Wigner-Kirkwood expansion for semi-infinite quantum fluids

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Abstract. For infinite (bulk) quantum fluids of particles interacting via pairwise sufficiently smooth interactions, the Wigner-Kirkwood formalism provides a semiclassical expansion of the Boltzmann density in configuration space in even powers of the thermal de Broglie wavelength λ. This result permits one to generate an analogous λ-expansion for the bulk free energy and many-body densities. The present paper brings a technically nontrivial generalization of the Wigner-Kirkwood technique to semi-infinite quantum fluids, constrained by a plane hard wall impenetrable to particles. In contrast to the bulk case, the resulting Boltzmann density involves also position-dependent terms which are non-analytic in λ. Under some condition, the analyticity in λ is restored by integrating the Boltzmann density over configuration space; however, in contrast to the bulk free energy, the semiclassical expansion of the surface part of the free energy (surface tension) contains odd powers of λ, too. Explicit expressions for the leading quantum corrections in the presence of the boundary are given for the one-body and two-body densities. As model systems for explicit calculations, we use Coulomb fluids, in particular the one-component plasma defined in the ν-dimensional (integer $\nu \geq 2$) space.

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1. Introduction

In this paper, we consider a quantum system of N identical particles $j = 1, 2, \ldots, N$ of mass m which position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ are confined to a region Λ of the ν-dimensional space R^ν. For the sake of brevity, we denote the νN-dimensional position vector in configuration space by $\vec{\mathbf{r}} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and the corresponding gradient by $\vec{\boldsymbol{\nabla}} = (\boldsymbol{\nabla}_1, \boldsymbol{\nabla}_2, \ldots, \boldsymbol{\nabla}_N)$. The Hamiltonian of the particles (in the absence of a magnetic field) is

$$H = \frac{1}{2m}\left(-\mathrm{i}\hbar\vec{\boldsymbol{\nabla}}\right)^2 + V(\vec{\mathbf{r}}), \tag{1.1}$$

where $\hbar$ is Planck's constant and the scalar potential $V(\vec{\mathbf{r}})$ includes pairwise particle interactions $\sum_{j<k} v(|\mathbf{r}_j - \mathbf{r}_k|)$ plus perhaps one-particle interactions $\sum_j u(\mathbf{r}_j)$ with some external potential $u(\mathbf{r})$. The equilibrium statistical mechanics of the particle system is studied in the canonical ensemble at the temperature T (or, alternatively, the inverse temperature $\beta = 1/k_\mathrm{B}T$ with k_B being Boltzmann's constant). In the classical regime, the Hamiltonian (1.1) is replaced by $H = \vec{\mathbf{p}}^2/(2m) + V(\vec{\mathbf{r}})$, where $\vec{\mathbf{p}} = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ is the vector in the classical momentum space. The integration of the Boltzmann density $\exp(-\beta H)$ over the momentum variables results in a trivial constant, so that the classical Boltzmann density in configuration $\vec{\mathbf{r}}$-space $\propto \exp[-\beta V(\vec{\mathbf{r}})]$. Quantum effects are related to the thermal de Broglie wavelength $\lambda = \hbar(\beta/m)^{1/2}$. A *nearly classical* regime of present interest is defined as being such that the dimensionless parameter λ/l (l being a typical microscopic length of the classical particle system) is sufficiently small.

For a nearly classical bulk system in an infinite ν-dimensional space $\Lambda = R^\nu$, the Boltzmann density in configuration space $\vec{\mathbf{r}}$ can be expanded in powers of λ^2 within the well-known Wigner-Kirkwood expansion [1, 2]. The coefficients of the λ^2-expansion of the partition function, which is given by the integration of the Boltzmann density over configuration space $\vec{\mathbf{r}}$, are expressible in terms of the classical averages of gradient operations applied to $V(\vec{\mathbf{r}})$ and of their products.

The applicability of the Wigner-Kirkwood expansion scheme depends on the form of the interaction potential $v(r)$: divergence of an expansion coefficient indicates a loss of analyticity of the corresponding quantum correction. For the 3D exponential, screened Coulomb and square barrier potentials, the leading expansion term was found to have the non-analytic form $(\lambda^2)^{1/2}$ [3]. In the case of an inverse-power-law repulsive potential $v(r) = v_0(a/r)^n$ with the exponent n from the range $1 < n < \infty$, the Wigner-Kirkwood expansion turns out to be analytic in λ^2 [3]. In the hard-core limit $n \to \infty$, the Wigner-Kirkwood expansion fails and one has once more the nonanalyticity of type $(\lambda^2)^{1/2}$, as was shown in numerous analytic studies (see, e.g., [4, 5, 6, 7]).

Much of effort has been devoted to the calculation of quantum corrections for 3D Coulomb fluids of $\pm e$ charges, in the high-temperature regime described adequately by the classical Debye-Hückel theory. The bulk equation of state exhibits quantum corrections non-analytic in λ^2 [8]. As concerns the two-body density, its leading quantum correction exhibits at large distances an inverse-power-law decay in contrast with the classical Debye-Hückel exponential screening (see the review [9]).

To our knowledge, there does not exist in the literature a boundary version of the Wigner-Kirkwood expansion applicable to fluids in domains Λ surrounded by hard walls impenetrable to particles (or, equivalently, there is an infinite external potential outside the domain Λ). Surface properties of quantum particle systems have been investigated only in the presence of some smooth confining external-potential barriers (see, e.g., [10, 11]). The sole exception is represented by the study of density profiles in 3D quantum Coulomb fluids near a plain hard wall, within the high-temperature Debye-Hückel limit [12].

The present paper brings a technically nontrivial generalization of the Wigner-Kirkwood technique to semi-infinite quantum fluids, constrained by a plane hard wall. In contrast to the bulk case, the resulting Boltzmann density involves also position-dependent terms which are non-analytic in λ. Under some condition about the classical density profile, the analyticity in λ is restored by integrating the Boltzmann density over configuration space; however, in contrast to the bulk free energy, the semiclassical expansion of the surface part of the free energy (surface tension) contains odd powers of λ, too. Explicit expressions for the leading quantum corrections in the presence of the boundary are given for one-body and two-body densities.

As a model system for explicit calculations, we shall use a special kind of Coulomb fluid, namely the one-component plasma (jellium) made of mobile pointlike charges e neutralized by a uniform oppositely charged fixed background, in the ν-dimensional space (because of some physical nontrivialities in 1D, we shall restrict ourselves to dimensions $\nu \geq 2$). In the infinite space $\Lambda = R^\nu$, or when the hard walls surrounding the confining domain Λ do not induce image charges (plain hard walls), the translationally invariant Coulomb interaction potential of two e-charges $v(r)$ with $r = |\mathbf{r}_j - \mathbf{r}_k|$ is defined as the solution of the Poisson equation $\boldsymbol{\nabla}^2 v = -s_\nu e^2 \delta(\mathbf{r})$, where $s_\nu = 2\pi^{\nu/2}/\Gamma(\nu/2)$ (Γ stands for the Gamma function) is the surface area of the ν-dimensional unit sphere. The resulting Coulomb interaction potential is logarithmic in $\nu = 2$ dimensions and of type $e^2 r^{2-\nu}/(\nu-2)$ in $\nu \geq 3$ dimensions. The present definition of the Coulomb potential maintains many generic properties of "real" 3D Coulomb systems, like screening and the corresponding sum rules (see the review [13]). The total potential $V(\vec{\mathbf{r}})$ then satisfies for each of the particle coordinates the differential equation

$$\boldsymbol{\nabla}_j^2 V(\vec{\mathbf{r}}) = -s_\nu e^2 \sum_{\substack{k=1 \\ (k\neq j)}}^{N} \delta(\mathbf{r}_j - \mathbf{r}_k) + s_\nu e^2 n, \quad j = 1, 2, \ldots, N. \tag{1.2}$$

Here, the second term on the rhs comes from the particle-background interaction and $n = N/|\Lambda|$ is the mean number density of the mobile charges; the background-background interaction constant contributes to the partition function.

The paper is organized as follows. In section 2, the method of the bulk Wigner-Kirkwood expansion is briefly reviewed in a format which can be relatively simply extended to the boundary case. The following sections are devoted to semi-infinite quantum systems constrained by a plane hard wall. In section 3, we propose a method for constructing the expansion of the Boltzmann density in configuration $\vec{\mathbf{r}}$-space. This expansion is subsequently used in section 4 for the generation of the expansion for statistical quantities, such as the partition function and the corresponding surface part of the free energy, one-body and two-body densities. Explicit calculations for Coulomb models with known classical statistical quantities are presented in section 5. A few concluding remarks are given in section 6.

