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The difference of boundary effects between Bose and Fermi systems

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Abstract

In this paper, we show that there exists an essential difference of boundary effects between Bose and Fermi systems both for Dirichlet and Neumann boundary conditions: at low temperatures and high densities the influence of the boundary on the Bose system depends on the temperature but is independent of the density, but for the Fermi case the influence of the boundary is independent of the temperature but depends on the density, after omitting the negligible high-order corrections. We also show that at high temperatures and low densities the difference of the influence of the boundary between Bose and Fermi systems appears in the next-to-leading order boundary contribution, and the leading boundary contribution is independent of the density. Moreover, for calculating the boundary effects at high temperatures and low densities, since the existence of the boundary modification causes the standard virial expansion to be invalid, we introduce a modified virial expansion.

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1. Introduction

In small-size and low-temperature systems, the mean thermal wavelength of particles is comparable with the size of the system, and the boundary effect becomes one of the most important quantum effects. The influence of boundaries is widely discussed. Based on Maxwell–Boltzmann statistics, the boundary effect on the classical ideal gas confined in a narrow box or in spherical and cylindrical geometries is studied theoretically in [1, 2]. For quantum gases, the influence of the boundary effect on ideal quantum gases confined in irregular containers is discussed in [4]; some exact and approximative solutions for quantum gases in

finite-size containers are provided in [5]; a general result for the boundary modification to ideal quantum gases in arbitrary dimensions is provided in [6]. In Bose systems, the choice of the boundary condition may play an important role. Especially, for Bose systems it may display a phase transition—the Bose–Einstein condensation. Systematic discussions on this subject are given in [7–10]. Moreover, some experimental studies (e.g., [11–15]) show that the influence of the boundary may be remarkable in low-temperature quantum gases confined in small volumes.

In the present paper, we pay special attention to two-dimensional systems. Many novel properties of the gases absorbed within a bundle of carbon nanotubes are reported [16], and, especially, under appropriate thermodynamic conditions gases adsorbed within the nanotubes and on the external surface of the bundle will display two-dimensional behaviour [17–19]. Moreover, we also provide some three-dimensional results.

Different boundary conditions lead to different boundary effects. Two kinds of boundary conditions are considered: the Dirichlet boundary condition and the Neumann boundary condition.

The primary motivation of this work is to compare the boundary effects on Bose and Fermi systems. The analysis given by [5] shows that the ideal quantum gas can be used as an efficient tool for studying the boundary effects in many quantum systems, including electron gases, interacting Bose gases, etc, since in an interacting system there are two kinds of effects: one arises from the classical interaction, e.g., the van der Waals interaction, and the other is the quantum effect. In ideal quantum gases, though there are no classical interactions the quantum effects, such as the exchange interaction, remain. The boundary effect is, however, a kind of quantum effect, which becomes important when the mean thermal wavelength of particles is comparable with the size of the system, so the boundary effects on ideal and interacting gases are similar and the conclusions of the ideal gases are of widespread applicability.

In finite volumes (areas), energy levels are discrete, and the spectra of the particles are shape dependent and sensitive to the topology [4]. To take boundary effects into account, strictly speaking, we need to perform the summation over all possible states directly, but that is in general hard to solve. In [4, 5] some methods are developed to perform the summation. Based on a mathematical work given by M Kac [20], a method for calculating the boundary modification to the ideal quantum gases in irregular-shaped containers is provided in [4]; some thermodynamic quantities for two- and three-dimensional systems are calculated in [5] and some of the results are exact solutions. Different boundary conditions lead to different boundary effects. The equation of state for ideal quantum gases with boundary modifications is provided in [4, 5]. The boundary condition used in these two papers is the Dirichlet boundary condition. In the following, we will consider the boundary effects corresponding to two kinds of boundary conditions: the Dirichlet boundary condition and the Neumann boundary condition. It is straightforward to obtain the equation of state with the Neumann boundary condition by use of the method given in [4, 5]. The equation of state of Fermi and Bose gases in confined space with Dirichlet and Neumann boundary conditions can be expressed as

$$\frac{P\Omega}{kT} = \sum_{\sigma} A_{\sigma} h_{\sigma}(z), \tag{1}$$

$$N = \sum_{\sigma} A_{\sigma} h_{\sigma-1}(z), \tag{2}$$

where $h_{\sigma}(z)$ equals the Bose–Einstein integral $g_{\sigma}(z)$ or the Fermi–Dirac integral $f_{\sigma}(z)$ in the Bose or the Fermi case, respectively:

