Semi-infinite jellium: Thermodynamic potential, chemical potential, and surface energy

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A general expression for the thermodynamic potential of the model of semi-infinite jellium is obtained. By using this expression, the surface energy for the infinite barrier model is calculated. The behavior of the surface energy and of the chemical potential as functions of the Wigner-Seitz radius and the influence of the Coulomb interaction between electrons on the calculated values is studied. It is shown that taking into account the Coulomb interaction between electrons leads to growth of the surface energy. The surface energy is positive in the entire area of the Wigner-Seitz radius. It is shown that taking into account the Coulomb interaction between electrons leads to a decrease of the chemical potential.

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I. INTRODUCTION

The development of a quantum-statistical theory of Fermi systems with interfaces is one of the most important problems of contemporary statistical physics. In particular, the richness of surface phenomena and the rapid development of experimental methods of investigation of surfaces requires the development of a theory of such systems.

The most popular theoretical method for studying this area of research is the density functional theory [1–3], which has been developed from the well-known Thomas-Fermi method for atoms. By construction, the density functional theory is a one-particle approach and can not properly take into account the many-body correlation effects. Therefore the energy functionals for inhomogeneous systems are mostly used in the local density approximation [2], namely, the electron density distribution $n(\mathbf{r})$ is substituted by the average electron density $n = $ const in the well-known expressions of the theory for homogeneous systems. This approach is questionable [4], since the presence of the interface brings both quantitative and qualitative changes of various characteristics of an electronic system, e.g., the image forces, which cannot be obtained from the density functional theory in principle.

The surface energy of semi-infinite jellium calculated in the density functional theory turns out to be negative for large values of the electron concentration ($r_s < 2.5\,a_B$, where r_s is the Wigner-Seitz radius) [5]. This is physically incorrect. The surface energy must be positive, otherwise the metal would spontaneously split. At present, the general belief is that the cause of negativity of the surface energy is the replacement of the discrete ionic lattice by a uniform positive background. Thus, in the work of Lang and Kohn [5], a discrete lattice is accounted for by using the first-order perturbation theory in the pseudopotential. As a result, the surface energy becomes positive and is satisfactorily consistent with the experimental data for a number of simple metals [5]. A variational procedure has been developed by Monnier and Perdew [6,7] to take into account the averaged effect with the introduction of discrete additions to the potential inside a metal, which depends on the structure of the lattice and the surface. The obtained results for the surface energy were very close to the results of Lang and Kohn and were in better agreement with the

experimental data. Later, Appelbaum, and Hamann [8] used the local density approximation and performed calculations for the Cu(111) surface, with the account of the discrete ionic lattice without perturbation theory. They have obtained a good agreement with the experimental data. The authors of all these studies have assumed that the nonlocal exchange-correlation effects are negligible and can be omitted. In the works found in Refs. [9,10], the calculations of the surface energy were performed with a varying position of the last (exposed) ion layer and a good agreement with experimental data for the surface energy of simple metals was obtained. In Refs. [11–13], a stabilized jellium model has been proposed. In this model, the pseudopotential correction, which is averaged over the Wigner-Seitz cell, is incorporated into the effective potential inside the metal. This model yields positive values for the surface energy. Thus the consideration of a discrete ionic lattice permits to solve the problem of negative values of the surface energy.

However, it is not clear that neglecting the discreteness is the principal and only reason of discrepancy between the theory and experiment. Probably, the theory could be improved, still remaining in the framework of the jellium model. There have been attempts to go beyond the local density approximation. Namely, Schmit and Lucas [14], Craig [15], and Peuckert [16] have considered certain nonlocal contributions to the exchange-correlation term to the surface energy, due to the change of zero energy of plasmons and the appearance of surface modes during the separation of crystal into fragments. From a good agreement of this contribution with the experimental data for the surface energy, the authors of these works proposed to identify this contribution with the total surface energy, suggesting that other contributions, which have not been accounted for, canceled each other. This approach is actively debated in Refs. [17–24]. The expressions for the exchange-correlation energy of a bounded electron gas have been obtained by Harris and Jones [22,23], Wikborg and Inglesfield [25], and Johnson and Srinivasan [27], focusing on the analysis of nonlocal effects. The exchange part of the surface energy was calculated for electrons in a potential box with infinitely high walls [22,23], and the exchange-correlation and exchange parts were calculated in the random phase approximation [25]. A comparison of these results with those calculated in the local density approximation has showed that the exchange-correlation parts differ by about 10%, the

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exchange parts differ by 50%, and the correlation parts differ by six times. The local density approximation works much better for the sum of the exchange and correlation parts of energy rather than for each individual contribution (see also Ref. [26]). Further calculations, using more realistic models of the surface barrier [28–32], namely, the gradient expansions [32–39], and the analysis of Langreth and Perdew [38,39], have found a decisive contribution of the local density approximation to the exchange-correlation part of energy as well. In particular, the calculations [35] show that the nonlocal corrections do not exceed 16%, although the relative contribution of nonlocality into the total surface energy can be much larger (up to 40%) because for many metals the exchange-correlation part of the surface energy is greater than the total surface energy [5].

More recent studies have renewed the debate about the correctness of the application of the local density approximation in the calculation of the surface energy. Using the Fermi hypernetted-chain equations [40,41] previous calculations obtained significantly higher values of the surface energy than calculated by Lang and Kohn in the local density approximation [5]. In contrast, the values of the surface energy obtained in the calculations using density functional theory [42] with the nonlocal functional of Langreth and Mehl [43] are much closer to the results obtained with the local density approximation. Calculations of the surface energy with the quantum Monte Carlo method [44,45] have shown that the values of the surface energy obtained at high concentrations ($r_s \leqslant 2.07\,a_B$) are in a good agreement with the results obtained using a nonlocal functional, but at lower concentrations ($r_s \geqslant 3.25\,a_B$) they are in good agreement with the results of Krotscheck and Kohn [40,41]. On the other hand, Pitarke has concluded that the local density approximation leads to a small error in the exchange-correlation of the surface energy [46]. In this work, the long-range correlations are taken into account self-consistently in the random phase approximation, while the short-range correlations are included in the time-dependent local density approximation [47,48].

In Ref. [49], the surface energy is calculated by using the one- and two-particle distribution functions of electrons, which are obtained in Ref. [50] by taking into account the Coulomb interaction between electrons. It is found that the surface energy is positive in the entire range of electron concentrations.

Takahashi and Onzawa have calculated the electron density distribution and the surface energy of the noninteracting electron gas for the finite barrier model [51]. It is interesting that the electron density without self-consistency is very close to the self-consistent calculations of Lang and Kohn [5], and the surface energy is positive for all concentrations of electrons. Moreover, their result is close to the result of Lang and Kohn at low concentrations.

In the present work, our principle objective is to construct a consistent quantum-statistical theory of a simple metal with the "metal-vacuum" interface in the framework of the jellium model. An effective potential of interelectron interaction, which we have studied recently in Refs. [52–56], is crucial for calculating the general expression for the thermodynamic potential. It is shown that within certain approximations the thermodynamic potential can be represented as a functional of the one- and two-particle distribution functions of electrons. At low temperatures, the nonlinear algebraic equation for the

chemical potential and a general expression for the internal energy are obtained from the thermodynamic potential. It is shown that the obtained equation for the chemical potential of a nonhomogeneous system is similar to the equation for a homogeneous system. The chemical potential is calculated as a function of the Wigner-Seitz radius. The one particle distribution function of electrons is calculated for the infinite barrier model. Expressions for the extensive and surface contributions to the internal energy are obtained. For the same model, a calculation of the surface contribution to the internal energy, which is the surface energy at low temperature, is performed. The behavior of the surface energy as a function of the Wigner-Seitz radius is studied. We have found that the surface energy calculated in the present work is positive in the entire concentration range typical for metals, and at low concentrations is consistent with the calculations of Lang and Kohn [5]. The influence of the Coulomb interaction between electrons on the calculated characteristics is studied. Detailed calculations of these properties are given in Ref. [57].

II. MODEL

We consider a system of N electrons in the volume $V = SL$ in the field of positive charge with the distribution

$$\varrho_{\text{jell}}(\mathbf{R}) \equiv \varrho_{\text{jell}}(\mathbf{R}_{||}, Z) \equiv \varrho_{\text{jell}}(Z)$$

$$= \varrho_0 \theta(-Z) = \begin{cases} \varrho_0, & Z \leqslant 0 \\ 0, & Z > 0 \end{cases}, \quad (1)$$

where $Z = 0$ is the dividing plane, $\theta(x)$ is the Heaviside step function, $\mathbf{R}_{||} = (X, Y)$, $X, Y \in [-\sqrt{S}/2, +\sqrt{S}/2]$, $Z \in [-L/2, +L/2]$. The condition of electroneutrality is satisfied,

$$\lim_{S,L \to \infty} \int_S d\mathbf{R}_{||} \int_{-L/2}^{+L/2} dZ \, \varrho_{\text{jell}}(\mathbf{R}_{||}, Z) = eN, \quad e > 0, \quad (2)$$

moreover, in the thermodynamic limit, we have

$$\lim_{N,S,L \to \infty} \frac{eN}{SL} = \lim_{N,V \to \infty} \frac{eN}{V/2} = \varrho_0. \quad (3)$$

This model system is known as "semi-infinite jellium" and it is one of the simplest models of semi-infinite metal, which satisfactorily describes simple metals. The Hamiltonian of the model is

$$H_{\text{jell}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \Delta_i + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$- \sum_{j=1}^{N} \int_V d\mathbf{R} \, \frac{e\varrho_{\text{jell}}(\mathbf{R})}{|\mathbf{r}_j - \mathbf{R}|}$$

$$+ \frac{1}{2} \int_V d\mathbf{R}_1 \int_V d\mathbf{R}_2 \, \frac{\varrho_{\text{jell}}(\mathbf{R}_1)\varrho_{\text{jell}}(\mathbf{R}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|}, \quad (4)$$

where $\mathbf{r}_j$ is the position of j-th electron; the first term is the kinetic energy of electrons (m is the electron mass), the second term is the potential energy of the interelectron interaction, the third term is the energy of interaction of electrons with a positive charge, and the fourth term is the potential energy of the positive charge.

From Hamiltonian (4), we extract the Hamiltonian of the infinite jellium model $H_{\text{jell}}^{\text{unif}}$:

$$H_{\text{jell}}^{\text{unif}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \Delta_i + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$- \sum_{j=1}^{N} \int_V d\mathbf{R} \, \frac{e^2 N/V}{|\mathbf{r}_j - \mathbf{R}|}$$
$$+ \frac{1}{2} \int_V d\mathbf{R}_1 \int_V d\mathbf{R}_2 \, \frac{(eN/V)^2}{|\mathbf{R}_1 - \mathbf{R}_2|}; \tag{5}$$

here, the physical meaning of the terms is similar to the terms of Hamiltonian (4).

Thus we get

$$H_{\text{jell}} = H_{\text{jell}}^{\text{unif}} + \sum_{j=1}^{N} V_{\text{surf}}(\mathbf{r}_j) + \frac{1}{2} \int_V d\mathbf{R}_1 \int_V d\mathbf{R}_2$$
$$\times \frac{\varrho_{\text{jell}}(\mathbf{R}_1)\varrho_{\text{jell}}(\mathbf{R}_2) - (eN/V)^2}{|\mathbf{R}_1 - \mathbf{R}_2|}, \tag{6}$$

where

$$V_{\text{surf}}(\mathbf{r}_j) = \int_V d\mathbf{R} \, \frac{e(eN/V - \varrho_{\text{jell}}(\mathbf{R}))}{|\mathbf{r}_j - \mathbf{R}|} \tag{7}$$

is the surface potential acting on the electron. This potential is formed by the deviation of the positive charge distribution from the uniform one. So, if instead of $\varrho_{\text{jell}}(\mathbf{R})$ we put the uniform distribution eN/V, then the surface potential and the last term in the Hamiltonian (5) disappear and one obtains

$$\lim_{\varrho_{\text{jell}} \to \frac{eN}{V}} H_{\text{jell}} = H_{\text{jell}}^{\text{unif}}.$$

It should be noted that as a consequence of the symmetry of the model, the surface potential $V_{\text{surf}}(\mathbf{r})$ is a function of the normal to the dividing plane coordinates of the electron only, the motion of the electron in a plane parallel to the dividing plane is free, i.e.,

$$V_{\text{surf}}(\mathbf{r}) \equiv V_{\text{surf}}(z).$$

In order to calculate the thermodynamic potential of the system, it is convenient to present Hamiltonian (6) in the second quantization representation.

