Quantum statistics of ideal gases in confined space

Wu-Sheng Dai *
School of Science, Tianjin University, Tianjin 300072, P. R. China

and

Mi Xie †
Department of Physics, Tianjin Normal University, Tianjin 300074, P. R. China

Abstract

In this paper, the effects of boundary and connectivity on ideal gases in two-dimensional confined space and three-dimensional tubes are discussed in detail based on the analytical result. The implication of such effects on the mesoscopic system is also revealed.

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1. Introduction

With the increasing interest in studying the quantum effects in mesoscopic systems [1, 2] which are so small that the boundary effect gets important and can not be neglected any more, the question of how to solve the sum of the states precisely, or, how to take the boundary effect of such system into consideration, is raised naturally. The properties of some systems found recently are shape dependent and sensitive to the topology [3, 4, 5].

*Email address: daiwusheng@tju.edu.cn
†Email address: xiemi@mail.tjnu.edu.cn
The key problem in statistical mechanics is to solve the sum over all possible states. In principle, when an ideal gas is confined in finite volume, the spectrum of single-particle states will be determined by the configuration of the boundary. In case the boundary is irregular, it is impossible to get the sum over all possible states exactly. However, if the mean thermal wavelength of the particles is much shorter than the size of the system, as an approximation, one can assume that the spectrum of single-particle states be continuous while the total number of states be independent of the shape of the boundary and simply proportional to the volume (in three dimensional case) or the area (in two dimensional case) of the system. In other words, if the thermal wavelength of particles is very short in relative to the size of the volume or area which the system occupies, the effect of boundary configuration on the spectrum can be ignored. Historically, such an assumption was advocated by radiation theory of Rayleigh-Jeans. It also aroused great interest to the mathematicians, and finally was proved by Weyl mathematically [6].

The above problem in statistical mechanics is related to such an inverse problem in mathematics, that is, if it is possible to determine the metric and topological features by the knowledge of the spectrum, which is still an open question. After Weyl’s leading work[6], some progress has been made in mathematics [7]. Now we know that, in two dimensions, for the eigenvalue problem

\[
\frac{1}{2} \nabla^2 U + \mu U = 0 \text{ in } \Omega \text{ with } U = 0 \text{ on } \Gamma,
\]

where \( \Omega \) is the region bounded by curve \( \Gamma \), the total number of eigenstates \( N \) can be written as [7]

\[
N \sim \sum_{n=1}^{\infty} e^{-\mu_n t} \rightarrow \frac{\Omega}{2\pi t} \frac{L}{4\sqrt{2\pi t}} + \frac{1-r}{6}, \quad (t \to 0). \tag{2}
\]

Here \( \Omega \) is the area of \( \Omega \), \( L \) the length of \( \Gamma \), and \( r \) the number of holes in \( \Omega \), while \( \{\mu_n\} \) is the spectrum of eigenvalues of the system. In the short-wavelength limit, Weyl proved for two-dimensional case that \( N \sim \frac{\Omega}{2\pi t} \), i.e., the total number of states is proportional to the area of the region, which is a fundamental assumption in statistical physics.
Nevertheless, Weyl’s result omits the last two terms in eq.(2) coming from the perimeter and the number of holes and hence loses part of the information related to the geometry of the region. Here, the relation between the perimeter $L$ and the area $\Omega$ contains some information of the shape of the region while the number of holes $r$ reflects the connectivity.

In this paper, the effects of the boundary and the connectivity on the quantum statistics are discussed. In Sec. II, the analytical result with the geometry effects being considered for ideal Bose and Fermi gases in two-dimensional space is given, based on which the relevant physical indications of such effects are revealed. In Sec. III, the quantum statistics in threedimensional tubes is discussed. The conclusions are summarized in Sec. IV while some expressions of useful thermodynamic quantities are given in Appendix.