2. Wigner-Kirkwood expansion in infinite space

Let the particle system be in the infinite space $\Lambda = R^\nu$. In this so-called "bulk" regime, its equilibrium quantities in the nearly classical regime can be expanded in powers of $\hbar^2$ within the standard Wigner-Kirkwood expansion [1, 2] which *neglects* fermion or boson exchange effects between quantum particles. In this section, we review shortly the derivation of this expansion by the Laplace transform method [4, 14] which is suitable for our next purposes.

2.1. Boltzmann density

The Boltzmann density B_β in configuration space $\vec{\mathbf{r}}$ can be formally written in the basis of plane waves as a νN-dimensional integral defined in an infinite domain R^ν:

$$B_\beta(\vec{\mathbf{r}}) \equiv \langle \vec{\mathbf{r}} | \mathrm{e}^{-\beta H} | \vec{\mathbf{r}} \rangle = \int \frac{\mathrm{d}\vec{\mathbf{p}}}{(2\pi\hbar)^{\nu N}} \mathrm{e}^{-(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}} \mathrm{e}^{-\beta H} \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}}, \tag{2.1}$$

where $\vec{\mathbf{p}} = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ is the νN-dimensional momentum vector. Instead of considering $\mathrm{e}^{-\beta H}$ we take the Laplace transform of this operator with respect to the inverse temperature β,

$$\frac{1}{H+z} = \int_0^\infty \mathrm{d}\beta \, \mathrm{e}^{-\beta z} \mathrm{e}^{-\beta H}, \tag{2.2}$$

and concentrate on

$$B_z(\vec{\mathbf{r}}) \equiv \int_0^\infty \mathrm{d}\beta \, \mathrm{e}^{-\beta z} B_\beta(\vec{\mathbf{r}}) = \int \frac{\mathrm{d}\vec{\mathbf{p}}}{(2\pi\hbar)^{\nu N}} \mathrm{e}^{-(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}} \frac{1}{H+z} \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}}. \tag{2.3}$$

Let us first rewrite $H+z$ as

$$H + z = D + \mathcal{O}, \tag{2.4}$$

where D is a c-number

$$D = \frac{1}{2m}\vec{\mathbf{p}}^2 + V(\vec{\mathbf{r}}) + z \tag{2.5}$$

and $\mathcal{O}$ an operator

$$\mathcal{O} = \frac{1}{2m}\left(-\mathrm{i}\hbar\vec{\boldsymbol{\nabla}}\right)^2 - \frac{1}{2m}\vec{\mathbf{p}}^2, \tag{2.6}$$

and then expand

$$\frac{1}{H+z} = \frac{1}{D} - \frac{1}{D}\mathcal{O}\frac{1}{D} + \frac{1}{D}\mathcal{O}\frac{1}{D}\mathcal{O}\frac{1}{D} - \cdots. \tag{2.7}$$

It can be verified that for any function $f(\vec{\mathbf{r}})$ the operator $\mathcal{O}$ acts as follows

$$\mathcal{O}\left[f(\vec{\mathbf{r}})\mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}}\right] = -\mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}}\left[\frac{\mathrm{i}\hbar}{m}\vec{\mathbf{p}}\cdot\vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2\right] f(\vec{\mathbf{r}}). \tag{2.8}$$

One thus finds that

$$\mathrm{e}^{-(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}}\,\frac{1}{H+z}\,\mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}} = \frac{1}{D}\sum_{n=0}^{\infty}\left\{\left[\frac{\mathrm{i}\hbar}{m}\vec{\mathbf{p}}\cdot\vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2\right]\frac{1}{D}\right\}^n. \tag{2.9}$$

This formula enables us to express the Laplace transform of the Boltzmann density (2.3) as the series

$$B_z(\vec{\mathbf{r}}) = \sum_{n=0}^{\infty} B_z^{(n)}(\vec{\mathbf{r}}), \tag{2.10a}$$

where the term of order n

$$B_z^{(n)}(\vec{\mathbf{r}}) = \int \frac{\mathrm{d}\vec{\mathbf{p}}}{(2\pi\hbar)^{\nu N}}\frac{1}{D}\left\{\left[\frac{\mathrm{i}\hbar}{m}\vec{\mathbf{p}}\cdot\vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2\right]\frac{1}{D}\right\}^n \tag{2.10b}$$

is a polynomial in $\hbar$ containing powers in the range from $\hbar^n$ up to $\hbar^{2n}$. This means that the truncation of the series (2.10a) at some given order n provides all $\hbar$-terms up to order $\hbar^n$ (or, equivalently, all λ-terms up to order λ^n). By carrying out the differentiations in (2.10b), taking subsequently the inverse Laplace-transforms using the formula

$$\begin{aligned}\frac{1}{D^j} &= \frac{(-1)^{j-1}}{(j-1)!}\frac{\partial^{j-1}}{\partial z^{j-1}}\frac{1}{z+\vec{\mathbf{p}}^2/(2m)+V(\vec{\mathbf{r}})}\\ &= \int_0^{\infty}\mathrm{d}\beta\,\mathrm{e}^{-\beta z}\frac{1}{(j-1)!}\beta^{j-1}\mathrm{e}^{-\beta[\vec{\mathbf{p}}^2/(2m)+V(\vec{\mathbf{r}})]}\end{aligned} \tag{2.11}$$

($j = 1, 2, \ldots$), and finally integrating on the momentum variables $\vec{\mathbf{p}}$, the Boltzmann density in configuration space (2.1) is obtained as the series

$$\langle\vec{\mathbf{r}}|\mathrm{e}^{-\beta H}|\vec{\mathbf{r}}\rangle = \sum_{n=0}^{\infty} B_\beta^{(n)}(\vec{\mathbf{r}}), \tag{2.12}$$

where

$$B_\beta^{(0)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}, \tag{2.13a}$$

$$B_\beta^{(1)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}\,\lambda^2\left[-\frac{\beta}{4}\vec{\boldsymbol{\nabla}}^2 V + \frac{\beta^2}{6}\left(\vec{\boldsymbol{\nabla}}V\right)^2\right], \tag{2.13b}$$

$$\begin{aligned}B_\beta^{(2)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}&\left\{\lambda^2\left[\frac{\beta}{6}\vec{\boldsymbol{\nabla}}^2 V - \frac{\beta^2}{8}\left(\vec{\boldsymbol{\nabla}}V\right)^2\right] + \lambda^4\left[-\frac{\beta}{24}\left(\vec{\boldsymbol{\nabla}}^2\right)^2 V\right.\right.\\ &+\frac{\beta^2}{16}\vec{\boldsymbol{\nabla}}V\cdot\vec{\boldsymbol{\nabla}}\left(\vec{\boldsymbol{\nabla}}^2 V\right) + \frac{\beta^2}{48}\vec{\boldsymbol{\nabla}}^2\left(\vec{\boldsymbol{\nabla}}V\right)^2 + \frac{\beta^2}{32}\left(\vec{\boldsymbol{\nabla}}^2 V\right)^2\\ &\left.\left.-\frac{\beta^3}{30}\vec{\boldsymbol{\nabla}}V\cdot\vec{\boldsymbol{\nabla}}\left(\vec{\boldsymbol{\nabla}}V\right)^2 - \frac{\beta^3}{24}\left(\vec{\boldsymbol{\nabla}}V\right)^2\vec{\boldsymbol{\nabla}}^2 V + \frac{\beta^4}{72}\left(\vec{\boldsymbol{\nabla}}V\right)^4\right]\right\},\end{aligned} \tag{2.13c}$$

etc. We conclude that the quantum Boltzmann density in configuration space is given, to order λ^2, by

$$\langle\vec{\mathbf{r}}|\mathrm{e}^{-\beta H}|\vec{\mathbf{r}}\rangle = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}\left\{1 + \lambda^2\left[-\frac{\beta}{12}\vec{\boldsymbol{\nabla}}^2 V + \frac{\beta^2}{24}\left(\vec{\boldsymbol{\nabla}}V\right)^2\right] + O(\lambda^4)\right\}$$

$$= \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}} \left\{ \mathrm{e}^{-\beta V} \left[1 - \frac{\lambda^2 \beta}{24} \vec{\nabla}^2 V \right] + \frac{\lambda^2}{24} \vec{\nabla}^2 \mathrm{e}^{-\beta V} + O(\lambda^4) \right\}. \tag{2.14}$$

When integrated over the coordinates of particle j, the corresponding term in $\sum_{j=1}^{N} \boldsymbol{\nabla}_j^2 \exp(-\beta V)$ gives no volume contribution. Notice that odd powers of λ do not appear in the Wigner-Kirkwood expansion, so that the bulk Boltzmann factor is invariant with respect to the transformation $\mathrm{i}\hbar \to -\mathrm{i}\hbar$. This is due to the fact that the integration of terms with odd powers of momentum components over the whole corresponding axis is 0.

