.33})$$

and

$$z(\mathcal{L}_a) \frac{\delta b_D(\mathcal{L}_i, \mathcal{L}_j)}{\delta z(\mathcal{L}_a)} = z(\mathcal{L}_a) b_D(\mathcal{L}_i, \mathcal{L}_a) b_D(\mathcal{L}_a, \mathcal{L}_j). \quad (\text{III.34})$$

Note that the functional derivatives of the dressed activities and of the other bonds, which can be all expressed in terms of  $b_D$ , are then obtained by using Eqn. (III.34). This calculation provides

$$\rho(\mathcal{L}_a) = z_R(\mathcal{L}_a) \sum_{\mathcal{P}_a} \frac{1}{S(\mathcal{P}_a)} \int \left[ \prod D(\mathcal{L}) z^*(\mathcal{L}) \right] \left[ \prod b^* \right]_{\mathcal{P}_a}. \quad (\text{III.35})$$

which can be also obtained by a direct Abe-Meeron summation of the Mayer diagrammatic series for the loop density [11]. The insertion of these series into the



identity

$$\rho_{\alpha_a} = \sum_{q_a=1}^{\infty} \int D_q(\boldsymbol{x}_a) \rho(\mathcal{L}_a). \quad (\text{III.36})$$

leads to required activity expansion of the species density.

The prototype diagrams  $\mathcal{P}_a$  have the same topological structure as the genuine Mayer diagrams for the loop density. They are built with the root (white) loop  $\mathcal{L}_a$  and  $N$  black loops  $\mathcal{L}$  ( $N=0,1,\dots$ ), simply connected and may contain articulation loops. Two loops can be connected by at most one bond  $b^*$  and each black loop carries a statistical weight  $z^*$ . As for the graphs  $\mathcal{P}$  in the series (III.28), there are again three possible bonds  $b^* = b_D, b_{AM}, b_{AME}$  and three possible activities  $z^* = z, z_R, z_{RT}$ , with the same occurrence rules. The sum  $\sum_{\mathcal{P}_a} \dots$  is carried out over all unlabeled prototype graphs with different topological structures. The symmetry factors  $S(\mathcal{P}_a)$  are defined as usual, like  $S(\mathcal{P})$ .

#### D. The pseudo-neutrality condition

Let us consider a given graph  $\mathcal{P}$  in the series (III.28), and the Debye dressed graph  $\mathcal{P}_{DD}$  obtained by adding a black loop  $\mathcal{L}$  with weight  $z(\mathcal{L})$  connected to  $\mathcal{P}$  via a single bond  $b_D(\mathcal{L}, \mathcal{L}')$  where  $\mathcal{L}'$  is a black loop inside  $\mathcal{P}$ . In the low activity limit, the potential  $\phi$  reduces to its classical Debye counterpart [12], so

$$b_D(\mathcal{L}, \mathcal{L}') \sim -\beta q_{\alpha} e_{\alpha} q_{\alpha'} e_{\alpha'} \frac{\exp(-\kappa_z |\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|} \quad (\text{III.37})$$

with

$$\kappa_z^2 = \kappa^2(0,0) \sim 4\pi\beta \sum_{\gamma} e_{\gamma}^2 z_{\gamma}. \quad (\text{III.38})$$

At leading order in the small activities, the contribution of the graph  $\mathcal{P}_{DD}$  is obtained by keeping only the loop  $\mathcal{L}$  made with a single particle, i.e.  $q_{\alpha} = 1$ , while the bond  $b_D(\mathcal{L}, \mathcal{L}')$  is replaced by its classical Debye expression (III.37). The corresponding leading contribution of  $\mathcal{P}_{DD}$  then reduces to that of graph  $\mathcal{P}$  multiplied by

$$\begin{aligned} \int D(\mathcal{L}) z(\mathcal{L}) b_D(\mathcal{L}, \mathcal{L}') &\sim -\beta q_{\alpha'} e_{\alpha'} \sum_{\alpha} e_{\alpha} z_{\alpha} \int d\mathbf{x} \frac{\exp(-\kappa_z |\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|} \\ &= -\frac{4\pi\beta q_{\alpha'} e_{\alpha'}}{\kappa_z^2} \sum_{\alpha} e_{\alpha} z_{\alpha}. \end{aligned} \quad (\text{III.39})$$