2. Statistics in two-dimensional space

Obviously, eq.(1) is just the Schrödinger equation for free particles in a two-dimensional container. Based on eq.(2), we have

$$\sum_s e^{-\beta \epsilon_s} = \frac{\Omega}{\lambda^2} - \frac{1}{4} \frac{L}{\lambda} + \frac{1}{6} \frac{r}{6}, \quad (\lambda^2 \to 0),$$

where $\lambda = h/\sqrt{2\pi mkT} = h\sqrt{\beta}/\sqrt{2\pi m}$ is the mean thermal wavelength, $\epsilon_s$ the energy of a free particle, and the subscript $s$ labels different states. In macroscopic systems, the area (volume) of the system is usually large enough so that the influence of boundary can be ignored. However, it may not be true for some special cases. The above formula is a more precise approximation which includes the influence of the shape and the connectivity. It means that the geometry of the container may result in observable effects in physics. The effects described by the last two terms of eq.(3) can be expected to be observable in such cases that, 1) the area (volume) of the system is small, 2) the area (volume) is not small but the boundary of the system is so complicated that $L \gg \sqrt{\Omega}$ or the system is in multiply connected space.

For ideal Bose and Fermi gases in two-dimensional space, when the influence of
boundary and connectivity is considered, the grand potential of the system reads as [8]

$$\ln \Xi = \pm \sum_s \ln(1 \mp ze^{-\beta \epsilon_s}). \quad (4)$$

In this equation and following, the upper sign stands for bosons and the lower sign for fermions. Substitute eq.(3) into eq.(4) and expand it as a series of $ze^{-\beta \epsilon_s}$, we have

$$\ln \Xi = \sum_s \sum_n [(\pm 1)^{n+1} \frac{1}{n}(ze^{-\beta \epsilon_s})^n]. \quad (5)$$

Of course, such expansion is valid only for $0 < z < 1$.

By using the eq.(3), we can perform the summation over $s$:

$$\ln \Xi = \sum_n (\pm 1)^{n+1} \frac{z^n}{n^n} \left( \frac{\Omega}{n} + \frac{L}{4\lambda} + \frac{1-r}{6} \right). \quad (6)$$

Now, the sum over $n$ gives Bose-Einstein or Fermi-Dirac integral

$$\sum_n (\pm 1)^{n+1} \frac{z^n}{n^n} = \frac{1}{\Gamma(\sigma)} \int_0^\infty \frac{x^{\sigma-1}}{z^{-1}e^x + 1} dx \equiv h_\sigma(z). \quad (7)$$

Here, we introduce a function $h_\sigma(z)$ which equals to Bose-Einstein integral $g_\sigma(z)$ or Fermi-Dirac integral $f_\sigma(z)$ in Bose or Fermi case, respectively. Finally, the grand potential can be expressed as

$$\ln \Xi = \frac{\Omega}{\lambda^2} h_2(z) - \frac{L}{4\lambda} h_2(z) + \frac{1-r}{6} h_1(z). \quad (8)$$

In comparison with the grand potential $\ln \Xi_{\text{free}} = \frac{\Omega}{\lambda^2} h_2(z)$ for ideal gas in two-dimensional free space without boundary, grand potential eq.(8) depends not only on the area but also on the boundary as well as the connectivity of the space. The term which is proportional to the perimeter $L$ of the area, represents the influence of the boundary while the another term reflects the effect of the connectivity.

In addition, it is easy to see from eq.(8) that, grand potential of a system in confined space is less than that in free space since the signs of these two terms are negative (when $r > 1$). It means that the existence of a boundary and holes tends
to reduce the number of states of the system. This is just because in free space the energy spectrum is continuous while in confined space the spectrum gets discrete. Thus the number of modes in confined space is less than that in free space.

The expansion in eq.(5) requires $0 < z < 1$. In Bose-Einstein statistics, such a constraint on the fugacity $z$ is naturally satisfied. In Fermi-Dirac statistics, we have $0 < z < \infty$. Strictly speaking, the grand potential $\ln \Xi$ can not be expanded as a series of $z e^{-\beta \epsilon}$ when $z > 1$. However, the first term of $\ln \Xi$ in eq.(8) is just the grand potential in free space $\ln \Xi_{\text{free}}$ though the expansion is not rigorous. Since such a treatment provides a correct result in free space, we may expect that the rest two terms of $\ln \Xi$, which describe the contributions of boundary and connectivity, are also valid for $z > 1$.

When the thermal wavelength $\lambda$ is much shorter than the size of container, particle can not feel the shape of boundary. In contrast, for low frequency waves whose wavelengths are comparable to the size of container, its spectrum will seriously depend on the boundary. Therefore, when the ratio between the wavelength and the size of container is extremely small, a good approximation can be given by the first term of eq.(8) which is just the result proven by Weyl, and is only related to the area of the container. However, when the ratio is not negligible, the influence of the container geometry has to be considered, which is provided by the last two terms in eq.(8).