III. SECOND QUANTIZATION REPRESENTATION

We introduce the single-particle wave functions $\Psi_a(\mathbf{r})$ and the corresponding energies E_a of the electron in the field of the surface potential $V_{\text{surf}}(z)$,

$$\left[-\frac{\hbar^2}{2m} \Delta + V_{\text{surf}}(z) \right] \Psi_a(\mathbf{r}) = E_a \Psi_a(\mathbf{r}), \tag{8}$$

which we use to construct the representation of the second quantization.

Since the potential in the stationary Schrödinger equation (8) depends only on the normal to the dividing plane coordinate of the electron, the variables can be separated. Then

we obtain

$$E_a = \frac{\hbar^2 k_{||}^2}{2m} + \varepsilon_\alpha, \quad a = (\mathbf{k}_{||}, \alpha), \tag{9}$$

$$\Psi_a(\mathbf{r}) = \frac{1}{\sqrt{S}} e^{i\mathbf{k}_{||}\mathbf{r}_{||}} \varphi_\alpha(z), \tag{10}$$

where $\mathbf{r}_{||}$ is the two-dimensional coordinate of the electron in the plane parallel to the dividing plane, $\mathbf{k}_{||}$ is the wave vector of the electron in this plane, and

$$\mathbf{k}_{||} = (k_{||x}, k_{||y}), \quad k_{||x,y} = \frac{2\pi n_{x,y}}{\sqrt{S}}, \quad n_{x,y} = 0, \pm1, \pm2, \ldots, \tag{11}$$

α is some quantum number that depends on the form of the surface potential, the functions $\varphi_\alpha(z)$ satisfy the one-dimensional stationary Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_{\text{surf}}(z) \right] \varphi_\alpha(z) = \varepsilon_\alpha \varphi_\alpha(z).$$

In the second quantization representation constructed by means of the wave functions (10), the Hamiltonian of the system becomes

$$H = \sum_{\mathbf{k}_{||}, \alpha} E_\alpha(\mathbf{k}_{||}) a_\alpha^\dagger(\mathbf{k}_{||}) a_\alpha(\mathbf{k}_{||}) - \frac{1}{2S} N \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q}, 0)$$
$$+ \frac{1}{2SL} \sum_{\mathbf{q} \neq 0} \sum_k \nu_k(\mathbf{q}) \rho_k(\mathbf{q}) \rho_{-k}(-\mathbf{q}), \tag{12}$$

where $a_\alpha^\dagger(\mathbf{k}_{||}), a_\alpha(\mathbf{k}_{||})$ are the operators of electron creation and annihilation, respectively, in the state $(\mathbf{k}_{||}, \alpha)$, and the standard commutation relations are

$$\{a_{\alpha_1}(\mathbf{k}_{||1}), a_{\alpha_2}^\dagger(\mathbf{k}_{||2})\} = \delta_{\mathbf{k}_{||1}, \mathbf{k}_{||2}} \delta_{\alpha_1, \alpha_2}, \tag{13}$$

$$N = \sum_{\mathbf{k}_{||}, \alpha} a_\alpha^\dagger(\mathbf{k}_{||}) a_\alpha(\mathbf{k}_{||}) \tag{14}$$

is the particle number operator, $\nu(\mathbf{q}, 0) = \frac{2\pi e^2}{q}$, $\nu_k(\mathbf{q}) = 4\pi e^2/(\mathbf{q}^2 + k^2)$ is the Fourier transform of the Coulomb interaction, $q_{x,y} = \frac{2\pi}{\sqrt{S}} m_{x,y}$, $m_{x,y} = 0, \pm1, \pm2, \ldots$, $k = \frac{2\pi}{L} n$, $n = 0, \pm1, \pm2, \ldots$, and

$$\rho_k(\mathbf{q}) = \sum_{\mathbf{k}_{||}, \alpha, \alpha'} \langle \alpha | e^{-ikz} | \alpha' \rangle a_\alpha^\dagger(\mathbf{k}_{||}) a_{\alpha'}(\mathbf{k}_{||} - \mathbf{q}) \tag{15}$$

is the mixed Fourier representation of the local density of electrons,

$$\langle \alpha | \cdots | \alpha' \rangle = \int_{-L/2}^{+L/2} dz \, \varphi_\alpha^*(z) \cdots \varphi_{\alpha'}(z). \tag{16}$$

It is worth noting that in Eq. (12), there are no terms with $\mathbf{q} = 0$, due to the electroneutrality condition (2). The Hamiltonian in form (12) is convenient for the calculation of the thermodynamic potential by the functional integration method.

IV. THERMODYNAMIC POTENTIAL

A. Functional representation

The grand partition function,

$$\Xi = \mathrm{Sp} \exp[-\beta(H - \mu N)], \tag{17}$$

which determines the thermodynamic potential of the system,

$$\Omega = -\frac{1}{\beta} \ln \Xi, \tag{18}$$

and other thermodynamic functions, in the interaction representation becomes

$$\Xi = \Xi_0 \exp\left(\frac{\beta}{2S} \langle N \rangle_0 \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q}, 0)\right) \Xi_{\mathrm{int}}, \tag{19}$$

where $\Xi_0 = \mathrm{Sp} \exp(-\beta(H_0 - \mu N))$, $H_0 = \sum_{\mathbf{k}_{||}, \alpha} E_\alpha(\mathbf{k}_{||}) a_\alpha^\dagger(\mathbf{k}_{||}) a_\alpha(\mathbf{k}_{||})$ is the Hamiltonian of the noninteracting system, μ is the chemical potential,

$$\langle \ldots \rangle_0 = \frac{1}{\Xi_0} \mathrm{Sp}(\mathrm{e}^{-\beta(H_0 - \mu N)} \ldots),$$

$$\langle N \rangle_0 = \sum_{\mathbf{k}_{||}, \alpha} \langle a_\alpha^\dagger(\mathbf{k}_{||}) a_\alpha(\mathbf{k}_{||}) \rangle_0 = \sum_{\mathbf{k}_{||}, \alpha} n_\alpha(\mathbf{k}_{||}), \tag{20}$$

$n_\alpha(\mathbf{k}_{||}) = \dfrac{1}{\mathrm{e}^{\beta(E_\alpha(\mathbf{k}_{||}) - \mu)} + 1}$ is the Fermi-Dirac distribution,

$$\Xi_{\mathrm{int}} = \langle \mathcal{S}(\beta) \rangle_0,$$

$$\mathcal{S}(\beta) = \mathrm{T} \exp\left[-\frac{1}{2SL} \int_0^\beta d\beta' \sum_{\mathbf{q} \neq 0} \sum_k \nu_k(\mathbf{q})\right.$$

$$\left. \times \rho_k(\mathbf{q}, \beta') \rho_{-k}(-\mathbf{q}, \beta') \right], \tag{21}$$

$$\rho_k(\mathbf{q}, \beta') = \mathrm{e}^{\beta'(H_0 - \mu N)} \rho_k(\mathbf{q}) \mathrm{e}^{-\beta'(H_0 - \mu N)}, \tag{22}$$

where T is the symbol of chronological ordering of "times", $\beta = 1/\theta$, and θ is the thermodynamic temperature.

For further calculations, it is convenient to switch to the spectral representation:

$$\rho_k(\mathbf{q}, \nu) = \frac{1}{\beta} \int_0^\beta d\beta' \mathrm{e}^{\mathrm{i}\nu\beta'} \rho_k(\mathbf{q}, \beta'), \tag{23}$$

$$\rho_k(\mathbf{q}, \beta') = \sum_\nu \mathrm{e}^{-\mathrm{i}\nu\beta'} \rho_k(\mathbf{q}, \nu), \tag{24}$$

where $\nu = \frac{2\pi}{\beta} n$ $(n = 0, \pm 1, \pm 2, \ldots)$ are Bose frequencies. Then (21) becomes

$$\mathcal{S}(\beta)$$

$$= \mathrm{T} \exp\left[-\frac{1}{2SL} \sum_{\mathbf{q} \neq 0} \sum_k \sum_\nu \nu_k(\mathbf{q}) \rho_k(\mathbf{q}, \nu) \rho_{-k}(-\mathbf{q}, -\nu)\right]. \tag{25}$$

In order to simplify the approximation $\mathcal{S}(\beta)$ according to (20), we switch to a functional representation for

$\mathcal{S}(\beta)$ [58,59], using the Stratonovich-Hubbard identity [60]

$$\exp\left[-\frac{1}{2} \mathbf{y}^{\mathrm{T}} \mathbb{A} \mathbf{y}\right]$$

$$= (\det \mathbb{A})^{-1/2} \int_{-\infty}^{+\infty} (d\mathbf{x}) \exp\left[-\frac{1}{2} \mathbf{x}^{\mathrm{T}} \mathbb{A}^{-1} \mathbf{x} + \mathrm{i} \mathbf{x}^{\mathrm{T}} \mathbf{y}\right], \tag{26}$$

where $(d\mathbf{x}) = \prod_{k=1}^n \frac{dx_k}{\sqrt{2\pi}}$, $\mathbf{y}^{\mathrm{T}} = (y_1, \ldots, y_n)$, $\mathbf{x}^{\mathrm{T}} = (x_1, \ldots, x_n)$, and $\mathbb{A}$ is a positively defined matrix. Then, for (25), we obtain

$$\mathcal{S}(\beta) = \prod_{\mathbf{q} \neq 0} \prod_k \prod_\nu \left(\frac{\beta}{SL} \nu_k(\mathbf{q})\right)^{-1/2} \int (d\omega)$$

$$\times \exp\left[-\frac{1}{2} \sum_{\mathbf{q} \neq 0} \sum_k \sum_\nu \left(\frac{\beta}{SL} \nu_k(\mathbf{q})\right)^{-1} \omega_k(\mathbf{q}, \nu)\right.$$

$$\left. \times \omega_{-k}(-\mathbf{q}, -\nu) \right]$$

$$\times \mathrm{T} \exp\left[\mathrm{i} \sum_{\mathbf{q} \neq 0} \sum_k \sum_\nu \omega_k(\mathbf{q}, \nu) \rho_k(\mathbf{q}, \nu)\right], \tag{27}$$

where $(d\omega)$ is the element of the phase space:

$$(d\omega) = \prod_{\mathbf{q} > 0} \prod_{k \geqslant 0} \prod_{\nu \geqslant 0} \frac{d\omega_k^c(\mathbf{q}, \nu)}{\sqrt{\pi}} \frac{d\omega_k^s(\mathbf{q}, \nu)}{\sqrt{\pi}},$$

$$\omega_k(\mathbf{q}, \nu) = \omega_k^c(\mathbf{q}, \nu) + \mathrm{i}\omega_k^s(\mathbf{q}, \nu),$$

$$\omega_k^c(\mathbf{q}, \nu) = \omega_{-k}^c(-\mathbf{q}, -\nu), \quad \omega_k^s(\mathbf{q}, \nu) = -\omega_{-k}^s(-\mathbf{q}, -\nu).$$

Note that due to the fact that the operator variables $\rho_k(\mathbf{q}, \nu)$ are under sign T ordering in (27), it is impossible to perform an integration by β' in Eq. (23).

By making an average of $\mathcal{S}(\beta)$ according to (20), we obtain

$$\Xi_{\mathrm{int}} = \langle \mathcal{S}(\beta) \rangle_0 = \prod_{\mathbf{q} \neq 0} \prod_k \prod_\nu \left(\frac{\beta}{SL} \nu_k(\mathbf{q})\right)^{-1/2} \int (d\omega) J(\omega), \tag{28}$$

where

$$J(\omega) = \exp\left[-\frac{1}{2} \sum_{\mathbf{q} \neq 0} \sum_k \sum_\nu \left(\frac{\beta}{SL} \nu_k(\mathbf{q})\right)^{-1}\right.$$

$$\left. \times \omega_k(\mathbf{q}, \nu) \omega_{-k}(-\mathbf{q}, -\nu)\right]$$

$$\times \exp\left[\sum_{n \geqslant 2} \frac{1}{n!} \sum_{\substack{\mathbf{q}_1 \neq 0, k_1, \nu_1 \\ \cdots\cdots\cdots \\ \mathbf{q}_n \neq 0, k_n, \nu_n}} \mathfrak{M}_{k_1, \ldots, k_n}^0(\mathbf{q}_1, \nu_1, \ldots, \mathbf{q}_n, \nu_n)\right.$$

$$\left. \times \omega_{k_1}(\mathbf{q}_1, \nu_1) \ldots \omega_{k_n}(\mathbf{q}_n, \nu_n)\right], \tag{29}$$

$$\mathfrak{M}_{k_1, \ldots, k_n}^0(\mathbf{q}_1, \nu_1, \ldots, \mathbf{q}_n, \nu_n) = \mathrm{i}^n \langle \mathrm{T} \rho_{k_1}(\mathbf{q}_1, \nu_1) \ldots \rho_{k_n}(\mathbf{q}_n, \nu_n) \rangle_{0,c}$$

$$\sim \delta_{\mathbf{q}_1 + \mathbf{q}_2 + \ldots + \mathbf{q}_n, 0} \, \delta_{\nu_1 + \nu_2 + \ldots + \nu_n, 0}$$

are the so-called irreducible mean values (cumulants), δ is the Kronecker delta, and $\mathfrak{M}_k^0(\mathbf{q}, \nu) \equiv 0$, because $\mathbf{q} \neq 0$.