2.2. Statistical quantities

According to the standard formalism of statistical quantum mechanics, the partition function of the N-particle fluid (with ignored exchange effects) is given by the integration of the Boltzmann density over configuration space:

$$Z_{\mathrm{qu}} = \frac{1}{N!} \int_{\Lambda} \mathrm{d}\vec{\mathbf{r}} \left\langle \vec{\mathbf{r}} | \mathrm{e}^{-\beta H} | \vec{\mathbf{r}} \right\rangle. \tag{2.15}$$

For expressing macroscopic physical quantities, one defines the quantum average of a function $f(\vec{\mathbf{r}})$ as follows

$$\langle f \rangle_{\mathrm{qu}} = \frac{1}{Z_{\mathrm{qu}}} \frac{1}{N!} \int_{\Lambda} \mathrm{d}\vec{\mathbf{r}} \left\langle \vec{\mathbf{r}} | \mathrm{e}^{-\beta H} | \vec{\mathbf{r}} \right\rangle f(\vec{\mathbf{r}}). \tag{2.16}$$

At the one-particle level, one introduces the particle density

$$n_{\mathrm{qu}}(\mathbf{r}) = \left\langle \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle_{\mathrm{qu}}, \tag{2.17}$$

At the two-particle level, the two-body density is given by

$$n_{\mathrm{qu}}^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{\substack{j,k=1 \\ (j \neq k)}}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r}' - \mathbf{r}_k) \right\rangle_{\mathrm{qu}}. \tag{2.18}$$

It will be useful to consider also the truncated two-body density

$$n_{\mathrm{qu}}^{(2)\mathrm{T}}(\mathbf{r}, \mathbf{r}') = n_{\mathrm{qu}}^{(2)}(\mathbf{r}, \mathbf{r}') - n_{\mathrm{qu}}(\mathbf{r}) n_{\mathrm{qu}}(\mathbf{r}') \tag{2.19}$$

vanishing at asymptotically large distances $|\mathbf{r} - \mathbf{r}'| \to \infty$, the pair distribution function $g_{\mathrm{qu}}(\mathbf{r}, \mathbf{r}') = n_{\mathrm{qu}}^{(2)}(\mathbf{r}, \mathbf{r}') / [n_{\mathrm{qu}}(\mathbf{r}) n_{\mathrm{qu}}(\mathbf{r}')]$ and the pair correlation function $h_{\mathrm{qu}}(\mathbf{r}, \mathbf{r}') = g_{\mathrm{qu}}(\mathbf{r}, \mathbf{r}') - 1$. The classical partition function and the classical average of a function $f(\vec{\mathbf{r}})$ are defined as follows

$$Z = \frac{1}{N!} \int_{\Lambda} \frac{\mathrm{d}\vec{\mathbf{r}}}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V(\vec{\mathbf{r}})}, \tag{2.20}$$

$$\langle f \rangle = \frac{1}{Z} \frac{1}{N!} \int_{\Lambda} \frac{\mathrm{d}\vec{\mathbf{r}}}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V(\vec{\mathbf{r}})} f(\vec{\mathbf{r}}). \tag{2.21}$$

According to our convention, the classical values of statistical quantities will be written without a subscript, like $n(\mathbf{r})$, $n^{(2)}(\mathbf{r}, \mathbf{r}')$, etc.

Substituting the λ-expansion of the Boltzmann density (2.14) into formula (2.15), the quantum partition function takes the expansion form

$$Z_{\rm qu} = Z \left[1 - \lambda^2 \frac{\beta}{24} \langle \vec{\boldsymbol{\nabla}}^2 V \rangle + O(\lambda^4) \right]. \tag{2.22}$$

It is important to note that the general applicability of the Wigner-Kirkwood expansion scheme depends on the particular form of the interaction potential V; a divergence of the classical average $\langle \vec{\boldsymbol{\nabla}}^2 V \rangle$ indicates a non-analytic λ^2-expansion of the free energy.

For the model system of the one-component plasma in ν dimensions, the summation over the particle index j of the set of Poisson equations (1.2) leads to

$$\vec{\boldsymbol{\nabla}}^2 V(\vec{\mathbf{r}}) = -s_\nu e^2 \sum_{\substack{j,k=1 \\ (j\neq k)}}^{N} \delta(\mathbf{r}_j - \mathbf{r}_k) + s_\nu N e^2 n. \tag{2.23}$$

The first term on the rhs of (2.23) does not give any contribution to $\langle \vec{\boldsymbol{\nabla}}^2 V \rangle$, because it is weighted by a classical Boltzmann factor which vanishes at zero interparticle distance. The replacement of $\vec{\boldsymbol{\nabla}}^2 V$ in Eq. (2.22) by the particles-background term $s_\nu N e^2 n$ leads to

$$Z_{\rm qu} = Z \left[1 - \lambda^2 N \frac{\beta s_\nu e^2 n}{24} + O(\lambda^4) \right]. \tag{2.24}$$

For the free energy $F_{\rm qu}$ defined by the relation $-\beta F_{\rm qu} = \ln Z_{\rm qu}$, one gets from (2.24) the leading λ^2-correction term

$$F_{\rm qu} = F + \lambda^2 N \frac{s_\nu e^2 n}{24} + O(\lambda^4), \tag{2.25}$$

which is, as one expects in the bulk regime, extensive in the number of particles N. Corrections to the free energy of higher order in λ are standardly obtained from the partition function with higher-order λ-terms by using the cumulant expansion (see, e.g., Ref. [14]).

The Wigner-Kirkwood formalism ignores the exchange effects. However, for the one-component plasma, they are exponentially small [15].

The λ-expansion of the particle density (2.17) for the one-component plasma reads

$$n_{\rm qu}(\mathbf{r}) = \left[1 + \frac{\lambda^2}{24} \boldsymbol{\nabla}^2 + O(\lambda^4) \right] n(\mathbf{r}). \tag{2.26}$$

Since the classical density of particles is homogeneous in the bulk regime, $n(\mathbf{r}) = n$, there is no λ^2-correction term in the expansion of the homogeneous $n_{\rm qu}(\mathbf{r}) = n_{\rm qu}$.

The radial distribution function of the bulk one-component plasma has a λ-expansion of the form [16]

$$g_{\rm qu}(r) = \left[1 + \frac{\lambda^2}{12} \boldsymbol{\nabla}^2 + O(\lambda^4) \right] g(r). \tag{2.27}$$

In the short-distance $r \to 0$ limit, $g(r)$ is proportional to the Boltzmann factor of the bare Coulomb potential, which causes the breaking down of the Wigner-Kirkwood expansion scheme for too small values of r [16].

3. Half-space geometry: Boltzmann density

Let the particles be constrained to the half-space Λ defined by Cartesian coordinates $\mathbf{r} = (x, \mathbf{r}^\perp)$, where $x > 0$ and $\mathbf{r}^\perp \in R^{\nu-1}$ denotes the set of $(\nu - 1)$ unbounded spatial coordinates normal to x. The hard wall in half-space $x < 0$ is considered to be impenetrable to particles. We group the components of the νN-dimensional vector in configuration space $\vec{\mathbf{r}} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ into two another vectors $\vec{x} = (x_1, x_2, \ldots, x_N)$ and $\vec{\mathbf{r}}^\perp = (\mathbf{r}_1^\perp, \mathbf{r}_2^\perp, \ldots, \mathbf{r}_N^\perp)$; the corresponding momentum vectors generated from $\vec{\mathbf{p}} = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ are $\vec{p}^x = (p_1^x, p_2^x, \ldots, p_N^x)$ and $\vec{\mathbf{p}}^\perp = (\mathbf{p}_1^\perp, \mathbf{p}_2^\perp, \ldots, \mathbf{p}_N^\perp)$. The Hamiltonian is still of the form (1.1), where the interaction potential $V(\vec{\mathbf{r}})$ may include also additional effective one-body and two-body terms induced by the hard wall, e.g., the Coulomb energy of images in the case of charged particles near a dielectric wall.