One point must be emphasized here. When solving statistics problem, one has got used to assume that, the number of states be only proportional to the area and neglect the effect of boundary. Eq.(8) provides a more complete and precise approximation.

Following general procedures, the relevant thermodynamic quantities of two-dimensional ideal gas can be achieved easily although the extra two terms in eq.(8) make the derivation get tedious. Eliminating $z$ in the two equations

$$\begin{align*}
\frac{P \Omega}{kT} &= \frac{\Omega}{\lambda^2} h_2(z) - \frac{1}{4 \lambda} h_2(z) + \frac{1 - r}{6} h_1(z), \\
\frac{N}{\lambda^2} &= \frac{\Omega}{\lambda^2} h_1(z) - \frac{1}{4 \lambda} h_2(z) + \frac{1 - r}{6} h_0(z),
\end{align*}
$$

we obtain the equation of state of the ideal gas. The other thermodynamic quantities
are given in Appendix.

The effect of boundary on the thermodynamic quantities (see Appendix) is of the order of $L/(\sqrt{N}\sqrt{\Omega})$. The factor $L/\sqrt{\Omega}$ reflects some information of the shape of the two-dimensional container. If the container shape is close to circle or square, the ratio $L/\sqrt{\Omega}$ is of order 1. Otherwise, for example, when the shape of the container is very complex, $L/\sqrt{\Omega}$ can be large and hence the boundary effect will become significant.

Besides, the boundary effect is suppressed by the factor $1/\sqrt{N}$. In macroscopic systems, the contribution of boundary is strongly suppressed. But, the suppression may not be so serious for mesoscopic systems, and so that is expectable to observe the boundary effect in such systems.

The influence of connectivity is of order $(1-r)/N$, so one may observe the effect of connectivity when $r$ is comparable to $N$. This result implies that in some porous media such effects may not be ignored.

### 3. Statistics in three-dimensional tubes

Based on eq.(3), we can also calculate the boundary effect of a three-dimensional ideal gas in a long tube, of which all transverse cross sections keep the same.

The $z$-component of the momentum $p_z$ is continuous since the length of the tube $L_z$ is made sufficiently large. This allows us to convert the summation over $p_z$ into an integral. Then, we only need to perform the summations over $p_x$ and $p_y$, which can be achieved by using the same procedure above. The grand potential is

\[
\ln \Xi = \sum_n (\pm 1)^{n+1} \frac{z^n}{n} \sum_s e^{-n\beta \epsilon_s} \\
= \sum_n (\pm 1)^{n+1} \frac{z^n}{n} \int \frac{dz dp_z}{\hbar} e^{-n\beta p_z^2/2m} \sum_{p_x, p_y} e^{-n\beta p_x^2 + p_y^2/2m}.
\]

Working out the summations over $p_x$ and $p_y$ by use of eq.(3), we obtain

\[
\ln \Xi = \frac{L_z \Omega}{\lambda^3} h_{\frac{3}{2}}(z) - \frac{1}{4} \frac{L_z L}{\lambda^2} h_2(z) + \frac{1 - r}{6} \frac{L_z}{\lambda} h_{\frac{3}{2}}(z).
\]
where Ω and $L$ denote the area and perimeter of the transverse cross section of the tube, respectively.

Directly, we can obtain the equation of state

$$
\begin{align*}
\frac{PV}{kT} &= \frac{L_z \Omega}{\lambda^3} h_2(z) - \frac{1}{4} \frac{L_z L}{\lambda^2} h_2(z) + \frac{1 - r}{6} \frac{L_z h_2(z)}{\lambda}, \\
N &= \frac{L_z \Omega}{\lambda^3} h_2(z) - \frac{1}{4} \frac{L_z L}{\lambda^2} h_1(z) + \frac{1 - r}{6} \frac{L_z h_1(z)}{\lambda},
\end{align*}
$$

(12)

The thermodynamics quantities are listed in Appendix. The Bose-Einstein condensation in a three-dimensional tube will be discussed in detail elsewhere.

A similar analysis indicates that the effects of boundary and connectivity in three-dimensional tube are of the same order as those in two-dimensional space.

4. Conclusions and discussions

In conclusion, the effects of boundary and connectivity on the statistical mechanics of ideal gases in two-dimensional confined space and in three-dimensional tubes are discussed.