In general terms, the calculation of integral (28) is a complicated problem due to the exponential index having terms with $n \geqslant 3$. Their neglect results in the Gaussian approximation (or the so-called random phase approximation). As a rule, the calculation of this integral is done by means of a series expansion of the non-Gaussian part of integral (29) with subsequent averaging with a Gaussian distribution and partial summing up of the terms that give the most important contribution. In contrast, in Ref. [52], it was shown that the integrand $J(\omega)$ can be approximated by a Gaussian form $J_G(\omega)$, introducing the unknown function $D_{k_1,k_2}(\mathbf{q}, \nu)$:

$$J_G(\omega) = \exp\left[-\frac{1}{2}\sum_{\mathbf{q}\neq 0}\sum_{k_1,k_2}\sum_{\nu}\left(\frac{\beta}{S}g_{k_1,k_2}(\mathbf{q},\nu)\right)^{-1}\right.$$
$$\left. \times\, \omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\right], \tag{30}$$

where $g_{k_1,k_2}(\mathbf{q},\nu)$ is the Fourier transform of effective interelectron interaction,

$$\left(\frac{\beta}{S}g_{k_1,k_2}(\mathbf{q},\nu)\right)^{-1} = \left(\frac{\beta}{SL}\nu_{k_1}(\mathbf{q})\right)^{-1}\delta_{k_1+k_2,0} - D_{k_1,k_2}(\mathbf{q},\nu). \tag{31}$$

We will seek the unknown function $D_{k_1,k_2}(\mathbf{q},\nu)$ from the condition that the mean value of $\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)$, calculated with the distribution $J(\omega)$, is equal to the mean value, obtained with the Gaussian distribution $J_G(\omega)$, namely, from the condition

$$\overline{\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)} = \langle \omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\rangle_G, \tag{32}$$

where we have introduced the following notation:

$$\overline{\cdots} = \frac{\int(d\omega)J(\omega)\cdots}{\int(d\omega)J(\omega)},$$
$$\langle\ldots\rangle_G = \frac{\int(d\omega)J_G(\omega)\cdots}{\int(d\omega)J_G(\omega)}. \tag{33}$$

In Ref. [52], it is shown that the solution of Eq. (32) in the matrix form is

$$\mathbb{D} = \overline{\mathfrak{M}}(\mathbb{I} + \mathbb{V}\overline{\mathfrak{M}})^{-1}, \tag{34}$$

where $\mathbb{I}$ is the identity matrix,

$$\mathbb{V} = \left\|\frac{\beta}{SL}\nu_{k_1}(\mathbf{q})\delta_{k_1+k_2,0}\right\|,$$
$$\overline{\mathfrak{M}} = \|\overline{\mathfrak{M}}_{k_1,k_2}(\mathbf{q},\nu,-\mathbf{q},-\nu)\|,$$
$$\overline{\mathfrak{M}}_{k_1,k_2}(\mathbf{q},\nu,-\mathbf{q},-\nu) = i^2\langle T\rho_{k_1}(\mathbf{q},\nu)\rho_{k_2}(-\mathbf{q},-\nu)\rangle$$

is the two-particle correlator, where the averaging is performed with the Hamiltonian of the system:

$$\langle\ldots\rangle = \frac{1}{\Xi}\text{Sp}(e^{-\beta(H-\mu N)}\ldots). \tag{35}$$

With this approximation, the functional representation for Ω_{int} is

$$\Omega_{\text{int}} = -\frac{1}{\beta}\ln\Xi_{\text{int}}$$
$$= -\frac{1}{\beta}\ln\prod_{\mathbf{q}\neq 0}\prod_{\nu}\prod_{k}\left(\frac{\beta}{SL}\nu_k(\mathbf{q})\right)^{-1/2}\int(d\omega)J_G(\omega). \tag{36}$$

This Gaussian functional integral can be easily calculated. The result is

$$\Omega_{\text{int}} = -\frac{1}{2\beta}\sum_{\mathbf{q}\neq 0}\sum_{\nu}\ln\frac{\det g(\mathbf{q},\nu)}{\prod_k\frac{1}{L}\nu_k(\mathbf{q})}. \tag{37}$$

Consequently, the following expression for the thermodynamic potential Ω (18) can be obtained:

$$\Omega = \Omega_0 - \frac{1}{2S}\langle N\rangle_0\sum_{\mathbf{q}\neq 0}\nu(\mathbf{q},0) + \Omega_{\text{int}}, \tag{38}$$

where

$$\Omega_0 = -\frac{1}{\beta}\ln\Xi_0 = -\frac{1}{\beta}\sum_{\mathbf{k}_\parallel,\alpha}\ln[1 + e^{\beta(\mu - E_\alpha(\mathbf{k}_\parallel))}] \tag{39}$$

is the thermodynamical potential of the noninteracting system[1] (the calculation of Ω_0 is done in Appendix B).

Therefore the calculation of the thermodynamic potential in this approach requires knowledge of the effective interelectron interaction by taking into account the presence of the dividing plane. Its Fourier transform satisfies the matrix equation (31). This equation can be written as

$$g_{k_1,k_2}(\mathbf{q},\nu) = \frac{1}{L}\nu_{k_1}(\mathbf{q})\delta_{k_1+k_2,0}$$
$$+ \frac{\beta}{SL}\sum_k\nu_{k_1}(\mathbf{q})D_{-k_1,k}(\mathbf{q},\nu)g_{k,k_2}(\mathbf{q},\nu). \tag{40}$$

Because

$$g_{k_1,k_2}(\mathbf{q},\nu) = \frac{1}{L^2}\int_{-\frac{L}{2}}^{+\frac{L}{2}}dz_1\int_{-\frac{L}{2}}^{+\frac{L}{2}}dz_2$$
$$\times e^{ik_1z_1+ik_2z_2}g(\mathbf{q},\nu,z_1,z_2),$$
$$g(\mathbf{q},\nu,z_1,z_2) = \sum_{k_1,k_2}e^{-ik_1z_1-ik_2z_2}g_{k_1,k_2}(\mathbf{q},\nu) \tag{41}$$

and

$$D_{k_1,k_2}(\mathbf{q},\nu) = \frac{1}{L^2}\int_{-\frac{L}{2}}^{+\frac{L}{2}}dz_1\int_{-\frac{L}{2}}^{+\frac{L}{2}}dz_2$$
$$\times e^{-ik_1z_1-ik_2z_2}D(\mathbf{q},\nu,z_1,z_2),$$
$$D(\mathbf{q},\nu,z_1,z_2) = \sum_{k_1,k_2}e^{ik_1z_1+ik_2z_2}D_{k_1,k_2}(\mathbf{q},\nu), \tag{42}$$

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[1]Because the form of the thermodynamic potential Ω_0 as a function of μ coincides with the thermodynamic potential of an ideal electron gas, the thermodynamic potential Ω_0 (39) is called by us thermodynamic potential of the noninteracting system though it indirectly takes into account the Coulomb interaction between electrons via the chemical potential μ of interacting electrons.

Eq. (40) in $(\mathbf{q},z)$ representation has the form

$$g(\mathbf{q},\nu,z_1,z_2) = \nu(\mathbf{q},z_1 - z_2) + \frac{\beta}{SL^2} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz'$$

$$\times \nu(\mathbf{q},z_1 - z')D(\mathbf{q},\nu,z',z)g(\mathbf{q},\nu,z,z_2). \quad (43)$$

This integral equation was solved with different approximations in Refs. [52–56].

B. The calculation of Ω_{int}

As shown in Eq. (37), the calculation of the thermodynamic potential requires the evaluation of the determinant of the matrix effective interelectron interaction. This is challenging, since the order of the matrix is infinite. We can use the well-known identity (see, for example, Ref. [61])

$$\ln \det \mathbb{A} = \text{Sp} \ln \mathbb{A},$$

with further expansions in series $\ln \mathbb{A}$, then we calculate the trace of each matrix term in the series and sum up the series.

To avoid this, we propose a different procedure (it is equivalent to the approach outlined above). The essence is to build a differential equation for the unknown quantity Ω_{int}. To this end, we introduce the function $J_{\text{G}}(\omega,\lambda)$ instead of $J_{\text{G}}(\omega)$ (30), which depends on the parameter λ:

$$J_{\text{G}}(\omega,\lambda) = \exp\left[-\frac{1}{2}\sum_{\mathbf{q}\neq 0}\sum_{k_1,k_2}\sum_{\nu}\left(\frac{\beta}{S}g_{k_1,k_2}(\mathbf{q},\nu,\lambda)\right)^{-1}\right.$$

$$\left. \times \omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\right], \quad (44)$$

where $g_{k_1,k_2}(\mathbf{q},\nu,\lambda)$ is the Fourier transform of the effective interelectron interaction, which depends on the parameter λ,

$$\left(\frac{\beta}{S}g_{k_1,k_2}(\mathbf{q},\nu,\lambda)\right)^{-1}$$

$$= \left(\frac{\beta}{SL}\nu_{k_1}(\mathbf{q})\right)^{-1}\delta_{k_1+k_2,0} - \lambda D_{k_1,k_2}(\mathbf{q},\nu), \quad (45)$$

moreover, $g_{k_1,k_2}(\mathbf{q},\nu) \equiv g_{k_1,k_2}(\mathbf{q},\nu,1)$, $J_{\text{G}}(\omega) \equiv J_{\text{G}}(\omega,1)$.

Then, Ω_{int} and Ξ_{int} will depend on this parameter as well:

$$\Omega_{\text{int}}(\lambda) = -\frac{1}{\beta}\ln \Xi_{\text{int}}(\lambda)$$

$$= -\frac{1}{\beta}\ln \prod_{\mathbf{q}\neq 0}\prod_{\nu}\prod_{k}\left(\frac{\beta}{SL}\nu_k(\mathbf{q})\right)^{-1/2}\int (d\omega)J_{\text{G}}(\omega,\lambda),$$

$$(46)$$

moreover, $\Omega_{\text{int}} = \Omega_{\text{int}}(1)$.

We need to perform differentiation of $\Omega_{\text{int}}(\lambda)$ with respect to the parameter λ, and arrive at the result

$$\frac{d\Omega_{\text{int}}(\lambda)}{d\lambda}$$

$$= -\frac{1}{2\beta}\sum_{\substack{\mathbf{q}\neq 0,\nu \\ k_1,k_2}} D_{k_1,k_2}(\mathbf{q},\nu)\langle\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\rangle_{\text{G}}(\lambda),$$

$$(47)$$

where we have introduced the average

$$\langle\ldots\rangle_{\text{G}}(\lambda) = \frac{\int (d\omega)J_{\text{G}}(\omega,\lambda)\ldots}{\int (d\omega)J_{\text{G}}(\omega,\lambda)}. \quad (48)$$

Averaging (33) is equivalent to averaging (48) when in the latter the parameter λ is 1, $\langle\ldots\rangle_{\text{G}} = \langle\ldots\rangle_{\text{G}}(1)$.

Therefore $\Omega_{\text{int}}(\lambda)$ satisfies a differential equation of the first order [see Eq. (47)]. In order to obtain an unambiguous solution of the first-order differential equation, it must be supplemented by a single additional condition. It is worth noting that

$$\Omega_{\text{int}}(0) = \frac{1}{\beta}\ln 1 = 0. \quad (49)$$

We easily find the solution of the Cauchy problem (47) and (49):

$$\Omega_{\text{int}} \equiv \Omega_{\text{int}}(1) = -\frac{1}{2\beta}\sum_{\substack{\mathbf{q}\neq 0,\nu \\ k_1,k_2}} D_{k_1,k_2}(\mathbf{q},\nu)$$

$$\times \int_0^1 \langle\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\rangle_{\text{G}}(\lambda)d\lambda. \quad (50)$$

Averaging $\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)$ with the Gaussian distribution $J_{\text{G}}(\omega,\lambda)$ yields

$$\langle\omega_{k_1}(\mathbf{q},\nu)\omega_{k_2}(-\mathbf{q},-\nu)\rangle_{\text{G}}(\lambda) = \frac{\beta}{S}g_{k_1,k_2}(\mathbf{q},\nu,\lambda). \quad (51)$$

Thus we have obtained a convenient expression for the calculation of Ω_{int}:

$$\Omega_{\text{int}} = -\frac{1}{2S}\sum_{\substack{\mathbf{q}\neq 0,\nu \\ k_1,k_2}} D_{k_1,k_2}(\mathbf{q},\nu)\int_0^1 g_{k_1,k_2}(\mathbf{q},\nu,\lambda)d\lambda. \quad (52)$$

Using the relations (41) (which holds for the effective interelectron interaction dependent on λ) and (42), we get

$$\Omega_{\text{int}} = -\frac{1}{2SL^2}\sum_{\mathbf{q}\neq 0,\nu}\int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2\, D(\mathbf{q},\nu,z_1,z_2)$$

$$\times \int_0^1 g(\mathbf{q},\nu,z_1,z_2,\lambda)d\lambda. \quad (53)$$

Further evaluation of Ω_{int} using this formula should be carried out numerically. In order to obtain the analytical results, we make the following approximation: (1) $D \approx \mathfrak{M}^0$, namely, we apply the random phase approximation; and (2) $g(\mathbf{q},\nu,z_1,z_2,\lambda) \approx g(\mathbf{q},0,z_1,z_2,\lambda) \equiv g(\mathbf{q},z_1,z_2,\lambda)$, i.e., we neglect the dependence of the effective interelectron interaction on Bose frequency ν.