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$$h_{\sigma}(z) = \begin{cases} g_{\sigma}(z) = \frac{1}{\Gamma(\sigma)} \int_{0}^{\infty} \frac{x^{\sigma-1} dx}{z^{-1} e^{x} - 1} = \sum_{l=1}^{\infty} \frac{z^{l}}{l^{\sigma}}, \\ f_{\sigma}(z) = \frac{1}{\Gamma(\sigma)} \int_{0}^{\infty} \frac{x^{\sigma-1} dx}{z^{-1} e^{x} + 1} = \sum_{l=1}^{\infty} (-1)^{l-1} \frac{z^{l}}{l^{\sigma}}. \end{cases}$$
(3)

In these equations and the following, the upper sign stands for the Dirichlet boundary condition and the lower sign for the Neumann boundary condition. In two dimensions, $\Omega = S$ is the area, $\sigma = 2, 3/2, 1$, and $A_2 = gS/\lambda^2$, $A_{3/2} = \mp (1/4)gL/\lambda$, $A_1 = g\chi/6$, where $\lambda = h/\sqrt{2\pi mkT}$ is the mean thermal wavelength, *L* is the perimeter of the boundary, χ is the Euler–Poincaré characteristic number (the Euler–Poincaré characteristic number reflects the connectivity—a topological property—of a two-dimensional system), and *g* denotes the number of internal degrees of freedom, the degeneracy number of spin states (for bosons we take g = 1). For the case of the gas confined in a three-dimensional box, $\Omega = V$ is the volume, $\sigma = 5/2, 2, 3/2, 1$, and $A_{5/2} = gV/\lambda^3$, $A_2 = \mp (1/4)gS/\lambda^2$, $A_{3/2} = (1/16)gL/\lambda$, $A_1 = \mp (1/8)g$, where *S* is the area of the surface of the box and $L = 4(L_x + L_y + L_z)$ is the total length of the sides of the box.

The difference between the Dirichlet case and Neumann case is that the leading contributions of these two kinds of boundaries have opposite signs: the contribution of the Dirichlet boundary is negative, and the contribution of the Neumann boundary is positive.

The standard virial expansion approach cannot be used due to the existence of the boundary modification. For analysing the boundary effect in high-temperature and low-density systems, we introduce a modified virial expansion.

In this paper, we compare the boundary effects on the Bose system and on the Fermi system. At low temperatures and high densities, our results will show that the boundary effects on Bose and Fermi systems are different essentially: after omitting the negligible high-order corrections, for Bose systems the influence of the boundary depends on the temperature but is independent of the density; however, contrary to the Bose case, the influence of the boundary on Fermi systems depends on the density but is independent of the temperature. At high temperatures and low densities, the difference of the boundary effects between Bose and Fermi systems appears in the next-to-leading boundary contributions: the next-to-leading boundary contributions to Bose systems and to Fermi systems have opposite signs; they are functions of both temperature and density, though the leading boundary contribution is independent of the density.

In section 2, we compare and discuss the difference of boundary effects between Bose and Fermi systems both for Dirichlet and Neumann boundary conditions. In section 3, by introducing a modified virial expansion, we calculate the boundary effects on Bose and Fermi systems at high temperatures and low densities. The conclusions are summarized in section 4.

2. The difference between Bose and Fermi systems at low temperatures and high densities

In this section, we compare the boundary effects on the two-dimensional Bose and Fermi systems at low temperatures and high densities. We show that the boundary effects on Bose and Fermi systems are different essentially, and discuss the reason of such a difference.

We will take the specific heat, a quantity directly accessible to experimental measurement, as an example, and our main conclusion holds also for other thermodynamic quantities.