According to the low-activity estimation (III.39), the contribution of  $\mathcal{P}_{\text{DD}}$  has the same order as that of  $\mathcal{P}$  for arbitrary sets  $\{z_\alpha\}$  of particle activities. In other words, in order to compute the pressure at a given order for such sets, one would have to keep an infinite number of graphs in the series (III.28). However, it turns out that the remarkable property of the function  $P(T; \{z_\alpha\})$  exposed in Section II allows us to circumvent this drawback. Indeed, since  $P(T; \{z_\alpha\})$  only depends on  $(\mathcal{S} - 1)$  independent combinations of the activities  $y_1 = K_1(\{z_\alpha\}), y_2 = K_2(\{z_\alpha\}), \dots, y_{\mathcal{S}-1} = K_{\mathcal{S}-1}(\{z_\alpha\})$ , the function  $P(T; \{y_i\})$  can be determined, without any loss of generality, by fixing an arbitrary relation between the  $z_\alpha$ 's. Hence, it is particularly useful to fix once for all the so-called pseudo-neutrality condition

$$\sum_{\alpha} e_{\alpha} z_{\alpha} = 0 . \quad (\text{III.40})$$

Then, the leading contribution of  $\mathcal{P}_{\text{DD}}$  has an higher order than that of  $\mathcal{P}$ . At a given order in small activities, only a finite number of graphs  $\mathcal{P}$  now have to be kept in the series (III.28). It then remains to invert the  $\mathcal{S}$  independent relations

$$\begin{aligned} y_1 = K_1(\{z_\alpha\}) ; y_2 = K_2(\{z_\alpha\}) ; \dots ; y_{\mathcal{S}-1} = K_{\mathcal{S}-1}(\{z_\alpha\}) \\ \sum_{\alpha} e_{\alpha} z_{\alpha} = 0 , \end{aligned} \quad (\text{III.41})$$

in order to obtain the corresponding small- $y$  expansion of the pressure  $P(T; \{y_i\})$ . Such simplification is crucial for further calculations of particle densities which do satisfy overall neutrality as exposed in the next Section IV.

#### IV. DERIVATION OF THE PARTICLE DENSITIES CONSISTENT WITH THE LOCAL CHARGE NEUTRALITY

Once the small- $y$  expansion of  $P(T; \{y_i\})$  has been obtained, the corresponding expansion of the particle densities is readily calculated via the identity (II.21). The corresponding set  $\{\rho_\alpha\}$  of particle densities do automatically satisfy the local charge neutrality as shown in Section II. This is illustrated here for the two-component plasma by considering the first two terms of activity or density expansions. We also briefly introduce the case of a three component plasma.

### A. Two-component plasma

There is a single vector  $\mathbf{e}_\perp^{(1)} = \mathbf{e}_\perp$  with components  $(-e_2, e_1)$ . The powers  $(\omega_1, \omega_2)$  in the function (II.19) which defines the effective activity

$$y = z_1^{\omega_1} z_2^{\omega_2} \quad (\text{IV.1})$$

are

$$\omega_1 = -\frac{e_2}{e_1 - e_2} \quad \text{and} \quad \omega_2 = \frac{e_1}{e_1 - e_2} . \quad (\text{IV.2})$$

The expression (II.21) for each species density becomes

$$\rho_1 = \omega_1 y \frac{\partial \beta P}{\partial y}(T; y) \quad \text{and} \quad \rho_2 = \omega_2 y \frac{\partial \beta P}{\partial y}(T; y) . \quad (\text{IV.3})$$

Note that the charge density  $(e_1 \rho_1 + e_2 \rho_2)$  indeed vanishes, while the total particle density is

$$\rho = \rho_1 + \rho_2 = y \frac{\partial \beta P}{\partial y}(T; y) . \quad (\text{IV.4})$$

Within the pseudo-neutrality condition (III.40), the expression of both  $z_1$  and  $z_2$  in terms of  $y$  is readily calculated as

$$z_1 = (\omega_1/\omega_2)^{\omega_2} y \quad \text{and} \quad z_2 = (\omega_2/\omega_1)^{\omega_1} y \quad (\text{IV.5})$$