Then, the expression for Ω_{int} is simplified:

$$\Omega_{\text{int}} \approx -\frac{1}{2SL^2}\sum_{\mathbf{q}\neq 0}\int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2 \sum_{\nu} \mathfrak{M}^0(\mathbf{q},\nu,z_1,z_2)$$

$$\times \int_0^1 g(\mathbf{q},z_1,z_2,\lambda)d\lambda. \quad (54)$$

In this expression, the summation by the frequency ν only applies to the function

$$\mathfrak{M}^0(\mathbf{q},\nu,z_1,z_2) = \frac{L^2}{\beta} \sum_{\mathbf{k}_{||},\alpha_1,\alpha_2} \frac{n_{\alpha_1}(\mathbf{k}_{||}) - n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q})}{-\mathrm{i}\nu + E_{\alpha_1}(\mathbf{k}_{||}) - E_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q})}$$
$$\times \varphi^*_{\alpha_1}(z_1)\varphi_{\alpha_2}(z_1)\varphi^*_{\alpha_2}(z_2)\varphi_{\alpha_1}(z_2)$$

and can be performed analytically

$$\sum_{\nu} \mathfrak{M}^0(\mathbf{q},\nu,z_1,z_2) = -L^2 \sum_{\mathbf{k}_{||},\alpha_1} n_{\alpha_1}(\mathbf{k}_{||})|\varphi_{\alpha_1}(z_1)|^2 \delta(z_1 - z_2)$$
$$+ L^2 \sum_{\mathbf{k}_{||},\alpha_1,\alpha_2} n_{\alpha_1}(\mathbf{k}_{||})n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q})\varphi^*_{\alpha_1}(z_1)$$
$$\times \varphi_{\alpha_2}(z_1)\varphi^*_{\alpha_2}(z_2)\varphi_{\alpha_1}(z_2), \quad (55)$$

where $\delta(z_1 - z_2)$ is the Dirac delta function.

The effective interelectron interaction $g(\mathbf{q},z_1,z_2,\lambda)$ is the solution of the integral equation

$$g(\mathbf{q},z_1,z_2,\lambda) = \nu(\mathbf{q},z_1 - z_2) + \frac{\beta}{SL^2}\lambda$$
$$\times \int_{-L/2}^{+L/2} dz \int_{-L/2}^{+L/2} dz' \, \nu(\mathbf{q}|z_1 - z'|)$$
$$\times \mathfrak{M}^0(\mathbf{q},0,z',z)g(\mathbf{q},z,z_2,\lambda). \quad (56)$$

Substituting Eq. (55) into Eq. (54) and Eq. (54) in Eq. (38), we find the thermodynamic potential

$$\Omega = \Omega_0 - \frac{1}{2S}\langle N\rangle_0 \sum_{\mathbf{q}\neq 0} \nu(\mathbf{q},0) + \frac{1}{2S}\sum_{\mathbf{q}\neq 0}\sum_{\mathbf{k}_{||},\alpha} n_\alpha(\mathbf{k}_{||})$$
$$\times \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz \, |\varphi_\alpha(z)|^2 \int_0^1 g(\mathbf{q},z,z,\lambda)d\lambda$$
$$- \frac{1}{2S}\sum_{\mathbf{q}\neq 0}\sum_{\mathbf{k}_{||},\alpha_1,\alpha_2} n_{\alpha_1}(\mathbf{k}_{||})n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q})$$
$$\times \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2 \, \varphi^*_{\alpha_1}(z_1)\varphi_{\alpha_2}(z_1)\varphi^*_{\alpha_2}(z_2)\varphi_{\alpha_1}(z_2)$$
$$\times \int_0^1 g(\mathbf{q},z_1,z_2,\lambda)d\lambda. \quad (57)$$

Taking into account the expressions for the one- and two-particle distribution functions of electrons in the semi-infinite jellium [50],

$$F_1^0(z) = \frac{V}{S\langle N\rangle_0}\sum_{\mathbf{k}_{||},\alpha} |\varphi_\alpha(z)|^2 n_\alpha(\mathbf{k}_{||}), \quad (58)$$

$$F_2^0(\mathbf{r}_{||},z_1,z_2) = F_1^0(z_1)F_1^0(z_2) - \frac{V^2}{S^2\langle N\rangle_0^2}$$
$$\times \sum_{\substack{\mathbf{k}_{||},\alpha_1 \\ \mathbf{k}'_{||},\alpha_2}} \mathrm{e}^{\mathrm{i}\mathbf{k}_{||}\mathbf{r}_{||}} n_{\alpha_1}(\mathbf{k}'_{||})n_{\alpha_2}(\mathbf{k}'_{||} - \mathbf{k}_{||})$$
$$\times \varphi^*_{\alpha_1}(z_1)\varphi_{\alpha_2}(z_1)\varphi^*_{\alpha_2}(z_2)\varphi_{\alpha_1}(z_2), \quad (59)$$

the thermodynamic potential can be represented as

$$\Omega = \Omega_0 - \frac{1}{2S}\langle N\rangle_0 \sum_{\mathbf{q}\neq 0} \nu(\mathbf{q},0) + \frac{1}{2}\frac{\langle N\rangle_0 S}{V}$$
$$\times \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz \, F_1^0(z) \int_0^1 d\lambda \, g(\mathbf{r}_{||},z,z,\lambda)\big|_{\mathbf{r}_{||}=0}$$
$$+ \frac{1}{2}\frac{\langle N\rangle_0^2 S}{V^2}\int_S d\mathbf{r}_{||} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2 \, \big(F_2^0(\mathbf{r}_{||},z_1,z_2)$$
$$- F_1^0(z_1)F_1^0(z_2)\big) \int_0^1 d\lambda \, g(\mathbf{r}_{||},z_1,z_2,\lambda), \quad (60)$$

where

$$g(\mathbf{r}_{||},z_1,z_2,\lambda) = \frac{1}{S}\sum_{\mathbf{q}} \mathrm{e}^{\mathrm{i}\mathbf{q}\mathbf{r}_{||}} g(\mathbf{q},z_1,z_2,\lambda) \quad (61)$$

is the effective interelectron interaction in the coordinate representation, which depends on the parameter λ.

It should be noted that the expressions (58) and (59) coincide by form with the expressions for the distribution functions of electrons without the Coulomb interaction, but these distribution functions depend on the chemical potential μ of interacting electrons.

C. Thermodynamic potential in the case of the infinite barrier model

The form of the surface potential $V_{\mathrm{surf}}(z)$ must be specified to perform further calculation of the thermodynamic potential according to the expressions (57) or (60). We use the infinite barrier model for the surface potential, namely,

$$V_{\mathrm{surf}}(z) = \begin{cases} \infty, & z > d, \\ 0, & z < d. \end{cases} \quad (62)$$

The wave functions and the corresponding energy levels for the model are

$$\varphi_\alpha(z) = \frac{2}{\sqrt{L+2d}} \begin{cases} \sin(\alpha(d-z)), & z \leqslant d, \\ 0, & z > d, \end{cases}$$
$$\varepsilon_\alpha = \frac{\hbar^2\alpha^2}{2m}, \quad (63)$$

where

$$\alpha = \frac{\pi n}{\left(\frac{L}{2}+d\right)}, \quad n = 1,2,3,\ldots. \quad (64)$$

The one-particle distribution function of the model is

$$F_1^0(z) = \left[1 + \frac{3\cos(2\mathcal{K}_F(d-z))}{(2\mathcal{K}_F(d-z))^2} - \frac{3\sin(2\mathcal{K}_F(d-z))}{(2\mathcal{K}_F(d-z))^3}\right]$$
$$\times \theta(d-z). \quad (65)$$

This expression for $d = 0$ coincides by form with the one-particle distribution function without the Coulomb interaction [62–65], but the expression (65) takes into account the Coulomb interaction through the magnitude of the Fermi wave vector $\mathcal{K}_F$ of interacting electrons.

The parameter d, which determines the position of the infinite potential barrier, is determined by the condition of

electroneutrality:

$$\lim_{L \to \infty} \int_{-L/2}^{L/2} dz \left(F_1^0(z) - \frac{1}{\varrho_0} \varrho_{\text{jell}}(z) \right)$$

$$= \lim_{L \to \infty} \int_{-L/2}^{L/2} dz \left(F_1^0(z) - \theta(-z) \right) = 0.$$

From this condition it follows that

$$d = \frac{3\pi}{8\mathcal{K}_F}, \tag{66}$$

i.e., this parameter is inversely proportional to the magnitude of the Fermi wave vector.

Using the technique to solve the integral equation (56) (see Refs. [53,54]), we obtain the following expression for the effective interelectron interaction $g(\mathbf{q}, z_1, z_2, \lambda)$,

$$g(q, z_1 \leqslant d, z_2 \leqslant d, \lambda)$$
$$= \frac{2\pi e^2}{Q(\lambda)} \left[e^{-Q(\lambda)|z_1 - z_2|} + \frac{Q(\lambda) - q}{Q(\lambda) + q} e^{Q(\lambda)(z_1 + z_2 - 2d)} \right],$$

$$g(q, z_1 \geqslant d, z_2 \geqslant d, \lambda)$$
$$= \frac{2\pi e^2}{q} \left[e^{-q|z_1 - z_2|} - \frac{Q(\lambda) - q}{Q(\lambda) + q} e^{-q(z_1 + z_2 - 2d)} \right],$$

$$g(q, z_1 \geqslant d, z_2 \leqslant d, \lambda) = \frac{4\pi e^2}{Q(\lambda) + q} e^{Q(\lambda)(z_2 - d) - q(z_1 - d)},$$

$$g(q, z_1 \leqslant d, z_2 \geqslant d, \lambda) = \frac{4\pi e^2}{Q(\lambda) + q} e^{Q(\lambda)(z_1 - d) - q(z_2 - d)},$$

where $Q(\lambda) = \sqrt{q^2 + \lambda \varkappa_{\text{TF}}^2 \text{L}(\frac{q}{2\mathcal{K}_F})}$, $\text{L}(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$, $\varkappa_{\text{TF}} = \sqrt{\frac{4}{\pi} \frac{\mathcal{K}_F}{a_B}}$ is the inverse Thomas-Fermi radius of screening, and a_B is the Bohr radius.