In ideal gas theory, one replace the summation over states by an integral over momentum: $\sum_s \rightarrow V \int \frac{d^d p}{h^d}$, where $d$ denotes the dimension. This replacement is based on the assumption that the momentum is independent of the boundary of container, which is valid only when $V \rightarrow \infty$, i.e., there is no boundary. In other words, such a replacement is equivalent to the assumption that the number of states is proportional to the area (in two dimensions) or volume (in three dimensions) of the container. In fact, this treatment is an approximation that ignores the influence of boundary.

Our analysis shows that, the influence of boundary and connectivity is of the order $L/(\sqrt{N} \sqrt{\Omega})$ and $(1 - r)/N$, respectively. In many cases, such influences are of order $1/\sqrt{N}$ and $1/N$, therefore, negligible. However, when these factors $L/\sqrt{\Omega}$ and $r$ are much bigger than 1, the effects may be observable. The factor $L/\sqrt{\Omega} \gg 1$ corresponds to such cases, for example, the boundary of the region is very complex or the two-dimensional container is long and narrow. $r \gg 1$ corresponds to the case that there are many holes in the region. In the meanwhile, the suppression by
$1/\sqrt{N}$ or $1/N$ could also be reduced in mesoscopic systems, so we can expect that the effect of container geometry may be observable in mesoscopic scale, especially in containers with complex boundary or in porous media.

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Appendix: Thermodynamic quantities

1. Thermodynamic quantities in two dimensions

Internal energy:

$$\frac{U}{NkT} = \frac{h_2(z)}{h_1(z)} \sigma_2 - \frac{1}{8\sqrt{N} \sqrt[4]{\Omega}} \frac{L}{h_1^{1/2}(z)} \sigma_2^{1/2}. $$

Free energy:

$$F = \ln z - \left( \frac{h_2(z)}{h_1(z)} \sigma_2 - \frac{1}{4\sqrt{N} \sqrt[4]{\Omega}} \frac{L}{h_1^{1/2}(z)} \sigma_2^{1/2} + \frac{1-r}{6N} h_1(z) \right).$$

Entropy:

$$S = 2 \frac{h_2(z)}{h_1(z)} \sigma_2 - \ln z - \frac{3}{8\sqrt{N} \sqrt[4]{\Omega}} \frac{L}{h_1^{1/2}(z)} \sigma_2^{1/2} + 1 - \frac{r}{6N} h_1(z).$$

Specific heat:

$$\frac{C_V}{Nk} = \sigma_2 \left( 2 \frac{h_2(z)}{h_1(z)} - \eta_2 \frac{h_1(z)}{h_0(z)} \right)$$

$$- \frac{1}{\sqrt{N} \sqrt[4]{\Omega}} \sigma_2^{1/2} \left( \frac{3}{16} \frac{h_3/2(z)}{h_1^{1/2}(z)} - \frac{1}{8} \frac{h_1^{1/2}(z) \eta_1/2(z)}{h_0(z)} \right),$$

where

$$\sigma_2 = \left( \frac{1 - \frac{1-r}{6N} h_0(z)}{1 + \frac{1}{64N} \frac{L^2}{h_1(z)} \frac{k^2_0(z)}{k^2_1(z)} - \frac{1-r}{6N} h_0(z) - \frac{1}{8N \sqrt[4]{\Omega}} \frac{L}{h_1^{1/2}(z)} \right)^2.$$
$\eta_2 = \frac{1 - \frac{1}{8\sqrt{N}} \frac{L}{\sqrt{\Omega}} h_{1/2}(z) \frac{1}{\sigma_2^{1/2}}}{1 - \frac{1}{4\sqrt{N}} \frac{L}{\sqrt{\Omega}} h_{1/2}(z) h_{1/2}(z) \frac{1}{h_0(z)} \frac{1}{\sigma_2^{1/2}}}.$

The following relation is used to calculate $C_V$

$$\frac{\partial z}{\partial T} = -\frac{z h_1(z)}{T h_0(z)} \eta_2.$$

2. Thermodynamic quantities in three dimensions

Internal energy:

$$\frac{U}{NkT} = \frac{3 h_{5/2}(z)}{2 h_{3/2}(z)} \sigma_3 - \frac{1}{4N^{1/3}} \frac{L_z^{1/3} L_z h_2(z)}{\Omega^{2/3} h_{3/2}^2(z)} \sigma_3^{2/3} + \frac{1 - r}{12N^{2/3} \Omega^{1/3}} h_{3/2}^3(z) \sigma_3^{1/3}.$$