The Bose case. For Bose cases, from the equation of state, equations (1) and (2), we can obtain the specific heat at low temperatures and high densities. From equation (2) one can

determine $\alpha = [1 \mp (\sqrt{\pi}/4)(L\lambda/S) e^{n\lambda^2/2}] e^{-n\lambda^2}$ approximately, where $\alpha = -\mu/(kT)$, with μ the chemical potential, and n = N/S is the mean number density, where N is the expectation value of the particle number in the grand canonical ensemble. Substituting α into equation (1), we obtain the grand potential. Starting from the grand potential we can calculate the specific heat,

$$\frac{C_V}{k} = \frac{S}{\lambda^2} \left\{ \frac{\pi^2}{3} - [(n\lambda^2)^2 + 2n\lambda^2 + 2] e^{-n\lambda^2} \right\}$$
$$\mp \frac{L}{8\lambda} \left\{ \frac{3}{2} \zeta \left(\frac{3}{2} \right) - \frac{\sqrt{\pi}}{2} [(n\lambda^2)^2 + 3n\lambda^2 + 6] e^{-n\lambda^2/2} \right\}.$$
(4)

In this section, we always drop the topological terms which are often negligible. The terms proportional to S/λ^2 in equation (4) are the specific heat in free space, and the remaining terms are the boundary modifications.

The percentage of the boundary modification to specific heat is

$$\frac{C_V - C_V^0}{C_V^0} = \mp 0.149 \frac{L}{\sqrt{S}} \frac{\lambda}{\sqrt{S}} [1 - 0.226(n\lambda^2)^2 e^{-n\lambda^2/2} + \cdots]$$
$$\approx \mp 0.149 \frac{L}{\sqrt{S}} \frac{\lambda}{\sqrt{S}} \propto \frac{1}{\sqrt{T}}.$$
(5)

We can see that the boundary effect on a Bose system, after omitting the negligible high-order corrections, is independent of the density; it is proportional to λ/\sqrt{S} , which is the ratio between the thermal wavelength and the linear size of the container, and L/\sqrt{S} , which reflects to some extent the information of the shape of the boundary. We can see that as the temperature falls, the contribution from the boundary will become more and more important.

The above result is obtained in low temperatures. It should be emphasized that this result will become invalid when the fugacity $z \rightarrow 1$ since the result provided in [4] and [5] is invalid when $z \to 1$. If the system can display Bose–Einstein condensation, the case $z \to 1$ corresponds to a non-zero temperature T_c . That is to say, if the Bose–Einstein condensation occurs, our result will be invalid at a certain non-zero temperature. However, in the above case (the two-dimensional ideal Bose gas with Dirichlet and Neumann boundaries) there is no Bose–Einstein condensation [7]. This means that only when $T \rightarrow 0$ the fugacity $z \rightarrow 1$. Nevertheless, the modification to the equation of state, equations (1) and (2), will be valid only when the boundary contribution is small [20]. Consequently, for the Bose case there exists a lower limit on temperatures in the range of applicability of the above result. This lowest temperature can be roughly estimated: the boundary modification should be less than the leading contribution. From equation (4) we can obtain this lower limit for a square two-dimensional system directly: the above result is valid only when the temperature $T > 0.057h^2(mka^2)^{-1}$, where a is the side length of the system. For illustration, such a temperature for ²³Na with size 50 nm is about 2×10^{-5} K. Moreover, the boundary influence on the condensation is a very important and interesting subject, which has been considered in [7–10].

The Fermi case. For Fermi cases, the specific heat is

$$\frac{C_V}{Nk} = \frac{\pi^2}{3} \frac{kT}{\varepsilon_F^0} \left[\left(1 \mp \frac{1}{2} \delta \right) \mp \frac{7\pi^2}{160} \delta \left(\frac{kT}{\varepsilon_F^0} \right)^2 + \cdots \right].$$
(6)

The ratio of the boundary modification to the specific heat in free space is

$$\frac{C_V - C_V^0}{C_V^0} = \pm \frac{1}{2} \delta \left[1 + \frac{7\pi^2}{80} \left(\frac{kT}{\varepsilon_F^0} \right)^2 + \cdots \right] \sim \pm \frac{1}{2} \delta, \tag{7}$$

where

$$\delta = \frac{1}{2}\sqrt{\frac{g}{\pi}}\frac{L}{\sqrt{S}}\frac{1}{\sqrt{S}}\sqrt{\frac{S}{N}}.$$

Unlike the Bose case, after omitting the contribution suppressed by $(kT/\varepsilon_F^0)^2$, the ratio $(C_V - C_V^0)/C_V^0 \propto \mp L/\sqrt{S}(1/\sqrt{S})\sqrt{S/N}$ is independent of the temperature but is determined by three factors: the number density N/S (or, the mean space between particles $\sqrt{S/N}$), the shape, which is described by L/\sqrt{S} to some extent, and the linear size \sqrt{S} . In other words, the boundary effects on two-dimensional Fermi systems depend on the density, the size, and the geometrical properties of the system, but are independent of the temperature.