Due to the presence of the hard wall impenetrable to particles, the one-body Boltzmann density in configuration space is written in the basis of stationary plane waves with zero boundary condition at $x = 0$:

$$B_\beta(\vec{\mathbf{r}}) \equiv \langle \vec{\mathbf{r}} | \mathrm{e}^{-\beta H} | \vec{\mathbf{r}} \rangle = \int_0^\infty \frac{\mathrm{d}\vec{p}^x}{(\pi\hbar)^N} \int \frac{\mathrm{d}\vec{\mathbf{p}}^\perp}{(2\pi\hbar)^{(\nu-1)N}} \psi_{\vec{\mathbf{p}}}^*(\vec{\mathbf{r}})\, \mathrm{e}^{-\beta H}\, \psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}}), \tag{3.1}$$

where

$$\psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}}) = \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}^\perp \cdot \vec{\mathbf{r}}^\perp} \prod_{j=1}^N \left[\sqrt{2} \sin\left(\frac{p_j^x x_j}{\hbar} \right) \right]. \tag{3.2}$$

To generate the $\hbar$-expansion of the matrix element (3.1), one introduces its Laplace transform

$$B_z(\vec{\mathbf{r}}) \equiv \int_0^\infty \mathrm{d}\beta\, \mathrm{e}^{-\beta z} B_\beta(\vec{\mathbf{r}}) = \int_0^\infty \frac{\mathrm{d}\vec{p}^x}{(\pi\hbar)^N} \int \frac{\mathrm{d}\vec{\mathbf{p}}^\perp}{(2\pi\hbar)^{(\nu-1)N}} \psi_{\vec{\mathbf{p}}}^*(\vec{\mathbf{r}})\, \frac{1}{H+z}\, \psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}}) \tag{3.3}$$

and proceeds formally as in the previous bulk case, up to the expansion (2.7). Afterwards, one needs the following generalization of the operator equation (2.8):

$$\mathcal{O}\left[f(\vec{\mathbf{r}}) \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}' \cdot \vec{\mathbf{r}}} \right] = -\mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}' \cdot \vec{\mathbf{r}}} \left[\frac{\mathrm{i}\hbar}{m} \vec{\mathbf{p}}' \cdot \vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m} \vec{\boldsymbol{\nabla}}^2 \right] f(\vec{\mathbf{r}}), \tag{3.4}$$

which is valid for any νN-dimensional momentum vector $\vec{\mathbf{p}}'$ such that $|\vec{\mathbf{p}}'| = |\vec{\mathbf{p}}|$. As a consequence, one finds from (2.7) that

$$\frac{1}{H+z} \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}' \cdot \vec{\mathbf{r}}} = \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}' \cdot \vec{\mathbf{r}}} \frac{1}{D} \sum_{n=0}^\infty \left\{ \left[\frac{\mathrm{i}\hbar}{m} \vec{\mathbf{p}}' \cdot \vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m} \vec{\boldsymbol{\nabla}}^2 \right] \frac{1}{D} \right\}^n. \tag{3.5}$$

To make use of this operator formula, we consider an exponential representation of the function $\psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}})$ given by Eq. (3.2):

$$\begin{aligned} \psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}}) &= \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}^\perp \cdot \vec{\mathbf{r}}^\perp} \frac{1}{(\sqrt{2}\mathrm{i})^N} \prod_{j=1}^N \sum_{\sigma_j = \pm 1} \sigma_j \mathrm{e}^{(\mathrm{i}/\hbar)\sigma_j p_j^x x_j} \\ &= \frac{1}{(\sqrt{2}\mathrm{i})^N} \sum_{\{\vec{\sigma}\}} \left(\prod_{j=1}^N \sigma_j \right) \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\mathbf{r}}}. \end{aligned} \tag{3.6}$$

Here, each of the σ-components of the "state" vector $\vec{\sigma} = (\sigma_1, \sigma_2, \ldots, \sigma_N)$ can take one of the values ± 1 (the sign determines the direction of the plane wave propagation) and the summation goes over all possible 2^N $\vec{\sigma}$-configurations. For a given state vector $\vec{\sigma}$, we have redefined the particle momenta $\mathbf{p}_j(\sigma_j) = (\sigma_j p_j^x, \mathbf{p}_j^\perp)$ $(j = 1, 2, \ldots, N)$ and grouped them into the νN-dimensional vector $\vec{\mathbf{p}}(\vec{\sigma}) = (\mathbf{p}_1(\sigma_1), \mathbf{p}_2(\sigma_2), \ldots, \mathbf{p}_N(\sigma_N))$, which couples via the scalar product to the $\vec{\mathbf{r}}$-vector in the exponential of Eq. (3.6). Since the momentum vector $\vec{\mathbf{p}}(\vec{\sigma})$ satisfies the requirement $|\vec{\mathbf{p}}(\vec{\sigma})| = |\vec{\mathbf{p}}|$ for an arbitrary state vector $\vec{\sigma}$, one can apply the key relation (3.5) to every summand in the exponential representation (3.6) of $\psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}})$:

$$\frac{1}{H+z}\psi_{\vec{\mathbf{p}}}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2}\mathrm{i})^N} \sum_{\{\vec{\sigma}\}} \left(\prod_{j=1}^N \sigma_j \right) \mathrm{e}^{(\mathrm{i}/\hbar)\vec{\mathbf{p}}(\vec{\sigma})\cdot\vec{\mathbf{r}}} \frac{1}{D} \sum_{n=0}^\infty \left\{ \left[\frac{\mathrm{i}\hbar}{m} \vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m} \vec{\boldsymbol{\nabla}}^2 \right] \frac{1}{D} \right\}^n . \quad (3.7)$$

Inserting this relation into Eq. (3.3), the Laplace transform of the Boltzmann density is expressed as the series

$$B_z(\vec{\mathbf{r}}) = \sum_{n=0}^\infty B_z^{(n)}(\vec{\mathbf{r}}), \quad (3.8a)$$

where

$$B_z^{(n)}(\vec{\mathbf{r}}) = \int_0^\infty \frac{\mathrm{d}\vec{p}^x}{(\pi\hbar)^N} \int \frac{\mathrm{d}\vec{\mathbf{p}}^\perp}{(2\pi\hbar)^{(\nu-1)N}} \prod_{j=1}^N \left[\sqrt{2} \sin\left(\frac{p_j^x x_j}{\hbar} \right) \right] \frac{1}{(\sqrt{2}\mathrm{i})^N} \sum_{\{\vec{\sigma}\}} \prod_{j=1}^N \left(\sigma_j \mathrm{e}^{(\mathrm{i}/\hbar)\sigma_j p_j^x x_j} \right)$$
$$\times \frac{1}{D} \left\{ \left[\frac{\mathrm{i}\hbar}{m} \vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}} + \frac{\hbar^2}{2m} \vec{\boldsymbol{\nabla}}^2 \right] \frac{1}{D} \right\}^n . \quad (3.8b)$$

To evaluate a given term $B_z^{(n)}(\vec{\mathbf{r}})$, one first carries out all differentiations in (3.8b). Since the scalar product

$$\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}} = \sum_{k=1}^N \sigma_k p_k^x \frac{\partial}{\partial x_k} + \sum_{k=1}^N \mathbf{p}_k^\perp \cdot \boldsymbol{\nabla}_{\mathbf{r}_k^\perp} \quad (3.9)$$

contains components of the state vector $\vec{\sigma}$, each of the components can take either odd or even power multiplied by the corresponding exponential; the summation over $\sigma_j = \pm 1$ then gives rise to the original stationary wave $\propto \sin(p_j^x x_j/\hbar)$ for odd powers of σ_j and to the shifted wave $\propto \cos(p_j^x x_j/\hbar)$ for even powers of σ_j. As the next step, one performs the inverse Laplace transform of $1/D^j$ $(j = 1, 2, \ldots)$ using the formula (2.11). The consequent relatively simple integrations over momenta lead to the final result; we have to keep in mind that while the integration of odd powers of the $\mathbf{p}^\perp$ components give zero contributions, this is no longer true for odd powers of p^x since the integration goes only over the positive values of p^x. We have performed the outlined procedure for the first terms $B_\beta^{(0)}$, $B_\beta^{(1)}$ and $B_\beta^{(2)}$. We do not go into details of the calculations, but only write down the final result and then discuss the origin of the obtained terms and their structure.