After the summation by the wave vector $\mathbf{k}_{||}$ in (57), we get

$$\Omega = \Omega_{\text{bulk}} + \Omega_{\text{surf}}, \tag{67}$$

where the first term is the extensive contribution to the thermodynamic potential (it is proportional to the volume of the system SL), the second term is the surface contribution (it is proportional to the area of the dividing plane S). The extensive contribution to the thermodynamic potential is

$$\Omega_{\text{bulk}} = \Omega_{0,\text{bulk}} + \Delta\Omega_{\text{bulk}}, \tag{68}$$

where

$$\frac{\Omega_{0,\text{bulk}}}{SL/2} = -\frac{\hbar^2}{15m\pi^2} \mathcal{K}_F^5 = -\frac{2}{15\pi^2} (\mathcal{K}_F a_B)^5 \frac{\text{Ry}}{a_B^3} \tag{69}$$

is the extensive contribution to the thermodynamic potential of the noninteracting system per unit volume [see Eq. (B3)]. This contribution depends on the magnitude of the Fermi wave vector $\mathcal{K}_F$ of interacting electrons. $\Delta\Omega_{\text{bulk}}$ has the form

$$\frac{\Delta\Omega_{\text{bulk}}}{SL/2} = \frac{e^2 \mathcal{K}_F^3}{6\pi^2} \int_0^\infty dq \left[\int_0^1 d\lambda \frac{q}{Q(\lambda)} - 1 \right]$$
$$- \frac{e^2}{2\pi^4} \int_0^\infty dq\, q \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2 \widetilde{J}(q, \alpha_1, \alpha_2)$$
$$\times \int_0^1 d\lambda\, g_1(q, \alpha_1, \alpha_2, \lambda), \tag{70}$$

where

$$\widetilde{J}(q, \alpha_1, \alpha_2)$$
$$= \begin{cases} \begin{cases} \pi c_1^2, & c_2 > c_1, \\ \pi c_2^2, & c_1 > c_2, \end{cases} & 0 \leqslant q < |c_1 - c_2|, \\ f(c_1, c_2, q) + f(c_2, c_1, q), & |c_1 - c_2| \leqslant q < c_1 + c_2, \\ 0, & q \geqslant c_1 + c_2, \end{cases}$$

$$c_1 = \sqrt{\mathcal{K}_F^2 - \alpha_1^2}, \quad c_2 = \sqrt{\mathcal{K}_F^2 - \alpha_2^2},$$

$$f(c_1, c_2, q) = c_1^2 \left(\frac{\pi}{2} - \arcsin \frac{c_1^2 - c_2^2 + q^2}{2q c_1} \right)$$
$$- \frac{c_1^2 - c_2^2 + q^2}{2q} \sqrt{c_1^2 - \frac{(c_1^2 - c_2^2 + q^2)^2}{4q^2}},$$

$$g_1(q, \alpha_1, \alpha_2, \lambda) = \frac{Q^2(\lambda) + \alpha_1^2 + \alpha_2^2}{\left(Q^2(\lambda) + \alpha_1^2 + \alpha_2^2 \right)^2 - 4\alpha_1^2 \alpha_2^2}.$$

It should be noted that the dividing plane has no effect on the expression given by Eq. (68) and actually this expression is the thermodynamic potential of the homogeneous system per unit volume. However, the thermodynamic potential of the homogeneous system can be calculated in a similar manner, based on the Hamiltonian of the infinite jellium (5). These calculations are much simpler, and at the similar level of approximations, we obtain

$$\frac{\Omega_{\text{unif}}}{V} = -\frac{\hbar^2}{15m\pi^2} \mathcal{K}_F^5 + \frac{\mathcal{K}_F^3}{12\pi^4} \int_0^\infty dq\, q^2$$
$$\times \left[\int_0^1 d\lambda\, g_{\text{unif}}(q, \lambda) - \nu(q) \right]$$
$$- \frac{\mathcal{K}_F^3}{12\pi^4} \int_0^\infty dq\, q^2 \widetilde{J}_{\text{unif}}(q) \int_0^1 d\lambda\, g_{\text{unif}}(q, \lambda), \tag{71}$$

where

$$\widetilde{J}_{\text{unif}}(q) = \begin{cases} 1 - \frac{3}{4} \frac{q}{\mathcal{K}_F} + \frac{1}{16} \frac{q^3}{\mathcal{K}_F^3}, & q < 2\mathcal{K}_F, \\ 0, & q \geqslant 2\mathcal{K}_F, \end{cases}$$

$\nu(q) = \frac{4\pi e^2}{q^2}$ is the three-dimensional Fourier transform of the Coulomb interaction,

$$g_{\text{unif}}(q, \lambda) = \frac{4\pi e^2}{q^2 + \lambda \varkappa_{\text{TF}}^2 \text{L}\left(\frac{q}{2\mathcal{K}_F} \right)}$$

is the three-dimensional Fourier transform of the effective interelectron interaction of the homogeneous system that depends on the parameter λ.

Integration by the parameter λ in the expression given by Eq. (71) can be easily performed and as a result we obtain

$$\frac{\Omega_{\text{unif}}}{V} = -\frac{\hbar^2}{15m\pi^2} \mathcal{K}_F^5 - \frac{e^2 \mathcal{K}_F^3}{3\pi^3} \int_0^\infty dq$$
$$\times \left[1 - \frac{q^2(1 - \widetilde{J}_{\text{unif}}(q))}{\varkappa_{\text{TF}}^2 \text{L}\left(\frac{q}{2\mathcal{K}_F} \right)} \ln \left(1 + \frac{\varkappa_{\text{TF}}^2}{q^2} \text{L}\left(\frac{q}{2\mathcal{K}_F} \right) \right) \right]. \tag{72}$$

Although Eqs. (68)–(70) and (72) are different by form, they both lead to the same result, namely to the thermodynamic potential of the homogeneous system in the random phase approximation.

The surface contribution to the thermodynamic potential has the form

$$\Omega_{\text{surf}} = \Omega_{0,\text{surf}} + \Delta\Omega_{\text{surf}}, \tag{73}$$

is the surface contribution to the thermodynamic potential of the noninteracting system per unit area [see Eq. (B4)], which depends on the magnitude of the Fermi wave vector $\mathcal{K}_F$ of interacting electrons,

$$\frac{\Delta\Omega_{\text{surf}}}{S} = \frac{e^2 d\,\mathcal{K}_F^3}{6\pi^2}\int_0^\infty dq\left[\int_0^1 d\lambda\,\frac{q}{Q(\lambda)} - 1\right] + \frac{e^2\mathcal{K}_F^2}{16\pi}\int_0^\infty dq$$

$$+ \frac{e^2\mathcal{K}_F^3}{12\pi^2}\int_0^\infty dq\int_0^1 d\lambda\,\frac{q}{Q^2(\lambda)}\frac{Q(\lambda)-q}{Q(\lambda)+q}\left[1 + \frac{3Q^2(\lambda)}{2\mathcal{K}_F^2} - \frac{3Q(\lambda)(\mathcal{K}_F^2 + Q^2(\lambda))}{2\mathcal{K}_F^2}\arctan\frac{\mathcal{K}_F}{Q(\lambda)}\right]$$

$$- \frac{e^2}{4\pi^4}\int_0^\infty dq\,q\int_0^{\mathcal{K}_F} d\alpha_1\int_0^{\mathcal{K}_F} d\alpha_2\,\widetilde{J}(q,\alpha_1,\alpha_2)\int_0^1 d\lambda\,g_2(q,\alpha_1,\alpha_2,\lambda), \tag{75}$$

$$g_2(q,\alpha_1,\alpha_2,\lambda) = \left\{2g_1(q,\alpha_1,\alpha_2,\lambda)\,d + \left(\frac{Q(\lambda)-q}{Q(\lambda)+q} - 2\right)\frac{16Q(\lambda)\alpha_1^2\alpha_2^2}{\left[\left(Q^2(\lambda)+\alpha_1^2+\alpha_2^2\right)^2 - 4\alpha_1^2\alpha_2^2\right]^2}\right\}.$$

It is worth mentioning that the second term in the expression given by Eq. (75) (it is linear on the chemical potential and is quadratic on the magnitude of the Fermi wave vector $\mathcal{K}_F$) contains the divergent integral. However, as we will see below, this divergent integral disappears in the calculation of the internal energy.

V. INTERNAL ENERGY

A. General expressions

By using the thermodynamic potential Ω and the Gibbs-Helmholtz equation generalized for the case of variable number of particles, we obtain the internal energy of the system U,

$$U = \Omega - \theta\frac{\partial\Omega}{\partial\theta} - \mu\frac{\partial\Omega}{\partial\mu}. \tag{76}$$

At low temperatures $\theta \to 0$, the second term of the right-hand side (r.h.s.) of this equation vanishes and we get

$$U = \Omega + \mu\langle N\rangle, \tag{77}$$

where we have used the relation

$$\langle N\rangle = \frac{1}{\Xi}\text{Sp}(e^{\beta(H-\mu N)}N) = -\frac{\partial\Omega}{\partial\mu}. \tag{78}$$

According to Eq. (67), the thermodynamic potential can be divided into the extensive and surface contributions. Then we get

$$\langle N\rangle = -\frac{\partial(\Omega_{\text{bulk}} + \Omega_{\text{surf}})}{\partial\mu} = N_{\text{bulk}} + N_{\text{surf}}, \tag{79}$$

where

$$N_{\text{bulk}} = -\frac{\partial\Omega_{\text{bulk}}}{\partial\mu}, \tag{80}$$

$$N_{\text{surf}} = -\frac{\partial\Omega_{\text{surf}}}{\partial\mu}, \tag{81}$$

where

$$\frac{\Omega_{0,\text{surf}}}{S} = \frac{\hbar^2\mathcal{K}_F^4}{m\pi^2}\left(\frac{\pi}{32} - \frac{d\,\mathcal{K}_F}{15}\right)$$

$$= \frac{2}{\pi^2}\left(\frac{\pi}{32} - \frac{d\,\mathcal{K}_F}{15}\right)(\mathcal{K}_F a_B)^4\frac{\text{Ry}}{a_B^2} \tag{74}$$

and

$$U = U_{\text{bulk}} + U_{\text{surf}},$$

$$U_{\text{bulk}} = \Omega_{\text{bulk}} - \mu\frac{\partial\Omega_{\text{bulk}}}{\partial\mu} = \Omega_{\text{bulk}} + \mu N_{\text{bulk}}, \tag{82}$$

$$U_{\text{surf}} = \Omega_{\text{surf}} - \mu\frac{\partial\Omega_{\text{surf}}}{\partial\mu} = \Omega_{\text{surf}} + \mu N_{\text{surf}} \tag{83}$$

are the extensive and surface contributions to the internal energy, respectively.

The chemical potential μ is the solution of Eq. (78). By using (79) in the thermodynamic limit, we get

$$\lim_{N,S,L\to\infty}\frac{\langle N\rangle}{SL/2} = \lim_{N,S,L\to\infty}\frac{N_{\text{bulk}}}{SL/2} = \frac{3}{4\pi}\frac{1}{r_s^3},$$

where r_s is the Wigner-Seitz radius in units of the Bohr radius a_B. Moreover, in the thermodynamic limit, the summand N_{surf} does not affect the chemical potential μ (but affects the surface contribution to the internal energy U_{surf}) and the equation for μ can be presented as

$$\langle N\rangle = -\frac{\partial\Omega_{\text{bulk}}}{\partial\mu}. \tag{84}$$

According to Eqs. (82) and (83), in order to calculate the extensive U_{bulk} and the surface U_{surf} contributions to the internal energy, we need to evaluate the extensive N_{bulk} and surface N_{surf} contributions to the average of the number operator of electrons $\langle N\rangle$.

B. Average of the number operator of electrons and the chemical potential

According to Eqs. (80) and (81), N_{bulk} and N_{surf} can be calculated by taking the derivatives of Ω_{bulk} and Ω_{surf} with respect to the chemical potential μ, respectively. However, it

is easier to use the functional representation of the thermodynamic potential Ω [see Eq. (36)] and compute the derivative of this expression (38) with respect to the chemical potential μ. As a result, we find that

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu}
$$
$$
+ \frac{1}{2\beta} \sum_{\substack{\mathbf{q} \neq 0, \nu \\ k_1, k_2}} \frac{\partial D_{k_1,k_2}(\mathbf{q},\nu)}{\partial \mu} \langle \omega_{k_1}(\mathbf{q},\nu) \omega_{k_2}(-\mathbf{q},-\nu) \rangle_G,
$$
$$
\tag{85}
$$

where averaging $\langle \ldots \rangle_G$ is performed according to Eq. (33).