The difference between Bose and Fermi systems. In a word, in addition to the size and shape, the boundary effect on Bose systems depends almost only on the temperature, but that on Fermi systems depends almost only on the density. Such a difference is quite essential. In the following we will analyse the reason.

Essentially, the influence of the boundary is determined by the thermal wavelength of the particles and the size of the system. The lower the energy of a particle, the longer is the wavelength and then the stronger is the boundary effect. Therefore, the particles in lower energy levels will be influenced more strongly than those in higher energy levels.

First, we discuss the influence of the temperature on the boundary effects.

For a Bose system, when the temperature falls, the particles will tend to occupy lower energy levels, so the boundary effect will become stronger. As a result, the boundary effect will be a function of the temperature.

For a Fermi system, there exists the Fermi energy. At low temperatures almost all the particles are in the states below the Fermi energy. The magnitude of the influence of the boundary on the particles is determined by the wavelength: the shorter the wavelength the weaker the boundary influence is. Generally speaking, the energy of the particles near the Fermi surface is relatively high, so the wavelength is short. Therefore in a low-temperature system the contribution of the boundary influence mainly comes from the particles far below the Fermi surface. At very low temperatures, a small change in the temperature only influences the particles near the Fermi surface; however, due to their short wavelengths, the boundary contribution from such particles is very small compared with the whole boundary effect. Therefore, in low-temperature Fermi systems the boundary effect is almost independent of the temperature.

Next, we discuss the influence of the density on the boundary effects.

For a Bose system with fixed size and shape, the change in the density will change the total number of particles, but almost has no influence on the relative distribution of particles. What we consider is the ratio between the boundary contribution and the result of free space, i.e., the percentage of the boundary contribution, which mainly depends on the distribution of the particles. Therefore, such a ratio will not change after changes in density.

For a Fermi system with fixed size and shape, the ratio of the boundary contribution to the free space result will get smaller as the density increases. When the volume is given, as the density increases, the number of particles increases. Roughly speaking, the energy of the newly added particle will be higher than the original Fermi energy, i.e., the wavelength of the newly added particle will be shorter than the original mean wavelength. As mentioned above, the boundary effect is mainly determined by the magnitude of the wavelength of the low-energy particles. Therefore with the density increasing the proportion of the influence of the boundary with respect to the result in free space will be suppressed. Particularly, it should be emphasized that in the Fermi case the influences on different thermodynamic quantities are different: for example, for the Dirichlet boundary condition, the influence on the specific heat is negative, but on the Fermi energy is positive. For illustrating this, we give the chemical potential and Fermi energy in a two-dimensional system,

$$\mu = \varepsilon_F^0 \left[(1 \pm \delta) \mp \delta \frac{\pi^2}{24} \left(\frac{kT}{\varepsilon_F^0} \right)^2 + \cdots \right],\tag{8}$$

$$\varepsilon_F = \varepsilon_F^0 (1 \pm \delta), \tag{9}$$

where $\varepsilon_F^0 = (\hbar^2/2m)(4\pi N/gS)$ is the Fermi energy in two-dimensional free space, and $(\varepsilon_F - \varepsilon_F^0)/\varepsilon_F^0 = \pm \delta$. Note that this boundary modification to the case of the Dirichlet boundary condition is positive and to the case of the Neumann boundary condition is negative; however, for the specific heat, equation (7), the modification to the Dirichlet case is negative, but to the Neumann case is positive.