The small-activity expansion of the pressure inferred from the screened Mayer series (III.28) then reads

$$\beta P = z_1 + z_2 + \frac{\kappa_z^3}{12\pi} + \dots \quad (\text{IV.6})$$

with  $\kappa_z = [4\pi\beta(e_1^2 z_1 + e_2^2 z_2)]^{1/2}$ , while the terms left over are  $o(z^{3/2})$ . Accordingly the small- $y$  expansion of the function  $\beta P(T, y)$  is

$$\beta P = \omega_1^{-\omega_1} \omega_2^{-\omega_2} y + \frac{\kappa_y^3}{12\pi} + o(y^{3/2}) \quad (\text{IV.7})$$

with  $\kappa_y = [4\pi\beta(e_1^2 (\omega_1/\omega_2)^{\omega_2} + e_2^2 (\omega_2/\omega_1)^{\omega_1}) y]^{1/2}$ . Inserting the expansion (IV.7) into the identities (IV.11), we find

$$\rho_1 = \frac{\omega_1^{\omega_2}}{\omega_2^{\omega_2}} y + \frac{\omega_1}{8\pi} \kappa_y^3 + o(y^{3/2}) \quad \text{and} \quad \rho_2 = \frac{\omega_2^{\omega_1}}{\omega_1^{\omega_1}} y + \frac{\omega_2}{8\pi} \kappa_y^3 + o(y^{3/2}) , \quad (\text{IV.8})$$

which can be recast in terms of the activities  $z_1$  and  $z_2$  as

$$\rho_1 = z_1 + \frac{\omega_1}{8\pi} \kappa_z^3 + o(z^{3/2}) \quad \text{and} \quad \rho_2 = z_2 + \frac{\omega_2}{8\pi} \kappa_z^3 + o(z^{3/2}) . \quad (\text{IV.9})$$

On another hand, the particle densities can be also calculated by inserting the screened activity expansion (III.35) of the loop density into the identity (III.36). Within the pseudo-neutrality condition (III.40), the first two terms of order  $O(z)$  and  $O(z^{3/2})$  are obtained by keeping two diagrams: (i) the diagram made with a single root (white) loop  $\mathcal{L}_a$  (ii) the diagram made with loop  $\mathcal{L}_a$  connected to a single black loop by a Debye bond  $b_D$ . This allows us to exactly recover the expressions (IV.9), as it should.

We stress that a direct calculation of  $\rho_1$  and  $\rho_2$  by taking the partial derivatives with respect to  $z_1$  and  $z_2$  respectively of the expression (IV.6), as if  $z_1$  and  $z_2$  were independent variables, would lead to wrong expressions, which in particular do not satisfy the local charge neutrality. In particular, if the leading terms of order  $O(z)$  would coincide with the ideal contributions in the correct expansions (IV.9), the terms of order  $o(z^{3/2})$  would differ of their exact counterparts for a charge-asymmetric system with  $\omega_1 \neq \omega_2$ . If we pursue the expansions beyond the terms  $O(z^{3/2})$ , the direct calculation of the densities would be wrong at sufficiently high orders, even for charge-symmetric systems. This sheds light on the importance of expressing the pressure in terms of the new activity  $y$ , in order to derive expansions consistent with the local charge neutrality.

The hydrogen plasma is an example of charge-symmetric two-component plasma, made with protons ( $e_1 = e$ ) and electrons  $e_2 = -e$ . Then, the powers  $\omega_1$  and  $\omega_2$  are identical,  $\omega_1 = \omega_2 = 1/2$ , so we find  $y = (z_1 z_2)^{1/2}$ . The helium plasma is an example of charge-asymmetric two-component plasma, made with  $\alpha$  nuclei ( $e_1 = 2e$ ) and electrons  $e_2 = -e$ . The corresponding powers are  $\omega_1 = 1/3$  and  $\omega_2 = 2/3$ , while the effective activity reduces to  $y = z_1^{1/3} z_2^{2/3}$ .