Considering that

$$
\left\langle \omega_{k_1}(\mathbf{q},\nu) \omega_{k_2}(-\mathbf{q},-\nu) \right\rangle_G = \frac{\beta}{S} g_{k_1,k_2}(\mathbf{q},\nu), \tag{86}
$$

Eq. (85) can be rewritten as

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu}
$$
$$
+ \frac{1}{2S} \sum_{\substack{\mathbf{q} \neq 0, \nu \\ k_1, k_2}} \frac{\partial D_{k_1,k_2}(\mathbf{q},\nu)}{\partial \mu} g_{k_1,k_2}(\mathbf{q},\nu). \tag{87}
$$

Taking into account Eqs. (41) and (42), we obtain

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu}
$$
$$
+ \frac{1}{2SL^2} \sum_{\mathbf{q} \neq 0, \nu} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2 \frac{\partial D(\mathbf{q},\nu,z_1,z_2)}{\partial \mu}
$$
$$
\times g(\mathbf{q},\nu,z_1,z_2). \tag{88}
$$

In order to simplify this expression, we make similar approximations as in the calculation of the thermodynamic potential (see page 15). Then the expression given by Eq. (88) is greatly simplified and

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu}
$$
$$
+ \frac{1}{2SL^2} \sum_{\mathbf{q} \neq 0} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2
$$
$$
\times \sum_{\nu} \frac{\partial \mathfrak{M}^0(\mathbf{q},\nu,z_1,z_2)}{\partial \mu} g(\mathbf{q},z_1,z_2), \tag{89}
$$

where the summation by the frequency ν applies only to the derivative of the two-particle correlator with respect to the chemical potential μ and can be performed analytically,

$$
\sum_{\nu} \frac{\partial \mathfrak{M}^0(\mathbf{q},\nu,z_1,z_2)}{\partial \mu}
$$
$$
= -L^2 \sum_{\mathbf{k}_{||},\alpha_1} \frac{\partial n_{\alpha_1}(\mathbf{k}_{||})}{\partial \mu} |\varphi_{\alpha_1}(z_1)|^2 \delta(z_1 - z_2)
$$

$$
+ L^2 \sum_{\mathbf{k}_{||},\alpha_1,\alpha_2} \frac{\partial n_{\alpha_1}(\mathbf{k}_{||})}{\partial \mu} (n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q}) + n_{\alpha_2}(\mathbf{k}_{||} + \mathbf{q}))
$$
$$
\times \varphi_{\alpha_1}^*(z_1) \varphi_{\alpha_2}(z_1) \varphi_{\alpha_2}^*(z_2) \varphi_{\alpha_1}(z_2). \tag{90}
$$

Substituting Eq. (90) into Eq. (89), we find

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu}
$$
$$
- \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \sum_{\mathbf{k}_{||},\alpha} \frac{\partial n_\alpha(\mathbf{k}_{||})}{\partial \mu} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz \, |\varphi_\alpha(z)|^2 g(\mathbf{q},z,z)
$$
$$
+ \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \sum_{\mathbf{k}_{||},\alpha_1,\alpha_2} \frac{\partial \big(n_{\alpha_1}(\mathbf{k}_{||}) n_{\alpha_2}(\mathbf{k}_{||} - \mathbf{q})\big)}{\partial \mu}
$$
$$
\times \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2 \, \varphi_{\alpha_1}^*(z_1) \varphi_{\alpha_2}(z_1) \varphi_{\alpha_2}^*(z_2)
$$
$$
\times \varphi_{\alpha_1}(z_2) g(\mathbf{q},z_1,z_2). \tag{91}
$$

Taking into account the expressions for the one- (58) and two-particle (59) distribution functions of electrons in the semi-infinite jellium [50], we get

$$
\langle N \rangle = \langle N \rangle_0 + \frac{1}{2S} \sum_{\mathbf{q} \neq 0} \nu(\mathbf{q},0) \frac{\partial \langle N \rangle_0}{\partial \mu} - \frac{1}{2} \frac{S}{V}
$$
$$
\times \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz \frac{\partial \big(\langle N \rangle_0 F_1^0(z)\big)}{\partial \mu} g(\mathbf{r}_{||},z,z)\big|_{\mathbf{r}_{||}=0}
$$
$$
- \frac{1}{2} \frac{S}{V^2} \int_S d\mathbf{r}_{||} \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{+\frac{L}{2}} dz_2
$$
$$
\times \frac{\partial \big(\langle N \rangle_0^2 \big(F_2^0(\mathbf{r}_{||},z_1,z_2) - F_1^0(z_1) F_1^0(z_2)\big)\big)}{\partial \mu}
$$
$$
\times g(\mathbf{r}_{||},z_1,z_2), \tag{92}
$$

where $g(\mathbf{r}_{||},z_1,z_2)$ is the effective interelectron interaction in the coordinate representation [note that the transition to the coordinate representation is similar to Eq. (61)]. The calculations of $\langle N \rangle_0$ and $\partial \langle N \rangle_0 / \partial \mu$ are done in Appendix C.

C. Average of the number operator of electrons for the infinite barrier model

For further calculation of (91) or (92), as in above, we consider the infinite barrier model (62) of the surface potential $V_{\text{surf}}(z)$. After the summation over the wave vector $\mathbf{k}_{||}$ in Eq. (91), we get

$$
N_{\text{bulk}} = N_{0,\text{bulk}} + \Delta N_{\text{bulk}}, \tag{93}
$$

where

$$
\frac{N_{0,\text{bulk}}}{SL/2} = \frac{\mathcal{K}_F^3}{3\pi^2} \tag{94}
$$

is the extensive contribution to the average of the number operator $\langle N \rangle$ of the noninteracting system per unit volume [see Eq. (C1)]. This contribution depends on the magnitude of the Fermi wave vector $\mathcal{K}_F$ of the interacting electrons. ΔN_{bulk}

has the form

$$\frac{\Delta N_{\text{bulk}}}{SL/2} = \frac{\mathcal{K}_{\text{F}}}{2\pi^2 a_{\text{B}}} \int_0^\infty dq \left(1 - \frac{q}{Q}\right) + \frac{2}{\pi^4 a_{\text{B}}} \int_0^\infty dq\, q \int_0^{\mathcal{K}_{\text{F}}} d\alpha_1 \int_0^{\mathcal{K}_{\text{F}}} d\alpha_2\, I(q,\alpha_1,\alpha_2)\, g_1(q,\alpha_1,\alpha_2,1), \qquad (95)$$

$Q \equiv Q(1)$,

$$I(q,\alpha_1,\alpha_2) = \begin{cases} \left\{ \begin{matrix} 0, & 0 \leqslant q \leqslant c_1 - c_2, \\ \arccos \frac{q^2 + c_1^2 - c_2^2}{2c_1 q}, & c_1 - c_2 < q \leqslant c_1 + c_2, \\ 0, & c_1 + c_2 < q < \infty, \end{matrix} \right\}, & c_1 > c_2, \\[3ex] \left\{ \begin{matrix} \pi, & 0 \leqslant q \leqslant c_2 - c_1, \\ \arccos \frac{q^2 + c_1^2 - c_2^2}{2c_1 q}, & c_2 - c_1 < q \leqslant c_1 + c_2, \\ 0, & c_1 + c_2 < q < \infty, \end{matrix} \right\}, & c_2 \geqslant c_1, \end{cases} \qquad (96)$$

where

$$c_1 = \sqrt{\mathcal{K}_{\text{F}}^2 - \alpha_1^2}, \quad c_2 = \sqrt{\mathcal{K}_{\text{F}}^2 - \alpha_2^2}.$$

It should be noted that the dividing plane has no effect on the expressions (93)–(95) and therefore Eq. (93) is the number of electrons of the homogeneous system per unit volume. However, the number of electrons of the homogeneous system can similarly be calculated from the Hamiltonian of the infinite jellium (5). These calculations are much simpler and with similar approximations we obtain

$$\frac{N_{\text{unif}}}{V} = \frac{\mathcal{K}_{\text{F}}^3}{3\pi^2} + \frac{\mathcal{K}_{\text{F}}}{4\pi^4} \frac{m}{\hbar^2} \int_0^\infty dq\, q^2 \left(v(q) - g_{\text{unif}}(q)\right)$$
$$+ \frac{\mathcal{K}_{\text{F}}}{4\pi^4} \frac{m}{\hbar^2} \int_0^\infty dq\, q^2\, \widetilde{I}_{\text{unif}}(q)\, g_{\text{unif}}(q), \qquad (97)$$

where

$$\widetilde{I}_{\text{unif}}(q) = \begin{cases} 2, & \frac{q}{2\mathcal{K}_{\text{F}}} \leqslant -1, \\ 1 - \frac{q}{2\mathcal{K}_{\text{F}}}, & -1 < \frac{q}{2\mathcal{K}_{\text{F}}} \leqslant 1, \\ 0, & \frac{q}{2\mathcal{K}_{\text{F}}} > 1, \end{cases}$$

$$g_{\text{unif}}(q) = \frac{4\pi e^2}{q^2 + \varkappa_{\text{TF}}^2 \text{L}\left(\frac{q}{2\mathcal{K}_{\text{F}}}\right)}$$

is the three-dimensional Fourier transform of the effective interelectron interaction of the homogeneous system.

Substituting the expressions for the three-dimensional Fourier transforms of the Coulomb interaction $v(q)$ and the effective interelectron interaction $g_{\text{unif}}(q)$ into Eq. (97), we get

$$\frac{N_{\text{unif}}}{V} = \frac{\mathcal{K}_{\text{F}}^3}{3\pi^2} + \frac{\mathcal{K}_{\text{F}}}{\pi^3 a_{\text{B}}} \int_0^\infty dq\, \frac{\left(\varkappa_{\text{TF}}^2 \text{L}\left(\frac{q}{2\mathcal{K}_{\text{F}}}\right) + q^2 \widetilde{I}_{\text{unif}}(q)\right)}{q^2 + \varkappa_{\text{TF}}^2 \text{L}\left(\frac{q}{2\mathcal{K}_{\text{F}}}\right)}. \qquad (98)$$

The expressions (93)–(95) and (98) are nonlinear algebraic equations for the chemical potential μ ($\mu = \frac{\hbar^2 \mathcal{K}_{\text{F}}^2}{2m}$). Although their form is different but they yield the same result, because the dividing plane does not affect the chemical potential.

In Fig. 1, the chemical potential as a function of the Wigner-Seitz radius r_{s} is presented. The nomenclature of lines is given in the figure caption. It is worth noting that the chemical potential is the solution of nonlinear algebraic equations (98), and the chemical potential of noninteracting

electrons is

$$\mu_0 = \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{(r_{\text{s}}/a_{\text{B}})^2} \text{ Ry}. \qquad (99)$$

It can be seen that taking into account the Coulomb interaction leads to a decrease of the chemical potential of electrons.

In Fig. 2, the parameter d, $d = 3\pi/(8\mathcal{K}_{\text{F}})$, as a function of the Wigner-Seitz radius r_{s} is given. The parameter d is the distance from the infinite potential barrier to the dividing plane ($z = 0$). The conclusion from the curves is that taking into account the Coulomb interaction between electrons leads to an increase of this distance and its nonlinear dependence on r_{s}, whereas the parameter d for the noninteracting system is a linear function of r_{s}.

In the case of noninteracting electrons, the distance d increases linearly with increasing Wigner-Seitz radius ($d \sim 1/\sqrt{\mu_0} \sim r_{\text{s}}$) because the average distance between the electrons increases, and electrons can travel farther into the region $z \geqslant 0$. The Coulomb repulsion between the electrons leads to an additional increase of the average distance between the electrons. Therefore electrons can travel even farther into the
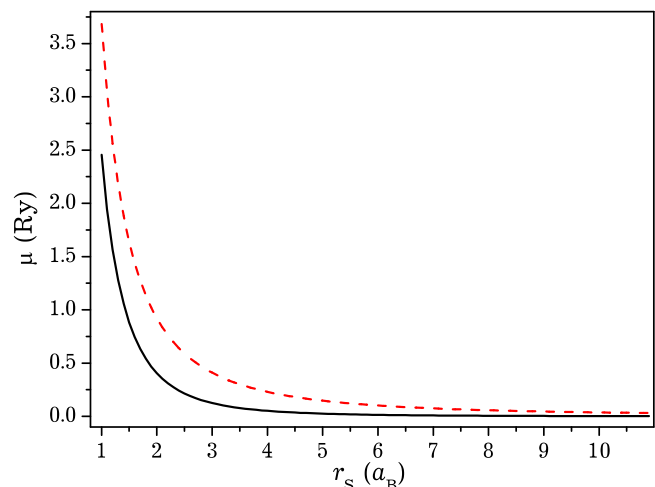

FIG. 1. (Color online) The chemical potential of the interacting electrons μ (solid line) and the chemical potential of the noninteracting electrons μ_0 (dashed line) as a function of the Wigner-Seitz radius.
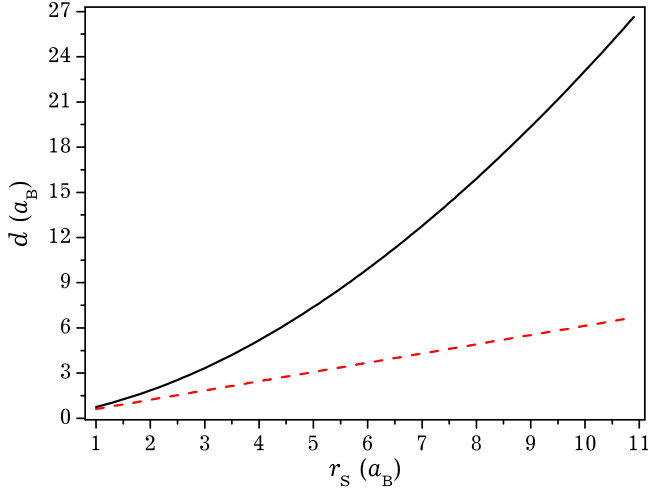
FIG. 2. (Color online) The parameter d as a function of the Wigner-Seitz radius (solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

region $z \geqslant 0$, the distance d as a function of Wigner-Seitz radius increases faster than linearly.

In Fig. 3, the one-particle distribution function of electrons (65) is presented for the following values of Wigner-Seitz radius: $r_s = 2\,a_B$ and $r_s = 6\,a_B$. The one-particle function of electrons (solid lines) depends on the chemical potential, which is the solution of the nonlinear algebraic equations (98) (here the Coulomb interaction is taken into account). The positive charge is located at $z \leqslant 0$. It can be concluded that taking into account the Coulomb interaction leads to an increase of the period of damped oscillations of the one-particle distribution function around its value in the body of the metal, which equals to unity.