Moreover, the boundary effect on the chemical potential deserves special attention. For illustrating this, we give the three-dimensional chemical potential and Fermi energy,

$$\mu_{3} = \varepsilon_{F3}^{0} \left[(1 \pm \Delta) - \frac{\pi^{2}}{12} \left(\frac{kT}{\varepsilon_{F3}^{0}} \right)^{2} + \cdots \right],$$
(10)

and

$$\varepsilon_{F3} = \varepsilon_{F3}^0 (1 \pm \Delta), \tag{11}$$

where $\varepsilon_{F3}^0 = (\hbar^2/2m)(6\pi^2 N/gV)^{2/3}$ is the Fermi energy in three-dimensional free space and

$$\Delta = \frac{1}{4} \left(\frac{\pi g}{6}\right)^{1/3} \frac{S}{V^{2/3}} \frac{1}{V^{1/3}} \left(\frac{V}{N}\right)^{1/3}.$$

The second-order term of the two-dimensional chemical potential (8) only includes the boundary contribution, while the second-order term of the three-dimensional chemical potential (10) is independent of the boundary; i.e., there is no second-order boundary correction to the three-dimensional chemical potential. This leads to such a result: in two dimensions, the second-order contribution to the ratio $(\mu - \mu^0)/\mu^0 = \pm \delta [1 - (\pi^2/24)(kT/\varepsilon_F^0)^2 + \cdots]$ is negative, but in three dimensions the second-order contribution to the ratio $(\mu_3 - \mu_3^0)/\mu_3^0 = \pm \Delta [1 + (\pi^2/12)(kT/\varepsilon_{F3}^0)^2 + \cdots]$ is positive. The reason is that in the result of the standard statistical mechanics, which is under the thermodynamic limit approximation, the two-dimensional chemical potential has no second-order term [21]³, so the second-order contribution in equation (8) only comes from the boundary effect. In three-dimensional free space, however, the chemical potential does have the second-order term, but the three-dimensional boundary correction, which behaves like the two-dimensional chemical potential, has no second-order term.

3. Boundary effects at high temperatures and low densities: a modified virial expansion

The existence of the boundary modification causes the standard virial expansion to be invalid. For analysing the boundary effect at high temperatures and low densities, we introduce a modified virial expansion approach.

In statistical mechanics, in the limit $T \to \infty$, hence $\lambda \to 0$, all the thermodynamic quantities can be expanded with respect to $n\lambda^2$ since $n\lambda^2 = N\lambda^2/S \ll 1$, which is the

³ In this paper, there is a misprint in equation (26); this equation should be $\mu = \epsilon_F [1 - \frac{\pi^2}{3} \frac{1}{n+1} (\frac{\nu}{s} - 1) (\frac{kT}{\epsilon_F})^2 + \cdots].$

so-called virial expansion. The main idea of the virial expansion in two dimensions is to suppose that the equation of state can be expanded as $PS/(NkT) = \sum_{l=1}^{\infty} a_l (n\lambda^2)^{l-1}$, where the coefficients a_l are referred to as the virial coefficients. Nevertheless, since equations (1) and (2) contain the terms which describe the influence of the boundary shape and topology, the expansion parameter of the virial expansion $n\lambda^2$ (or $N\lambda^2/S$) is not the unique expansion parameter, so the thermodynamic quantities cannot be expressed as the series of $n\lambda^2$. In other words, it is impossible to perform the standard virial expansion.

For calculating the thermodynamic quantities at high temperatures and low densities, we introduce a new approach which is, in fact, a modified virial expansion. We suppose that the equation of state can be expressed as a series,

$$\frac{PS}{NkT} = \sum_{l=1}^{\infty} a_{(l+1)/2} (n\lambda^2)^{(l-1)/2},$$
(12)

where $a_{(l+1)/2}$ are the modified virial coefficients.

Using equations (2) and (3), we obtain

$$n\lambda^2 = \left(z + \eta \frac{z^2}{2} + \cdots\right) \mp \frac{1}{4} \frac{L\lambda}{S} \left(z + \eta \frac{z^2}{\sqrt{2}} + \cdots\right) + \frac{\chi}{6} \frac{\lambda^2}{S} (z + \eta z^2 + \cdots).$$
(13)