## B. Three component plasmas

For three component plasmas, the two effective activities  $y_1$  and  $y_2$  are defined by choosing two independent vectors  $\{\mathbf{e}_\perp^{(1)}, \mathbf{e}_\perp^{(2)}\}$  orthogonal to  $\mathbf{e}$ . For fixing ideas, let us consider the case of the hydrogen-helium mixture made with protons ( $e_1 = e$ ),  $\alpha$ -nuclei ( $e_2 = 2e$ ) and electrons ( $e_3 = -e$ ). Since the components of  $\mathbf{e}$  are  $e(1, 2, -1)$ ,

we can choose  $\mathbf{e}_\perp^{(1)} = e(1, 0, 1)$  and  $\mathbf{e}_\perp^{(2)} = e(0, 1, 2)$ . The corresponding effective activities are

$$y_1 = z_1^{1/2} z_3^{1/2} \quad \text{and} \quad y_2 = z_2^{1/3} z_3^{2/3}. \quad (\text{IV.10})$$

The identity (II.21) provides the species densities

$$\begin{aligned} \rho_1 &= \frac{y_1}{2} \frac{\partial \beta P}{\partial y_1}(T; y_1, y_2) \\ \rho_2 &= \frac{y_2}{3} \frac{\partial \beta P}{\partial y_2}(T; y_1, y_2) \\ \rho_3 &= \frac{y_1}{2} \frac{\partial \beta P}{\partial y_1}(T; y_1, y_2) + \frac{2y_2}{3} \frac{\partial \beta P}{\partial y_2}(T; y_1, y_2). \end{aligned} \quad (\text{IV.11})$$

The local charge neutrality,  $e\rho_1 + 2e\rho_2 - e\rho_3 = 0$ , is satisfied, while the total particle density reads

$$\rho = \rho_1 + \rho_2 + \rho_3 = y_1 \frac{\partial \beta P}{\partial y_1}(T; y_1, y_2) + y_2 \frac{\partial \beta P}{\partial y_2}(T; y_1, y_2). \quad (\text{IV.12})$$

Like in the two-component case, we can compute the small- $z$  expansion of the particle densities by using in the identities (IV.11) the small- $y$  expansion of the pressure inferred from the screened activity series (III.28). Again, and unsurprisingly, we check explicitly that the lowest-order terms in this small- $z$  expansion are exactly retrieved by using the screened activity series (III.35) for the loop density combined with the pseudo-neutrality condition (III.40).

## V. CONCLUDING COMMENTS

The various tools presented here should be quite useful for improving the equation of state of various quantum plasma at moderately low densities  $\rho$ . If the well-known virial expansions up to order  $\rho^{5/2}$  provide an accurate description of the almost fully ionized regime observed at sufficiently low densities, recombination processes into entities made with three or more particles may become important when the density increases. In such situations, where the density still remains relatively small, the corresponding contributions can be easily identified in the screened activity series for the pressure in terms of a few simple prototype graphs made with three or more loops. This defines a finite cluster function  $Z_\mathcal{E}$  for any entity (chemical species)  $\mathcal{E}$ .

The function  $Z_{\mathcal{E}}$  has to be expressed in terms of the effective activities  $\{y_i\}$ , in order to determine, consistently with charge neutrality, the corresponding contributions to the particle densities. Once all the relevant physical contributions have been calculated along similar lines, the expressions of the particle densities in terms of the effective activities are inverted. This provides the required equation of state in terms of particle densities, which correctly accounts, in a non-perturbative way, for the emergence of recombined entities.

The physical content of the above scheme is very close to that of the celebrated ACTEX expansion introduced by Rogers [13]. However, we stress that the cluster functions  $Z_{\mathcal{E}}$  are defined within systematic prescriptions which avoid double counting problems. Moreover they properly account for the collective screening effects which ensure their finiteness, without introducing ad-hoc regularisations as in the phenomenological Planck-Larkin partition functions. Note that the cluster functions  $Z_{\mathcal{E}}$  were first introduced within the screened activity series for the particle densities [11]. It was shown that their zero-density limit leads to a natural definition of the bare partition function of chemical species in the vacuum.

Eventually, let us mention two applications of the previous general scheme. First, for the hydrogen plasma, atoms H and molecules  $H_2$  successively emerge when the density increases starting from the very dilute regime where all protons and electrons are ionized. In order to describe the cross-over regimes between the ionized, atomic and molecular phases, one has to first determine properly the various cluster functions describing atoms H, ions  $H_2^+$ ,  $H^-$  and molecules  $H_2$  as functions of the effective activity  $y = (z_p z_e)^{1/2}$ . The accurate computation of the cluster functions involving more than two particles, *i.e.*  $Z_{H_2^+}$ ,  $Z_{H^-}$  and  $Z_{H_2}$  require the introduction of suitable quantum Monte Carlo techniques [14]. Within a suitable double zero-density and zero-temperature limit which defines a partially ionized atomic phase, exact asymptotic expansion beyond the familiar Saha theory [15] have been already derived [16].