The surface contribution to the average number of electrons $\langle N \rangle$ has the form

$$N_{\text{surf}} = N_{0,\text{surf}} + \Delta N_{\text{surf}}, \tag{100}$$

where

$$\frac{N_{0,\text{surf}}}{S} = \frac{\mathcal{K}_F^2}{\pi^2}\left(\frac{d\,\mathcal{K}_F}{3} - \frac{\pi}{8}\right) \tag{101}$$
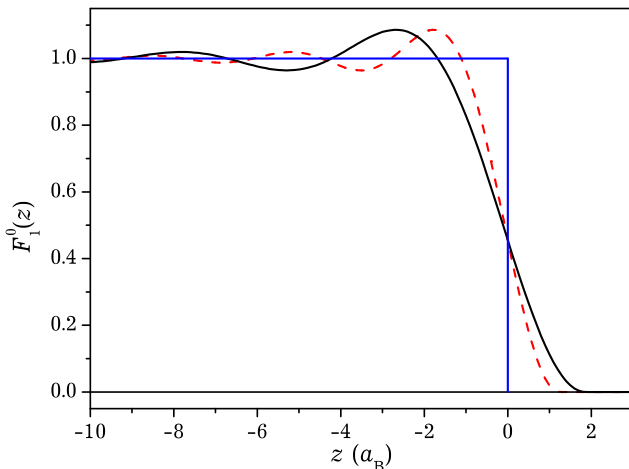
is the surface contribution to the average number of the noninteracting electron system per unit area [see Eq. (C2)], which depends on the magnitude of the Fermi wave vector $\mathcal{K}_F$ of the interacting electrons, and

$$\begin{aligned}
\frac{\Delta N_{\text{surf}}}{S} &= \frac{d\,\mathcal{K}_F}{2\pi^2 a_B}\int_0^\infty dq\left(1 - \frac{q}{Q}\right) - \frac{1}{8\pi a_B}\int_0^\infty dq \\
&\quad - \frac{\mathcal{K}_F}{4\pi^2 a_B}\int_0^\infty dq\,\frac{q}{Q^2}\frac{Q-q}{Q+q}\left(1 - \frac{Q}{\mathcal{K}_F}\arctan\frac{\mathcal{K}_F}{Q}\right) \\
&\quad + \frac{1}{\pi^4 a_B}\int_0^\infty dq\,q\int_0^{\mathcal{K}_F}d\alpha_1\int_0^{\mathcal{K}_F}d\alpha_2\,I(q,\alpha_1,\alpha_2) \\
&\quad \times g_1(q,\alpha_1,\alpha_2,1).
\end{aligned} \tag{102}$$

By placing the parameter d (66) in Eq. (101), we obtain

$$N_{0,\text{surf}} = 0$$

and

$$N_{\text{surf}} = \Delta N_{\text{surf}}.$$

Namely, if we take into account the Coulomb interaction between electrons, then the surface contribution to the average number of electrons $\langle N \rangle$ is not zero.

It should be noted that the second term in Eq. (102), (which is linear on the chemical potential and is quadratic on the magnitude of the Fermi wave vector $\mathcal{K}_F$) contains the divergent integral. However, as we will see below, this divergent integral disappears in the calculation of the internal energy.

D. Surface energy

Substituting Eqs. (60) and (92) into Eq. (77), we obtain the internal energy. This expression can be considered as one possible energy functional that, in contrast to the functionals used in the density functional theory, depends not only on the one-particle distribution function of the electrons, but also on the two-particle distribution function and the effective interelectron interaction.

The extensive contribution to the internal energy per unit volume follows from the substitution of Ω_{bulk} and N_{bulk} (or
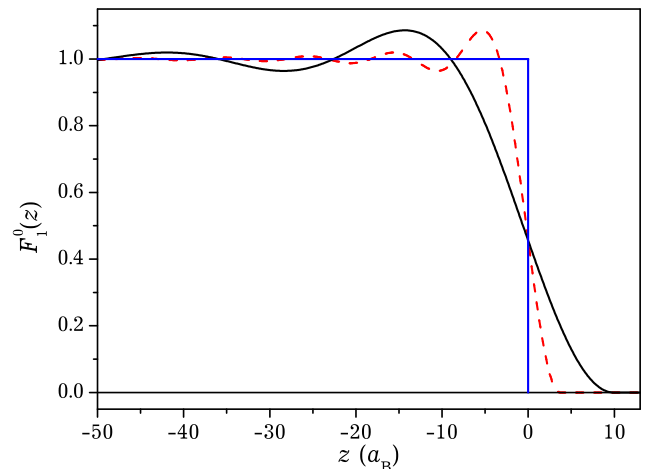

FIG. 3. (Color online) The one-particle distribution function of electrons as a function of the electron coordinate normal to the dividing plane at $r_s = 2\,a_B$ (left) and $r_s = 6\,a_B$ (right) (the solid line is for interacting electrons whereas the dashed line is for noninteracting electrons).

Ω_{unif} and N_{unif}) into Eq. (82). Then we get

$$
\frac{U_{\text{bulk}}}{SL/2} = \frac{\hbar^2}{10m\pi^2}\mathcal{K}_F^5 - \frac{e^2\mathcal{K}_F^3}{6\pi^2}\int_0^\infty dq\left[1 - \int_0^1 d\lambda\,\frac{q}{Q(\lambda)}\right] + \frac{e^2\mathcal{K}_F^3}{4\pi^2}\int_0^\infty dq\left(1 - \frac{q}{Q}\right) + \frac{e^2\mathcal{K}_F^2}{\pi^4}\int_0^\infty dq\,q
$$
$$
\times \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2\, I(q,\alpha_1,\alpha_2)\, g_1(q,\alpha_1,\alpha_2,1) - \frac{e^2}{2\pi^4}\int_0^\infty dq\,q \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2\,\tilde{J}(q,\alpha_1,\alpha_2)\int_0^1 d\lambda\, g_1(q,\alpha_1,\alpha_2,\lambda)
$$

(103)

or

$$
\frac{U_{\text{unif}}}{V} = \frac{\hbar^2}{10m\pi^2}\mathcal{K}_F^5 + \frac{e^2\mathcal{K}_F^3}{\pi^3}\int_0^\infty dq\left[\frac{1}{2}\frac{\left(\varkappa_{\text{TF}}^2\mathrm{L}\left(\frac{q}{2\mathcal{K}_F}\right) + q^2\tilde{I}_{\text{unif}}(q)\right)}{q^2 + \varkappa_{\text{TF}}^2\mathrm{L}\left(\frac{q}{2\mathcal{K}_F}\right)} - \frac{1}{3} + \frac{q^2(1 - \tilde{J}_{\text{unif}}(q))}{3\varkappa_{\text{TF}}^2\mathrm{L}\left(\frac{q}{2\mathcal{K}_F}\right)}\ln\left(1 + \frac{\varkappa_{\text{TF}}^2}{q^2}\mathrm{L}\left(\frac{q}{2\mathcal{K}_F}\right)\right)\right], \quad (104)
$$

where the first term of the expression (103), or (104), is the internal energy of the noninteracting system.

By using the expressions for Ω_{surf} and N_{surf} in Eq. (83), we obtain the surface contribution to the internal energy per unit area. We are interested in the case of low temperatures ($\theta \to 0$). Then according to Refs. [67,68], the ratio U_{surf}/S is the free surface energy σ, and the magnitude of $U_{\text{surf}} = \sigma S$ is the work that is necessary for the irreversible process of creating a new free surface S. The quantity σ describes the excess energy of the surface area compared with the energy inside the body of the metal. Then, the surface energy σ can be presented as

$$
\sigma = \sigma_0 + \Delta\sigma, \quad (105)
$$

where

$$
\sigma_0 = \frac{\hbar^2\mathcal{K}_F^4}{2m\pi^2}\left(\frac{d\,\mathcal{K}_F}{5} - \frac{\pi}{16}\right), \quad (106)
$$

$$
\Delta\sigma = \frac{e^2 d\,\mathcal{K}_F^3}{4\pi^2}\int_0^\infty dq\left(1 - \frac{q}{Q}\right) - \frac{e^2 d\,\mathcal{K}_F^3}{6\pi^2}\int_0^\infty dq\left[1 - \int_0^1 d\lambda\,\frac{q}{Q(\lambda)}\right] - \frac{e^2\mathcal{K}_F^3}{8\pi^2}\int_0^\infty dq\,\frac{q}{Q^2}\frac{Q - q}{Q + q}\left(1 - \frac{Q}{\mathcal{K}_F}\arctan\frac{\mathcal{K}_F}{Q}\right)
$$
$$
+ \frac{e^2\mathcal{K}_F^3}{12\pi^2}\int_0^\infty dq\int_0^1 d\lambda\,\frac{q}{Q^2(\lambda)}\frac{Q(\lambda) - q}{Q(\lambda) + q}\left[1 + \frac{3Q^2(\lambda)}{2\mathcal{K}_F^2} - \frac{3Q(\lambda)\left(\mathcal{K}_F^2 + Q^2(\lambda)\right)}{2\mathcal{K}_F^2}\arctan\frac{\mathcal{K}_F}{Q(\lambda)}\right]
$$
$$
+ \frac{e^2\mathcal{K}_F^2}{2\pi^4}\int_0^\infty dq\,q \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2\, I(q,\alpha_1,\alpha_2)\, g_1(q,\alpha_1,\alpha_2,1)
$$
$$
- \frac{e^2}{4\pi^4}\int_0^\infty dq\,q \int_0^{\mathcal{K}_F} d\alpha_1 \int_0^{\mathcal{K}_F} d\alpha_2\,\tilde{J}(q,\alpha_1,\alpha_2)\int_0^1 d\lambda\, g_2(q,\alpha_1,\alpha_2,\lambda).
$$

(107)

By placing the parameter d (66) in Eq. (106), we obtain

$$
\sigma_0 = \frac{\hbar^2\mathcal{K}_F^4}{160m\pi} = \frac{(\mathcal{K}_F a_B)^4}{80\pi}\frac{\text{Ry}}{a_B^2}. \quad (108)
$$

It coincides by form with the surface energy of the noninteracting system [63,64,69–71], but in Eq. (108), $\mathcal{K}_F$ is the magnitude of the Fermi wave vector that takes into account the Coulomb interaction between electrons.

In Fig. 4, the dependence of the surface energy on the Wigner-Seitz radius r_s is presented. The solid line is the surface energy calculated using the formulas (105), (107), and (108); the solution of the nonlinear algebraic equation (98) yields the chemical potential. The dashed line is the surface energy of the noninteracting system (108), the dash-dotted line is the result of Lang and Kohn [5].

The result given in this figure shows that taking into account the Coulomb interaction leads to an increase of the surface energy compared to the surface energy of the noninteracting system. In addition, the surface energy calculated by us is positive in the entire region of r_s and in the interval

$r_s = 5.5 - 6\,a_B$ it coincides with the surface energy calculated by Lang and Kohn.

VI. CONCLUSIONS

The general expression for the thermodynamic potential of the semi-infinite jellium model is obtained by using the method of functional integration. The knowledge of the two-particle correlation function of electrons and the effective interelectron is required for the practical application of this expression.

It is shown that taking into account the Coulomb interaction between electrons leads to a decrease of the chemical potential. It is also shown that the surface contribution to the thermodynamic potential does not affect the chemical potential.

By using the infinite barrier model, the extensive and surface contributions to the thermodynamic potential, the average of the number operator of electrons and the internal energy are obtained and studied at low temperatures.

The influence of the Coulomb interactions between electrons on the behavior of the one-particle distribution function is studied as well. We obtained that taking into account the Coulomb interaction between electrons leads to an increase of
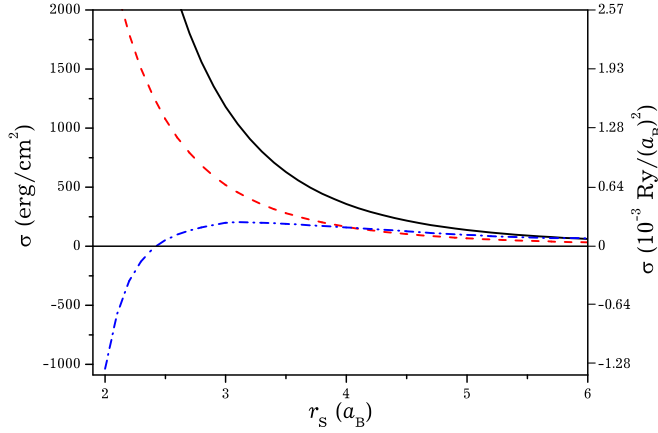
FIG. 4. (Color online) The surface energy as a function of the Wigner-Seitz radius (the solid line is for the interacting system, the dashed line is for the noninteracting system, whereas the dash-dotted line is the result of Lang and Kohn [5]).

the period of damped oscillations around its average value in the body of the metal.