In this equation and the following, for the Bose case $\eta = +1$ and for the Fermi case $\eta = -1$. In this equation, the expansion parameters include $N\lambda^2/S$, $L\lambda/S$, $\lambda^3/(LS)$ and $(\lambda^2/S)\chi/6$. Therefore we write z in the form

$$z = n\lambda^2 \sum_{l=1}^{\infty} b_{(l+1)/2} (n\lambda^2)^{(l-1)/2},$$
(14)

where $b_{(l+1)/2}$ are the coefficients of the expansion. Then we can obtain an equation of λ . By equating the coefficients of each power of λ , we can obtain the coefficients $b_{(l+1)/2}$ and then obtain the modified virial coefficients $a_{(l+1)/2}$:

$$a_{1} = 1, a_{3/2} = 0, \qquad a_{2} = -0.25\eta, a_{5/2} = \mp 0.037\eta \frac{1}{\sqrt{N}} \frac{L}{\sqrt{S}}, \qquad a_{3} = 0.028 - 0.003\eta \frac{1}{N} \frac{L^{2}}{S}, \dots$$
(15)

One can see that $a_{(l+1)/2}$ are related to the geometry of the system, and if the thermodynamic limit approximation is taken, they will return to the common virial coefficients. By $a_{(l+1)/2}$, we can express the expansions for the thermodynamic quantities. As an example, we give the expansions of chemical potential and specific heat:

$$\frac{\mu}{kT} = \ln(n\lambda^2) \pm 0.25 \frac{L\lambda}{S} + 0.031 \left(\frac{L\lambda}{S}\right)^2 - 0.167 \frac{\chi\lambda^2}{S} + \cdots$$
$$- 0.5\eta n\lambda^2 \left[1 \pm 0.146 \frac{L\lambda}{S} + 0.011 \left(\frac{L\lambda}{S}\right)^2 + \cdots \right]$$
$$+ 0.042(n\lambda^2)^2 \left[1 \pm 0.100 \frac{L\lambda}{S} + \cdots \right] + \cdots,$$
$$\frac{C_V}{Nk} = \left[1 \pm 0.063 \frac{L\lambda}{S} + \cdots \right] + 0.25\eta n\lambda^2 \left[\pm 0.110 \frac{L\lambda}{S} + 0.021 \left(\frac{L\lambda}{S}\right)^2 + \cdots \right]$$
$$- 0.028(n\lambda^2)^2 \left[1 \pm 0.188 \frac{L\lambda}{S} + \cdots \right].$$

In comparison with the virial expansion, one can see that the boundary effects are reflected mainly by the terms which are proportional to $L\lambda/S$ and its powers.

The result shows that at high temperatures and low densities, both for Bose and Fermi cases, the leading contribution of the boundary to the chemical potential and the specific heat is a function of temperature and geometrical property of the system, but is independent of the density of the system. In the next-to-leading order boundary contribution, the difference between Bose and Fermi systems appears: the modifications to Bose systems and to Fermi systems have opposite signs. Moreover, the boundary modifications to different thermodynamic quantities are different. One can also verify that the properties we have drawn in this section are also satisfied by the other thermodynamic quantities.

Note that the same procedures can be used for the three-dimensional case directly by expressing the equation of state and the fugacity z as

$$\frac{PV}{NkT} = \sum_{l=1}^{\infty} c_{(l+2)/3} (n\lambda^3)^{(l-1)/3} \quad \text{and} \quad z = n\lambda^3 \sum_{l=1}^{\infty} d_{(l+2)/3} (n\lambda^3)^{(l-1)/3}.$$
(16)

4. Conclusion

In conclusion, we show the essential difference of boundary effects on Bose and Fermi systems in two dimensions: at low temperatures and high densities, for Bose systems, boundary effects are almost independent of the density but depend on the temperature; while for Fermi systems, the effects are almost independent of the temperature but depend on the density. At high temperatures and low densities, the difference of boundary effects between Bose and Fermi systems appears in the next-to-leading order boundary contributions: the next-to-leading order contributions to Bose systems and to Fermi systems have opposite signs; moreover, the leading boundary contribution is independent of the density.

Strictly speaking, for a finite-size system one should use the canonical formalism, but it is shown in [5] that the result based on the grand canonical formalism for finite-size systems is valid for most realistic cases. A detailed discussion for the canonical ensemble formalism is given by [22, 23]. In this paper attention is concentrated on the difference of boundary effects between Bose and Fermi systems, and we have not considered the Bose–Einstein condensation since there is no corresponding phase transition in the Fermi system at low temperatures. Of course, the boundary effect on the Bose–Einstein condensation is very important. Systematic discussions on this subject can be found in [7–10]. Note that in this paper though our attention focuses mainly on the two-dimensional cases, it is easy to check that most of our conclusion is also valid for three dimensions.

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