For the hydrogen-helium mixture at low densities, the presence of helium atoms He, as well as ions like  $H^-$  or  $H_2^+$ , requires to consider prototype graphs made three loops. Once the corresponding cluster functions  $Z_{He}$ ,  $Z_{H^-}$  and  $Z_{H_2^+}$  have been

computed within the same quantum Monte Carlo techniques [14] as above, it remains to express them in terms of the effective activities  $(y_1, y_2)$  (IV.10) with  $z_1 = z_p$ ,  $z_2 = z_\alpha$  and  $z_3 = z_e$ . A partial account of the corresponding calculations along the Sun adiabat is given in Refs. [17, 18].

### Acknowledgements

Financial support from the CNRS (contract 081912) and from the Conseil régional de Franche-Comté (contract 362887) are gratefully acknowledged. The calculations were run on computers from the Institute UTINAM of the University de Franche-Comté, supported by the Région Franche-Comté and the Institut des Sciences de l'Univers (INSU).

- 
- [1] J. Ginibre, Some applications of functional integration in statistical mechanics, in *Statistical Mechanics and Quantum Field Theory*, edited by C. DeWitt and R. Stora (les Houches, Gordon and Breach, 1971)
  - [2] F. Cornu, Correlations in quantum plasmas: I. Resummations in Mayer-like diagrammatics, *Phys. Rev. E* **53**:4562 (1996)
  - [3] Ph.A. Martin, Quantum Mayer graphs: applications to Bose and Coulomb gases, *Acta Physica Polonica B* **34**:3629 (2003)
  - [4] A. Alastuey and A. Perez, Virial expansion of the equation of state of a quantum plasma, *Europhys. Lett.* **20**:19-24 (1992)
  - [5] A. Alastuey, V. Ballenegger and W. Ebeling, Comment on "Direct linear term in the equation of state of plasmas", *Phys. Rev. E* **92**:047101 (2015)
  - [6] W. Ebeling, *Ann. Phys. Leipzig* **19**:104 (1967)
  - [7] W.D. Kraeft, D. Kremp, W. Ebeling, and G. Ropke, *Quantum Statistics of Charged Particle Systems* (Plenum Press, New York, 1986)
  - [8] H.E. DeWitt, M. Schlanges, A.Y. Sakakura, W.D. Kraeft, Low density expansion of the equation of state for a quantum electron gas, *Phys. Lett. A*, **197**:326 (1995).
  - [9] L. S. Brown and L. G. Yaffe. Effective Field theory for highly ionized plasmas *Phys.*

*Rep.* **340**:1-164 (2001)

- [10] E.H. Lieb and J. Lebowitz, The constitution of matter: existence of thermodynamics for systems composed of electrons and nuclei, *Adv. Math.* **9**: 316-398 (1972)
- [11] A. Alastuey, V. Ballenegger, F. Cornu and Ph.A. Martin, Screened cluster expansions for partially ionized gases, *J. Stat. Phys.* **113**:455-503 (2003)
- [12] V. Ballenegger, Ph.A. Martin and A. Alastuey, Quantum Mayer graphs for Coulomb systems and the analog of the Debye potential, *J. Stat. Phys.* **108**:169-211 (2002)
- [13] F.J. Rogers, Statistical mechanics of Coulomb gases of arbitrary charge, *Phys. Rev. A* **10**:2441 (1974)
- [14] D. Wendland, V. Ballenegger, and A. Alastuey, Quantum partition functions of composite particles in a hydrogen-helium plasma via path integral Monte Carlo, *J. Chem. Phys.* **141**:184109 (2014)
- [15] M. Saha, *Philos. Mag.* **40**:472 (1920)
- [16] A. Alastuey, V. Ballenegger, F. Cornu and Ph.A. Martin, *J. Stat. Phys.* **113**:455-503 (2008)
- [17] D. Wendland, The equation of state of the Hydrogen-Helium mixture with application to the Sun, Theses, Ecole normale suprieure de Lyon ENS LYON, October 2015
- [18] V. Ballenegger, A. Alastuey and D. Wendland, The screened cluster equation of state for hydrogen-helium mixtures: Atomic, molecular, and ionic contributions from first principles, *Contr. Plasma Phys.* **58**:114-121 (2018)