The result for $B_\beta^{(0)}(\vec{\mathbf{r}})$ reads

$$B_\beta^{(0)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V} \prod_{j=1}^N \left(1 - \mathrm{e}^{-2x_j^2/\lambda^2} \right) . \quad (3.10)$$

In comparison with the corresponding bulk term (2.13a), each particle gets an additional "boundary" factor $1-\exp(-2x^2/\lambda^2)$ which goes from 0 at the boundary $x=0$ to 1 in the bulk interior $x\to\infty$ on the length scale $\sim\lambda$. The product of boundary factors ensures that the quantum Boltzmann density vanishes as soon as one of the particles lies on the boundary. The dependence of the boundary factor on the de Broglie wavelength λ is non-analytic; this fact prevents one from a simple classification of contributions to the Boltzmann density according to integer powers of λ like it was in the bulk case. However, as will be shown explicitly in the next section on the evaluation of the partition function, when the exponential part $\exp(-2x^2/\lambda^2)$ of the boundary factor (multiplied eventually by another λ-independent function of x) is integrated over the x-coordinate, the analyticity in the parameter λ is restored. At this stage we only notice that the integrated product of boundary factors should be expanded in the following way

$$\prod_{j=1}^{N}\left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right)=1-\sum_{j=1}^{N}\mathrm{e}^{-2x_j^2/\lambda^2}+\frac{1}{2!}\sum_{\substack{j,k=1\\(j\neq k)}}^{N}\mathrm{e}^{-2x_j^2/\lambda^2}\mathrm{e}^{-2x_k^2/\lambda^2}+\cdots,\tag{3.11}$$

where each exponential term $\exp(-2x^2/\lambda^2)$, when integrated over x, produces one λ-factor as the result of the evoqued substitution of variables $x=\lambda x'$.

The result for $B_\beta^{(1)}(\vec{\mathbf{r}})$ is found in the form

$$B_\beta^{(1)}(\vec{\mathbf{r}})=\frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}\left\{-\sum_{k=1}^{N}\prod_{\substack{j=1\\(j\neq k)}}^{N}\left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right)x_k\mathrm{e}^{-2x_k^2/\lambda^2}\beta\frac{\partial V}{\partial x_k}\right.$$
$$\left.+\prod_{j=1}^{N}\left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right)\lambda^2\left[-\frac{\beta}{4}\vec{\boldsymbol{\nabla}}^2V+\frac{\beta^2}{6}\left(\vec{\boldsymbol{\nabla}}V\right)^2\right]\right\}.\tag{3.12}$$

Here, the first term corresponds to the source operator $D^{-1}\vec{\mathbf{p}}(\vec{\sigma})\cdot\vec{\boldsymbol{\nabla}}D^{-1}$ which does contribute to the Boltzmann density in the bulk case. The dependence on λ appears, besides the product of the particle boundary factors $1-\exp(-2x^2/\lambda^2)$, also via the combination $x\exp(-2x^2/\lambda^2)$. This function has a maximum of order λ and the integration of this function over x gives a contribution of order λ^2. These properties make the function $x\exp(-2x^2/\lambda^2)$ of an order equal to or "weaker" than λ, and therefore this function is a legitimate expansion parameter. The second term on the rhs of Eq. (3.12), having the origin in the source operator $D^{-1}\vec{\boldsymbol{\nabla}}^2D^{-1}$, corresponds to the simple multiplication of its bulk counterpart (2.13b) by the product of particle boundary factors $1-\exp(-2x^2/\lambda^2)$.

The final formula for $B_\beta^{(2)}(\vec{\mathbf{r}})$ consists in four terms

$$B_\beta^{(2)}(\vec{\mathbf{r}})=B_\beta^{(2,1)}(\vec{\mathbf{r}})+B_\beta^{(2.2)}(\vec{\mathbf{r}})+B_\beta^{(2,3)}(\vec{\mathbf{r}})+B_\beta^{(2,4)}(\vec{\mathbf{r}}),\tag{3.13}$$

where

$$B_\beta^{(2,1)}(\vec{\mathbf{r}})=\frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}}\mathrm{e}^{-\beta V}\left\{\prod_{j=1}^{N}\left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right)\lambda^2\left[\frac{\beta}{6}\vec{\boldsymbol{\nabla}}^2V-\frac{\beta^2}{8}\left(\vec{\boldsymbol{\nabla}}V\right)^2\right]\right.$$
$$+\sum_{k=1}^{N}\prod_{\substack{j=1\\(j\neq k)}}^{N}\left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right)x_k^2\mathrm{e}^{-2x_k^2/\lambda^2}\left[\frac{2\beta}{3}\frac{\partial^2V}{\partial x_k^2}-\frac{\beta^2}{2}\left(\frac{\partial V}{\partial x_k}\right)^2\right]\tag{3.14a}$$

$$- \sum_{\substack{k,l=1\\(k\neq l)}}^{N} \prod_{\substack{j=1\\(j\neq k,l)}}^{N} \left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right) x_k \mathrm{e}^{-2x_k^2/\lambda^2} x_l \mathrm{e}^{-2x_l^2/\lambda^2} \left[\frac{2\beta}{3}\frac{\partial^2 V}{\partial x_k \partial x_l} - \frac{\beta^2}{2}\frac{\partial V}{\partial x_k}\frac{\partial V}{\partial x_l}\right] \Bigg\}$$

corresponds to the source operator $D^{-1}\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}}[D^{-1}\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}} D^{-1}]$,

$$B_\beta^{(2,2)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V} \sum_{k=1}^{N} \prod_{\substack{j=1\\(j\neq k)}}^{N} \left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right) x_k \mathrm{e}^{-2x_k^2/\lambda^2} \lambda^2 \left[-\frac{\beta}{6}\frac{\partial}{\partial x_k}\left(\vec{\boldsymbol{\nabla}}^2 V\right) + \frac{\beta^2}{8}\left(\vec{\boldsymbol{\nabla}}^2 V\right)\frac{\partial V}{\partial x_k} + \frac{\beta^2}{12}\frac{\partial}{\partial x_k}\left(\vec{\boldsymbol{\nabla}} V\right)^2 - \frac{\beta^3}{15}\left(\vec{\boldsymbol{\nabla}} V\right)^2 \frac{\partial V}{\partial x_k}\right] \tag{3.14b}$$

has its origin in the source operator $D^{-1}\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}}[D^{-1}\vec{\boldsymbol{\nabla}}^2 D^{-1}]$,

$$B_\beta^{(2,3)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V} \sum_{k=1}^{N} \prod_{\substack{j=1\\(j\neq k)}}^{N} \left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right) x_k \mathrm{e}^{-2x_k^2/\lambda^2} \lambda^2 \left[-\frac{\beta}{6}\frac{\partial}{\partial x_k}\left(\vec{\boldsymbol{\nabla}}^2 V\right) + \frac{\beta^2}{8}\left(\vec{\boldsymbol{\nabla}}^2 V\right)\frac{\partial V}{\partial x_k} + \frac{\beta^2}{8}\frac{\partial}{\partial x_k}\left(\vec{\boldsymbol{\nabla}} V\right)^2 - \frac{\beta^3}{10}\left(\vec{\boldsymbol{\nabla}} V\right)^2 \frac{\partial V}{\partial x_k}\right] \tag{3.14c}$$

comes from the source operator $D^{-1}\vec{\boldsymbol{\nabla}}^2[D^{-1}\vec{\mathbf{p}}(\vec{\sigma}) \cdot \vec{\boldsymbol{\nabla}} D^{-1}]$, and

$$B_\beta^{(2,4)}(\vec{\mathbf{r}}) = \frac{1}{(\sqrt{2\pi}\lambda)^{\nu N}} \mathrm{e}^{-\beta V} \prod_{j=1}^{N} \left(1-\mathrm{e}^{-2x_j^2/\lambda^2}\right) \lambda^4 \left[-\frac{\beta}{24}\left(\vec{\boldsymbol{\nabla}}^2\right)^2 V + \frac{\beta^2}{16}\vec{\boldsymbol{\nabla}} V \cdot \vec{\boldsymbol{\nabla}}\left(\vec{\boldsymbol{\nabla}}^2 V\right) + \frac{\beta^2}{48}\vec{\boldsymbol{\nabla}}^2\left(\vec{\boldsymbol{\nabla}} V\right)^2 + \frac{\beta^2}{32}\left(\vec{\boldsymbol{\nabla}}^2 V\right)^2 - \frac{\beta^3}{30}\vec{\boldsymbol{\nabla}} V \cdot \vec{\boldsymbol{\nabla}}\left(\vec{\boldsymbol{\nabla}} V\right)^2 - \frac{\beta^3}{24}\left(\vec{\boldsymbol{\nabla}} V\right)^2 \vec{\boldsymbol{\nabla}}^2 V + \frac{\beta^4}{72}\left(\vec{\boldsymbol{\nabla}} V\right)^4\right] \tag{3.14d}$$

results from the source operator $D^{-1}\vec{\boldsymbol{\nabla}}^2[D^{-1}\vec{\boldsymbol{\nabla}}^2 D^{-1}]$. It is easy to check that the term $B_\beta^{(2)}(\vec{\mathbf{r}})$ as a whole is of the leading order λ^2, like it was in the bulk regime (see Eq. (2.13*c*)).