Free energy:

$$\frac{F}{NkT} = \ln z - \frac{h_{5/2}(z)}{h_{3/2}(z)} \sigma_3 - \frac{1}{4N^{1/3}} \frac{L_z^{1/3} L_z h_2(z)}{\Omega^{2/3} h_{3/2}^2(z)} \sigma_3^{2/3} + \frac{1 - r}{6N^{2/3} \Omega^{1/3}} h_{3/2}^2(z) \sigma_3^{1/3}.$$

Entropy:

$$\frac{S}{Nk} = \frac{5 h_{5/2}(z)}{2 h_{3/2}(z)} \sigma_3 - \ln z - \frac{1}{2N^{1/3}} \frac{L_z^{1/3} L_z h_2(z)}{\Omega^{2/3} h_{3/2}^2(z)} \sigma_3^{2/3} + \frac{1 - r}{4N^{2/3} \Omega^{1/3}} h_{3/2}^2(z) \sigma_3^{1/3}.$$

Specific heat:

$$C_V = Nk\{\sigma_3\left[\frac{15}{4} h_{5/2}(z) - \frac{9}{4} \eta_3 h_{3/2}(z) h_{1/2}(z)\right] - \frac{1}{N^{1/3}} \frac{L_z^{1/3} \sigma_{3/3}^2}{\Omega^{2/3}} h_2(z) \sigma_3^{2/3} + \frac{1}{8} \eta_3 h_{3/2}(z) h_1(z) \sigma_3^{1/3}\} + \frac{1 - r}{6N^{2/3} \Omega^{1/3}} \sigma_3^{1/3} \left[\frac{3}{4} (1 - \eta_3) h_{3/2}^2(z) \right],$$

where

$$\sigma_3 = \left(1 - \frac{L_z L_z h_1(z) h_{1/2}(z)}{\Omega h_{3/2}(z)} + \frac{L_z^2}{2916N^2} h_{3/2}^2(z)\right)^{-1} \xi_1^{-1}.$$
\[ \eta_3 = \frac{1 - \frac{1}{6N^{1/3}} \frac{L^{1/3} L_1(z)}{\Theta^{1/3} \eta(z)} \frac{1}{\sigma_3^{1/3}} + \frac{1 - r}{18N^{2/3} \Omega^{1/3} \eta(z)} \frac{1}{\sigma_3^{1/3}}}{1 - \frac{1}{4N^{1/3}} \frac{L^{1/3} L_1(z)}{\Theta^{1/3} \eta(z)} \frac{1}{\sigma_3^{1/3}} + \frac{1 - r}{6N^{2/3} \Omega^{1/3} \eta(z)} \frac{1}{\sigma_3^{1/3}}} , \]

\[ \xi_1 = \xi_2 - \frac{1}{\xi_2 12N^{1/3} \Omega^{2/3} \eta(z)} \frac{1}{\sigma_3^{1/3}} + \frac{1 - r}{18N^{2/3} \Omega^{1/3} \eta(z)} \frac{1}{\sigma_3^{1/3}} \frac{1}{\xi_3^{1/3}} , \]

\[ \xi_2 = \left( \frac{1}{2} + \frac{1}{2} \right)^{1/3} \left[ 1 + \frac{1}{432N} \frac{L_z L^3 h_1(z)}{\Omega^2 \eta^{2/3} \eta(z)} \right] , \xi_3 = \frac{\xi_2^{3/4}}{\xi_2^{1/4}} , \]

\[ \xi_4 = 1 - \frac{1 - r}{72N} \frac{L_z L h_1(z)}{\Omega} \frac{1}{h_3/2(z)} + \frac{(1 - r)^3}{291N^2} \frac{L_z h_3(z)}{\Omega} \frac{1}{h_3/2(z)} , \]

\[ \xi_5 = 1 - \frac{(1 - r)^2}{27N} \frac{L_z h_3^2(z)}{L} \frac{h_1(z)}{h_3/2(z)} . \]

We also have

\[ \frac{\partial z}{\partial T} = -\frac{3}{2} \frac{z}{T} \frac{h_3/2(z)}{h_1(z)} \eta_3. \]

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