It is found that taking into account the Coulomb interaction between electrons, the distance between the dividing plane and the surface potential as a function of the Wigner-Seitz radius looses its linear behavior. Namely, it grows faster.

Based on the expression for the surface contribution to the internal energy and modeling the surface potential by the infinite barrier, the surface energy is calculated at low temperatures. It is shown that taking into account the Coulomb interaction between electrons leads approximately to a double increase in the surface energy. The surface energy is positive in the entire range of Wigner-Seitz radius. In the interval $r_s > 5\,a_B$, the surface energy calculated by us is in good agreement with the calculations of Lang and Kohn [5]. Thus the consideration of a discrete ionic lattice is not a necessary condition for solving the problem of the surface energy negative values, instead the proper treatment of the Coulomb interaction between electrons in the framework of the semi-infinite jellium model is the key to solving this problem.

APPENDIX A: DENSITY OF STATES

Let us calculate the density of states of electrons without Coulomb interaction,

$$\rho(E) = \sum_{\mathbf{k}_{\|},\alpha} \delta(E - E_\alpha(\mathbf{k}_{\|})), \tag{A1}$$

where according to (9)

$$E_\alpha(\mathbf{k}_{\|}) = \frac{\hbar^2(k_{\|}^2 + \alpha^2)}{2m}.$$

In the thermodynamic limit ($S \to \infty$ and $L \to \infty$), the sum can be replaced by the integral, according to the Euler-Maclaurin formula [28,66],

$$\sum_{n=0}^{\infty} f(n) = \int_0^\infty f(x)\,dx - \frac{1}{2}[f(\infty) - f(0)]$$

$$+ \frac{B_1}{2!}[f'(\infty) - f'(0)] - \frac{B_2}{4!}[f'''(\infty) - f'''(0)]$$

$$+ \cdots,$$

where B_k are the Bernoulli numbers.

We perform a summation over the two-dimensional vector according to Eq. (11) and obtain

$$\sum_{\mathbf{k}_{\|}} f(\mathbf{k}_{\|}) = 2 \int_{-\infty}^{+\infty} dn_x \int_{-\infty}^{+\infty} dn_y f(\mathbf{k}_{\|})$$

$$= \frac{2S}{(2\pi)^2} \int_{-\infty}^{+\infty} dk_{\|x} \int_{-\infty}^{+\infty} dk_{\|y}\, f(\mathbf{k}_{\|})$$

$$= \frac{2S}{(2\pi)^2} \int_{-\infty}^{+\infty} d\mathbf{k}_{\|}\, f(\mathbf{k}_{\|}), \tag{A2}$$

where two possible orientations of the electron spin are taken into account.

The summation over the three-dimensional vector $\mathbf{k}_{\|}$ yields

$$\sum_{\mathbf{k}_{\|}} f(\mathbf{k}_{\|}) = \frac{2V}{(2\pi)^3} \int_{-\infty}^{+\infty} d\mathbf{k}_{\|}\, f(\mathbf{k}_{\|}). \tag{A3}$$

Now we consider the summation over α. Equation (64) implies that

$$\frac{dn}{d\alpha} = \frac{L}{2\pi}\left(1 + \frac{2d}{L}\right),$$

then

$$\sum_\alpha f(\alpha) = \int_0^{+\infty} dn\, f(\alpha) - \frac{1}{2}f(0)$$

$$= \int_0^{+\infty} d\alpha\left[\frac{L}{2\pi}\left(1 + \frac{2d}{L}\right) - \frac{1}{2}\delta(\alpha)\right]f(\alpha). \tag{A4}$$

The transition from the sum over $\mathbf{k}_{\|}$ to the integral is performed according to Eq. (A2). Then the density of states (A1) is

$$\rho(E) = \frac{2S}{(2\pi)^2} \sum_\alpha \int d\mathbf{k}_{\|}\, \delta\left(E - \frac{\hbar^2(k_{\|}^2 + \alpha^2)}{2m}\right)$$

$$= \frac{S}{\pi} \sum_\alpha \int_0^\infty dk_{\|}\, k_{\|}\, \delta\left(E - \frac{\hbar^2(k_{\|}^2 + \alpha^2)}{2m}\right)$$

$$= \frac{S}{2\pi}\frac{2m}{\hbar^2} \sum_\alpha \theta\left(\frac{2mE}{\hbar^2} - \alpha^2\right).$$

Transformation from the sum over α to the integral according to Eq. (A4) leads to

$$\rho(E) = \frac{S}{2\pi}\frac{2m}{\hbar^2} \int_0^{+\infty} d\alpha\left[\frac{L}{2\pi}\left(1 + \frac{2d}{L}\right) - \frac{1}{2}\delta(\alpha)\right]$$

$$\times \theta\left(\frac{2mE}{\hbar^2} - \alpha^2\right)$$

$$= \frac{SL}{2}\frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\sqrt{E} + S\left(\frac{\sqrt{2}m^{3/2}d}{\pi^2\hbar^3}\sqrt{E} - \frac{m}{4\pi\hbar^2}\right), \tag{A5}$$

where the first term (which is proportional to the volume SL) is the extensive contribution, and the second term is the surface contribution to the density of states. This expression coincides with the expression for the density of states, obtained in Ref. [28], if we put $d = 0$ in Eq. (A5).

It should be noted that the density of states of the noninteracting homogeneous system is

$$\rho_{\text{unif}}(E) = V \frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\sqrt{E},$$

which coincides with the first term of Eq. (A5).

APPENDIX B: THE CALCULATION OF Ω_0

Let us now calculate the thermodynamic potential of the noninteracting system

$$\Omega_0 = -\frac{1}{\beta}\sum_{\mathbf{k}_{||},\alpha}\ln[1 + e^{\beta(\mu - E_\alpha(\mathbf{k}_{||}))}]. \quad \text{(B1)}$$

Because here μ is the chemical potential of interacting electrons, this expression takes into account the Coulomb interaction indirectly.

In order to perform the summation by $\mathbf{k}_{||}$ and α, we use the density of states calculated in Appendix A. Then, the thermodynamic potential is

$$\begin{aligned}
\Omega_0 &= -\frac{1}{\beta}\int_0^\infty dE\,\rho(E)\ln[1 + e^{\beta(\mu - E)}]\\
&= -\frac{1}{\beta}\frac{SL}{2}\frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\int_0^\infty dE\,\sqrt{E}\,\ln[1 + e^{\beta(\mu - E)}]\\
&\quad -\frac{1}{\beta}S\frac{\sqrt{2}m^{3/2}d}{\pi^2\hbar^3}\int_0^\infty dE\,\sqrt{E}\,\ln[1 + e^{\beta(\mu - E)}]\\
&\quad +\frac{1}{\beta}S\frac{m}{4\pi\hbar^2}\int_0^\infty dE\,\ln[1 + e^{\beta(\mu - E)}].
\end{aligned}$$

Integrating by parts each of the terms, we get

$$\begin{aligned}
\Omega_0 &= -\frac{SL}{2}\frac{2\sqrt{2}m^{3/2}}{3\pi^2\hbar^3}\int_0^\infty dE\,E^{3/2}\frac{1}{e^{\beta(E-\mu)}+1}\\
&\quad -S\frac{2\sqrt{2}m^{3/2}d}{3\pi^2\hbar^3}\int_0^\infty dE\,E^{3/2}\frac{1}{e^{\beta(E-\mu)}+1}\\
&\quad +S\frac{m}{4\pi\hbar^2}\int_0^\infty dE\,E\frac{1}{e^{\beta(E-\mu)}+1}.
\end{aligned}$$

In the limit of low temperatures ($\beta \to \infty$), we get the following expression:

$$\Omega_0 = \Omega_{0,\text{bulk}} + \Omega_{0,\text{surf}}, \quad \text{(B2)}$$

where

$$\Omega_{0,\text{bulk}} = -\frac{SL}{2}\frac{4\sqrt{2}m^{3/2}}{15\pi^2\hbar^3}\mu^{5/2} = -\frac{SL}{2}\frac{\hbar^2}{15m\pi^2}\mathcal{K}_{\text{F}}^5 \quad \text{(B3)}$$

is the extensive contribution to the thermodynamic potential of the noninteracting system (it is proportional to the volume SL), which depends on the magnitude of the Fermi wave vector $\mathcal{K}_{\text{F}}$ of interacting electrons and

$$\begin{aligned}
\Omega_{0,\text{surf}} &= -S\left(\frac{4\sqrt{2}m^{3/2}d}{15\pi^2\hbar^3}\mu^{5/2} - \frac{m}{8\pi\hbar^2}\mu^2\right)\\
&= S\frac{\hbar^2\mathcal{K}_{\text{F}}^4}{m\pi^2}\left(\frac{\pi}{32} - \frac{d\,\mathcal{K}_{\text{F}}}{15}\right) \quad \text{(B4)}
\end{aligned}$$

is the surface contribution (it is proportional to the area of the dividing plane S).

It should be noted that the thermodynamic potential of the noninteracting homogeneous system is

$$\Omega_{0,\text{unif}} = -V\frac{4\sqrt{2}m^{3/2}}{15\pi^2\hbar^3}\mu^{5/2} = -V\frac{\hbar^2}{15m\pi^2}\mathcal{K}_{\text{F}}^5, \quad \text{(B5)}$$

which coincides with (B3).

APPENDIX C: THE CALCULATION OF $\langle N\rangle_0$ AND $\partial\langle N\rangle_0/\partial\mu$

By using the thermodynamic potential of the noninteracting system Ω_0 [see Eq. (B2)], we calculate $\langle N\rangle_0$ at low temperatures:

$$\langle N\rangle_0 = -\frac{\partial\Omega_0}{\partial\mu} = -\frac{\partial(\Omega_{0,\text{bulk}} + \Omega_{0,\text{surf}})}{\partial\mu} = N_{0,\text{bulk}} + N_{0,\text{surf}},$$

where

$$N_{0,\text{bulk}} = -\frac{\partial\Omega_{0,\text{bulk}}}{\partial\mu} = \frac{SL}{2}\frac{2\sqrt{2}m^{3/2}}{3\pi^2\hbar^3}\mu^{3/2} = \frac{SL}{2}\frac{\mathcal{K}_{\text{F}}^3}{3\pi^2} \quad \text{(C1)}$$

is the extensive contribution $\langle N\rangle_0$, and

$$\begin{aligned}
N_{0,\text{surf}} &= -\frac{\partial\Omega_{0,\text{surf}}}{\partial\mu} = S\left(\frac{2\sqrt{2}m^{3/2}d}{3\pi^2\hbar^3}\mu^{3/2} - \frac{m}{4\pi\hbar^2}\mu\right)\\
&= S\frac{\mathcal{K}_{\text{F}}^2}{\pi^2}\left(\frac{d\,\mathcal{K}_{\text{F}}}{3} - \frac{\pi}{8}\right) \quad \text{(C2)}
\end{aligned}$$

is the surface contribution $\langle N\rangle_0$. The latter result reduces to the one obtained previously in Refs. [64,71], if we put $d = 0$ in Eq. (C2).

By using $\langle N\rangle_0$, we calculate $\partial\langle N\rangle_0/\partial\mu$:

$$\frac{\partial\langle N\rangle_0}{\partial\mu} = \frac{\partial N_{0,\text{bulk}}}{\partial\mu} + \frac{\partial N_{0,\text{surf}}}{\partial\mu},$$

where the extensive contribution is

$$\frac{\partial N_{0,\text{bulk}}}{\partial\mu} = \frac{SL}{2}\frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\mu^{1/2} = \frac{SL}{2}\frac{m}{\hbar^2}\frac{\mathcal{K}_{\text{F}}}{\pi^2} \quad \text{(C3)}$$

and the surface contribution is

$$\begin{aligned}
\frac{\partial N_{0,\text{surf}}}{\partial\mu} &= S\left(\frac{\sqrt{2}m^{3/2}d}{\pi^2\hbar^3}\mu^{1/2} - \frac{m}{4\pi\hbar^2}\right)\\
&= S\frac{m}{\hbar^2\pi^2}\left(d\,\mathcal{K}_{\text{F}} - \frac{\pi}{4}\right). \quad \text{(C4)}
\end{aligned}$$

It should be noted that the following relations are valid for the noninteracting homogeneous system:

$$N_{0,\text{unif}} = V \frac{\mathcal{K}_F^3}{3\pi^2},$$ (C5)

$$\frac{\partial N_{0,\text{unif}}}{\partial \mu} = V \frac{m}{\hbar^2} \frac{\mathcal{K}_F}{\pi^2}.$$ (C6)

They coincide with the extensive contributions given by Eqs. (C1) and (C3), respectively.

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