We would like to note that in the bulk interior far away from the boundary, i.e., when all x-coordinates of particles $\{x_j \to \infty\}_{j=1}^N$, the results for the boundary Boltzmann density must reduce to the bulk ones (2.13*a*)–(2.13*c*). It is easy to verify that the obtained results pass this test.

To summarize, the λ-expansion of the Boltzmann density in the presence of a boundary is more complex than the analytic one in the bulk. The expansion involves not only powers of λ, but also non-analytic position-dependent terms of type $1-\exp(-2x^2/\lambda^2)$, $x\exp(-2x^2/\lambda^2)$, etc. The first three Boltzmann terms $B_\beta^{(0)}(\vec{\mathbf{r}})$, $B_\beta^{(1)}(\vec{\mathbf{r}})$ and $B_\beta^{(2)}(\vec{\mathbf{r}})$ exhibit properties similar to their bulk counterparts (2.13*a*)–(2.13*b*): The maximum of $B_\beta^{(n)}(\vec{\mathbf{r}})$ is of order λ^n. We anticipate that this formal structure of the Boltzmann terms is maintained also on higher levels.

4. Half-space geometry: statistical quantities

4.1. Partition function and free energy

Since the Boltzmann density is represented by the series $\sum_{n=0}^{\infty} B_\beta^{(n)}(\vec{\mathbf{r}})$, the partition function (2.15) is expressible as

$$Z_{\rm qu} = \sum_{n=0}^{\infty} Z_{\rm qu}^{(n)}, \quad Z_{\rm qu}^{(n)} = \frac{1}{N!}\int_\Lambda {\rm d}\vec{\mathbf{r}}\, B_\beta^{(n)}(\vec{\mathbf{r}}). \tag{4.1}$$

In the next paragraphs we evaluate consecutively the λ-expansion of the first three terms $Z_{\rm qu}^{(0)}$, $Z_{\rm qu}^{(1)}$ and $Z_{\rm qu}^{(2)}$, up to the order λ^2. According to the analysis in the previous section, higher-order $Z_{\rm qu}^{(n)}$ terms are expected to contribute only to λ^3 and higher powers of λ.

Inserting the Boltzmann term $B_\beta^{(0)}$ (3.10) into the definition (4.1) of $Z_{\rm qu}^{(0)}$ and performing the expansion (3.11) for the product of boundary factors, we obtain

$$\frac{Z_{\rm qu}^{(0)}}{Z} = 1 - \int_\Lambda {\rm d}\mathbf{r}\, {\rm e}^{-2x^2/\lambda^2} n(\mathbf{r}) + \frac{1}{2!}\int_\Lambda {\rm d}\mathbf{r}_1 \int_\Lambda {\rm d}\mathbf{r}_2\, {\rm e}^{-2x_1^2/\lambda^2}{\rm e}^{-2x_2^2/\lambda^2} n^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \cdots. \tag{4.2}$$

The system is translationally invariant in the $\mathbf{r}^\perp$ space, i.e. $n(\mathbf{r}) = n(x)$, $n^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = n^{(2)}(x_1,x_2;|\mathbf{r}_1^\perp - \mathbf{r}_2^\perp|)$, etc. This property enables us to rewrite Eq. (4.2) in a more convenient form

$$\begin{aligned}\frac{Z_{\rm qu}^{(0)}}{Z} = {} & 1 - |\partial\Lambda| \int_0^\infty {\rm d}x\, {\rm e}^{-2x^2/\lambda^2} n(x) + \frac{1}{2!}|\partial\Lambda|^2 \left[\int_0^\infty {\rm d}x\, {\rm e}^{-2x^2/\lambda^2} n(x)\right]^2 \\ & + \frac{1}{2!}|\partial\Lambda| \int {\rm d}\mathbf{r}^\perp \int_0^\infty {\rm d}x_1 \int_0^\infty {\rm d}x_2\, {\rm e}^{-2x_1^2/\lambda^2}{\rm e}^{-2x_2^2/\lambda^2} n^{(2){\rm T}}(x_1,x_2;|\mathbf{r}^\perp|) + \cdots, \end{aligned} \tag{4.3}$$

where $|\partial\Lambda|$ denotes the surface of the half-space domain Λ at $x = 0$, and the third term has been added to the rhs and subsequently subtracted from the double integral (inducing in this way the truncation of the two-body density) in order to arrange the series for the application of the cumulant method. Assuming that the classical density profile $n(x)$ is analytic at the boundary $x = 0$, i.e. $n(x) = n(0) + n'(0)x + n''(0)x^2/2! + \cdots$ (this condition is not always fulfilled, see subsection 5.1.), the integral

$$\begin{aligned}\int_0^\infty {\rm d}x\, {\rm e}^{-2x^2/\lambda^2} n(x) &= \lambda \int_0^\infty {\rm d}x'\, {\rm e}^{-2x'^2} n(\lambda x') \\ &= \lambda \frac{1}{2}\sqrt{\frac{\pi}{2}} n(0) + \lambda^2 \frac{1}{4} n'(0) + O(\lambda^3). \end{aligned} \tag{4.4}$$

Performing an analogous procedure in the double integral on the rhs of Eq. (4.3), we finally arrive at

$$\begin{aligned}\frac{Z_{\rm qu}^{(0)}}{Z} = {} & 1 - |\partial\Lambda|\lambda\frac{1}{2}\sqrt{\frac{\pi}{2}} n(0) + \frac{1}{2!}\left[|\partial\Lambda|\lambda\frac{1}{2}\sqrt{\frac{\pi}{2}} n(0)\right]^2 - |\partial\Lambda|\lambda^2\frac{1}{4}n'(0) \\ & + |\partial\Lambda|\lambda^2 \frac{\pi}{16}\int {\rm d}\mathbf{r}^\perp\, n^{(2){\rm T}}(0,0;|\mathbf{r}^\perp|) + O(\lambda^3). \end{aligned} \tag{4.5}$$

We recall that the boundary values of the classical statistical quantities $n(0)$, $n'(0)$ and $n^{(2){\rm T}}(0,0;|\mathbf{r}^\perp|)$ are, in general, nonzero.

The boundary factors $1-\exp(-2x^2/\lambda^2)$ do not play any role in the Boltzmann term $B_\beta^{(1)}$ (3.12) when one is interested in the λ-expansion of the corresponding $Z_{\rm qu}^{(1)}$ up to the λ^2 order, so we can ignore them. After simple algebra, $Z_{\rm qu}^{(1)}$ is written as

$$\frac{Z_{\rm qu}^{(1)}}{Z} = \int_\Lambda {\rm d}\mathbf{r}\,{\rm e}^{-2x^2/\lambda^2} x n'(x) + \lambda^2 \left[-\frac{\beta}{4} \left\langle \vec{\nabla}^2 V \right\rangle + \frac{\beta^2}{6} \left\langle (\vec{\nabla} V)^2 \right\rangle \right] + O(\lambda^3), \tag{4.6}$$

where the classical average is taken over the half-space Λ. The integral on the rhs of (4.6) can be treated in the way outlined in the previous paragraph, with the result

$$\int_\Lambda {\rm d}\mathbf{r}\,{\rm e}^{-2x^2/\lambda^2} x n'(x) = |\partial\Lambda| \lambda^2 \frac{1}{4} n'(0) + O(\lambda^3), \tag{4.7}$$

the second term can be simplified by using the evident equality

$$\begin{aligned} \beta^2 \left\langle (\vec{\nabla} V)^2 \right\rangle &= \beta \left\langle \vec{\nabla}^2 V \right\rangle + \int_\Lambda {\rm d}\mathbf{r}\,\boldsymbol{\nabla}^2 n(\mathbf{r}) \\ &= \beta \left\langle \vec{\nabla}^2 V \right\rangle - |\partial\Lambda| n'(0), \end{aligned} \tag{4.8}$$

provided that $n'(0)$ is finite, see subsection 5.1.

From the four contributions to the Boltzmann term $B_\beta^{(2)}(\vec{\mathbf{r}})$ in (3.13), only the first one implies the λ^2 term:

$$\frac{Z_{\rm qu}^{(2)}}{Z} = \lambda^2 \left[\frac{\beta}{6} \left\langle \vec{\nabla}^2 V \right\rangle - \frac{\beta^2}{8} \left\langle (\vec{\nabla} V)^2 \right\rangle \right] + O(\lambda^3). \tag{4.9}$$

Also here we can apply the relation (4.8) to eliminate the term $\beta^2 \langle (\vec{\nabla} V)^2 \rangle$ in favour of the Laplacian term.

The results obtained in this subsection can be summarized by the expansion formula for the free energy, expanding in powers of λ the logarithm in $\beta F_{\rm qu} = -\ln Z_{\rm qu}$,

$$\begin{aligned} \beta F_{\rm qu} = \beta F + \lambda^2 \frac{\beta}{24} \left\langle \vec{\nabla}^2 V \right\rangle + |\partial\Lambda| \Big\{ \lambda \frac{1}{2} \sqrt{\frac{\pi}{2}} n(0) \\ + \lambda^2 \frac{1}{24} n'(0) - \lambda^2 \frac{\pi}{16} \int {\rm d}\mathbf{r}^\perp\, n^{(2){\rm T}}(0,0;|\mathbf{r}^\perp|) \Big\} + O(\lambda^3). \end{aligned} \tag{4.10}$$

The free energy of a quantum particle system constrained to a domain Λ of volume $|\Lambda|$ and surface $|\partial\Lambda|$ possesses the following general form

$$F_{\rm qu} = f_{\rm qu}^b |\Lambda| + \gamma_{\rm qu} |\partial\Lambda|, \tag{4.11}$$

where $f_{\rm qu}^b$ is the bulk free energy per unit volume and $\gamma_{\rm qu}$ is the surface tension. In the formula (4.10), the quantum contribution to the bulk part of the free energy comes only from the potential-dependent term $\propto \langle \vec{\nabla}^2 V \rangle$. This term can, in principle, give also some surface contribution. But for our model system of the semi-infinite one-component plasma constrained by the plain hard wall, the potential V fulfills the Poisson equation (2.23) and therefore the term $\propto \langle \vec{\nabla}^2 V \rangle$ produces only the bulk quantum contribution to the classical free energy, as shown in Eq. (2.25). By comparing (4.10) with (4.11), the surface tension is found to be

$$\beta\gamma_{\rm qu} = \beta\gamma + \lambda \frac{1}{2} \sqrt{\frac{\pi}{2}} n(0) + \lambda^2 \frac{1}{24} n'(0) - \lambda^2 \frac{\pi}{16} \int {\rm d}\mathbf{r}^\perp\, n^{(2){\rm T}}(0,0;|\mathbf{r}^\perp|) + O(\lambda^3). \tag{4.12}$$

It is interesting that up to the λ^2 order the interaction potential V enters into the formula for the surface tension only implicitly via the classical one-body and two-body averages. We note that, although for the one-component plasma the boundary truncated two-body density $n^{(2)\mathrm{T}}(0,0;|\mathbf{r}^\perp|)$ in (4.12) exhibits a long-range decay of type $1/|\mathbf{r}^\perp|^\nu$ at asymptotically large $|\mathbf{r}^\perp| \to \infty$ [17, 18], this makes no divergence problem at large distances in the integration over the $(\nu-1)$-dimensional $\mathbf{r}^\perp$ space.

Without going into details, the result for the surface tension (4.12) can be straightforwardly generalized to many-component quantum fluids composed of different species $\alpha = 1,2,\ldots,L$ with masses $\{m_\alpha\}_{\alpha=1}^L$ and the corresponding de Broglie wavelengths $\lambda_\alpha = \hbar(\beta/m_\alpha)^{1/2}$:

$$\beta\gamma_{\mathrm{qu}} = \beta\gamma + \frac{1}{2}\sqrt{\frac{\pi}{2}}\sum_\alpha \lambda_\alpha n_\alpha(0) + \frac{1}{24}\sum_\alpha \lambda_\alpha^2 n'_\alpha(0) - \frac{\pi}{16}\int \mathrm{d}\mathbf{r}^\perp \sum_{\alpha,\beta} \lambda_\alpha\lambda_\beta n_{\alpha\beta}^{(2)\mathrm{T}}(0,0;|\mathbf{r}^\perp|) + O(\lambda_\alpha\lambda_\beta\lambda_\gamma). \tag{4.13}$$

4.2. Particle density profile

As concerns the quantum corrections to the classical density profile and two-body density, since they involve a quantum Boltzmann factor which is not integrated on all variables, their expansion will contain, in addition to powers of λ, non-analytic terms $\exp(-2x^2/\lambda^2)$. Here, we shall restrict ourselves to the leading correction of order λ, considering a factor $x\exp(-2x^2/\lambda^2)$ as being of order λ since its maximum is of order λ, as pointed out in section 3., using the expansion technique presented in the previous subsection 4.1.

The one-body density profile (2.17) is obtained in the form

$$n_{\mathrm{qu}}(x) = \left(1 - \mathrm{e}^{-2x^2/\lambda^2}\right)\left[n(x) - \lambda\frac{1}{2}\sqrt{\frac{\pi}{2}}\int \mathrm{d}\mathbf{r}^\perp\, n^{(2)\mathrm{T}}(x,0;|\mathbf{r}^\perp|)\right] + x\mathrm{e}^{-2x^2/\lambda^2} n'(x) + O(\lambda^2), \tag{4.14}$$

where the first (product) term has its origin in the Boltzmann term $B_\beta^{(0)}(\vec{\mathbf{r}})$ (3.10) and the second term comes from $B_\beta^{(1)}(\vec{\mathbf{r}})$ (3.12).

In the classical description of the one-component Coulomb plasma, the system is neutral as a whole,

$$\int_0^\infty \mathrm{d}x\ [n(x) - n] = 0, \tag{4.15}$$

and a particle of charge e is surrounded by a screening cloud the average charge of which is exactly $-e$,

$$n(x) = -\int \mathrm{d}\mathbf{r}^\perp \int_0^\infty \mathrm{d}x'\, n^{(2)\mathrm{T}}(x,x';|\mathbf{r}^\perp|). \tag{4.16}$$

The neutrality sum rule (4.15) is valid also in the quantum regime. For our purposes it can be reexpressed in the form

$$\int_0^\infty \mathrm{d}x\,[n_{\mathrm{qu}}(x) - n(x)] = 0. \tag{4.17}$$

It is easy to check that for the density profile (4.14) this relation is fulfilled in the linear λ order.

The formula (4.14) can be straightforwardly extended to a quantum fluid with many-components $\alpha = 1, 2, \ldots, L$:

$$n_{\rm qu}^{(\alpha)}(x) = \left(1 - {\rm e}^{-2x^2/\lambda_\alpha^2}\right) \left[n_\alpha(x) - \frac{1}{2}\sqrt{\frac{\pi}{2}} \int {\rm d}\mathbf{r}^\perp \sum_\beta \lambda_\beta n_{\alpha\beta}^{(2){\rm T}}(x, 0; |\mathbf{r}^\perp|) \right] + x{\rm e}^{-2x^2/\lambda_\alpha^2} n'_\alpha(x) + O(\lambda^2). \qquad (4.18)$$

4.3. Two-body density

The leading quantum correction for the truncated two-body density (2.19) is found to be

$$\begin{aligned} n_{\rm qu}^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_2) = & \left(1 - {\rm e}^{-2x_1^2/\lambda^2}\right)\left(1 - {\rm e}^{-2x_2^2/\lambda^2}\right) \Big\{ n^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_2) \\ & - \lambda \frac{1}{2}\sqrt{\frac{\pi}{2}} \int {\rm d}\mathbf{r}^\perp\, n^{(3){\rm T}}[\mathbf{r}_1, \mathbf{r}_2, (0, \mathbf{r}^\perp)] \Big\} \\ & + \left(1 - {\rm e}^{-2x_2^2/\lambda^2}\right) x_1 {\rm e}^{-2x_1^2/\lambda^2} \frac{\partial}{\partial x_1} n^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_2) \qquad (4.19a) \\ & + \left(1 - {\rm e}^{-2x_1^2/\lambda^2}\right) x_2 {\rm e}^{-2x_2^2/\lambda^2} \frac{\partial}{\partial x_2} n^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_2) + O(\lambda^2), \end{aligned}$$

where

$$\begin{aligned} n^{(3){\rm T}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & \, n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - n^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_2)\, n(\mathbf{r}_3) - n^{(2){\rm T}}(\mathbf{r}_1, \mathbf{r}_3)\, n(\mathbf{r}_2) \\ & - n^{(2){\rm T}}(\mathbf{r}_2, \mathbf{r}_3)\, n(\mathbf{r}_1) - n(\mathbf{r}_1) n(\mathbf{r}_2) n(\mathbf{r}_3). \qquad (4.19b) \end{aligned}$$

5. Coulomb models with known classical statistical quantities

5.1. High-temperature Debye-Hückel limit

For the semi-infinite one-component plasma, at least in two and three dimensions, the classical truncated two-body density and density profile are known in this limit (see, e.g., eqs.(3.12) and (3.27) in [17]). The classical surface tension is also known (see eqs. (4.6) and (4.7) in [19]). The integrals which appear in (4.12) and (4.14) are easily computed:

$$\int {\rm d}\mathbf{r}^\perp n^{(2){\rm T}}(x, 0; |\mathbf{r}^\perp|) = -n\kappa {\rm e}^{-\kappa x}, \qquad (5.1)$$

where $\kappa = [2(\nu - 1)\pi\beta e^2 n]^{1/2}$ is the inverse Debye length. It should be noted that the density profile

$$n(x) = n + \frac{\kappa^\nu}{2\pi(\nu - 1)} \times \int_0^\infty \frac{{\rm e}^{-\kappa x} - 2(1 + t^2)^{1/2} \exp[-2(1 + t^2)^{1/2}\kappa x]}{[(1 + t^2)^{1/2} + t]^2 (3 + 4t^2)} t^{\nu-2} {\rm d}t, \qquad (5.2)$$

contrarily to the assumption in subsection 4.1., can be expanded in powers of x only up to order $x^{3-\nu}$: the nth derivative of $n(x)$ is infinite for $n \geq 4 - \nu$.

In two dimensions, $n'(0)$ is finite and the quantum surface tension up to order λ^2 (4.12) becomes

$$\beta\gamma_{\rm qu} = \frac{\kappa}{2\pi}\left(1-\frac{\pi}{4}\right) + \lambda\frac{1}{2}\sqrt{\frac{\pi}{2}}\left[n - \left(\ln 3 - 1 + \frac{\pi\sqrt{3}}{9}\right)\frac{\kappa^2}{8\pi}\right] + \lambda^2\left(\frac{\kappa^3}{72\pi} + \frac{\pi}{16}n\kappa\right) + o(\lambda^2). \quad (5.3)$$

It is likely that $n''(0)$, which is infinite, would appear if we attempted to compute the term of order λ^3. This is an indication that the Wigner-Kirkwood expansion of the surface tension is *not* in integer powers of λ in the present case; some singular term (logarithmic for instance) appears beyond the order λ^2.

In three dimensions, $n'(0)$ is infinite. The integral (4.4) is nevertheless finite, although it cannot be expanded up to order λ^2 (instead, a term of order $\lambda^2 \ln\lambda$ appears). Also, using (4.8) in the contributions (4.6) and (4.9) to the partition function shows that these contributions, formally of order λ^2, are infinite. This is an indication that some singular term, which we are unable to estimate, appears in the Wigner-Kirkwood expansion of the surface tension beyond the order λ. At order λ, (4.12) gives

$$\beta\gamma_{\rm qu} = \frac{2\ln 2 - 1}{32\pi}\kappa^2 + \lambda\frac{1}{2}\sqrt{\frac{\pi}{2}}\left[n - \left(\frac{1 - 3\ln 3 + \pi\sqrt{3}}{4}\frac{\kappa^3}{24\pi}\right)\right] + o(\lambda). \quad (5.4)$$

For the two-component plasma, the classical density profiles (see eq.(4.9) in [17]), which contain the singular Bessel function $K_2(2\kappa x)$, also cannot be expanded in powers of x to all orders.

It is also interesting to compare the density profiles (4.18) for a many-component semi-infinite fluid with the results of Aqua and Cornu [12], which have been obtained by a very different method, for a three-dimensional multi-component semi-infinite quantum Coulomb fluid. Let the charge of a particle of species α be e_α. The inverse Debye length now is $\kappa = (4\pi\beta\sum_\alpha n_\alpha e_\alpha^2)^{1/2}$. An easy generalization of (5.1) shows that

$$\int d\mathbf{r}^\perp n^{(2)\rm T}_{\alpha\beta}(x,0;|\mathbf{r}^\perp|) = -\frac{4\pi\beta n_\alpha e_\alpha n_\beta e_\beta}{\kappa}{\rm e}^{-\kappa x}. \quad (5.5)$$

Thus, (4.18) becomes

$$n^{(\alpha)}_{\rm qu}(x) = \left(1 - {\rm e}^{-2x^2/\lambda_\alpha^2}\right)\left[n_\alpha(x) + \frac{\sqrt{2}\pi^{3/2}\beta n_\alpha e_\alpha}{\kappa}\left(\sum_\gamma \lambda_\gamma n_\gamma e_\gamma\right){\rm e}^{-\kappa x}\right] + x{\rm e}^{-2x^2/\lambda_\alpha^2}n'_\alpha(x) + O(\lambda^2). \quad (5.6)$$

The first line of (5.6) is identical to the result (1.14) in Aqua and Cornu [12]. However, they do not have the second line, since this second line is of higher order in $\kappa\beta e^2$ and $\kappa\lambda$ than in the regime they have considered.

5.2. Exactly solvable two-dimensional one-component plasma

The classical two-dimensional one component plasma is an exactly solvable model when $\beta e^2 = 2$. In particular, for the semi-infinite geometry, the density profile and the two-body densities are exactly known [17]. Now, the density profile

$$n(x) = n\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\exp[-(t-x\sqrt{2})^2]}{1+\Phi(t)}\mathrm{d}t, \tag{5.7}$$

where Φ is the error function, can be expanded in integer powers of x: all the derivatives of $n(x)$ at $x = 0$ are finite (this might be a property of even integer values of $\beta e^2 = 2$). In particular,

$$n(0) = n\ln 2, \tag{5.8}$$

$$n'(0) = -\sqrt{\pi}(2n)^{3/2}\int_0^\infty \ln\left(\frac{1+\Phi(t)}{2}\right)\mathrm{d}t, \tag{5.9}$$

where the integral has the numerical value -0.3377. The integral which appears in (4.12) can be computed:

$$\int \mathrm{d}\mathbf{r}^\perp n^{(2)\mathrm{T}}(0,0;|\mathbf{r}^\perp|) = -4\sqrt{\frac{2}{\pi}}n^{3/2}\int_0^\infty \frac{\mathrm{e}^{-2t^2}}{[1+\Phi(t)]^2}\mathrm{d}t, \tag{5.10}$$

where the integral on t is related to the previous one: by integrations per partes, one finds

$$\int_0^\infty \frac{\mathrm{e}^{-2t^2}}{[1+\Phi(t)]^2}\mathrm{d}t = \frac{\sqrt{\pi}}{2} + \frac{\pi}{2}\int_0^\infty \ln\left(\frac{1+\Phi(t)}{2}\right)\mathrm{d}t = 0.3558. \tag{5.11}$$

The classical surface tension is also known [19]:

$$\beta\gamma = -\sqrt{\frac{n}{2\pi}}\int_0^\infty \ln\left(\frac{1+\Phi(t)}{2}\right)\mathrm{d}t. \tag{5.12}$$

Using (5.12), (5.8), (5.9), and (5.10) in (4.12) gives the surface tension.

6. Conclusion

For nearly classical quantum fluids (nearly classical means that the quantum effects are weak), the Wigner-Kirkwood formalism can be generalized to semi-infinite fluids, i.e. to fluids confined to a half-space $x \geq 0$ by a hard plane wall at $x = 0$: the boundary condition for the wave functions is that they have to vanish at $x = 0$. Under the condition that the classical density profile has all its derivatives with respect to x finite at $x = 0$, the surface tension can be expanded in powers, including odd powers, of the thermal de Broglie wavelength λ; this is to be compared with the case of infinite homogeneous fluids with sufficiently smooth interactions, which have a free energy the expansion of which contains only even powers of λ. The one-body and many-body densities are more complicated. Their expansions contain not only powers of λ, but also non-analytic position-dependent terms, localized near the wall, of the types $\exp(-2x^2/\lambda^2)$, $x\exp(-2x^2/\lambda^2)$, etc.

The above assumption of the classical density profile having all its derivatives with respect to x finite at $x = 0$ is not always fulfilled; in particular, it fails for Coulomb fluids in the high-temperature Debye-Hückel regime. For such cases, the surface tension cannot be expanded in powers of λ; singular terms appear, for instance of the type $\lambda^n \ln \lambda$.

As a task for the future, one should consider the exchange effects for the half-space system geometry. We anticipate that, for the considered one-component plasma, the exchange effects are exponentially small and therefore negligible in the nearly classical regime, like in the bulk case.

The present formalism can be extended to more general boundary conditions and geometries of the confining domain (e.g., a strip of finite width).

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