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Low-temperature behaviour of an ideal Bose gas and some forbidden thermodynamic cycles

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Abstract

Based on the equation of state of an ideal Bose gas, the heat capacities at constant volume and constant pressure of the Bose system are derived and used to analyse the low-temperature behaviour of the Bose system. It is expounded that some important thermodynamic processes such as a constant pressure and an adiabatic process cannot be carried out from the region of $T > T_c$ to that of $T < T_c$, where T_c is the critical temperature of Bose–Einstein condensation of the Bose system. Consequently, some typical thermodynamic cycles such as the Carnot cycle, Brayton cycle, Otto cycle, Ericsson cycle, Diesel cycle and Atkinson cycle cannot be operated across the critical temperature T_c of Bose–Einstein condensation of an ideal Bose gas.

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1. Introduction

When the gas temperature is low enough or density is high enough, the gas will deviate from its classical behaviour and the quantum degeneracy of the gas will become important [1-3]. Especially for thermodynamic cycles at low temperatures, the quantum degeneracy of the working gas has to be considered. Because of the cause, quantum thermodynamic cycles working with the Bose and Fermi gases have become one of the interesting research subjects [3–6].

It is well known that the quantum gas obeys Bose–Einstein or Fermi–Dirac statistics. According to the Bose–Einstein distribution function, Bose–Einstein condensation (BEC) of the Bose gas will occur when temperature is lower than the critical temperature of BEC [7, 8]. This will result in some restrictions on thermodynamic cycles using the Bose gas as the working substance.

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In the present paper, we will give the expressions of some important parameters, based on the equation of state of an ideal Bose gas. The expressions are used to discuss the properties of isobaric and adiabatic processes of an ideal Bose gas system. The performance of some typical thermodynamic cycles working with the Bose gas is analysed and consequently it is expounded which typical thermodynamic cycles will be forbidden to be operated across the critical temperature of BEC.

2. Thermodynamic properties of an ideal Bose gas

Although many authors have investigated the thermodynamic properties of an ideal Bose gas and obtained a large number of important results [9-11], it is necessary to give the expressions of some thermodynamic parameters of the ideal Bose gas in order to discuss conveniently the properties of some important thermodynamic processes.

Based on quantum statistics, the expressions for the pressure and particle number of an ideal Bose gas are given by [12]

$$P = \frac{kT}{\lambda^3} g_{5/2}(z) \tag{1}$$

and

$$N - N_0 = \frac{V}{\lambda^3} g_{3/2}(z)$$
 (2)

where $\lambda = h/(2\pi m kT)^{1/2}$ is the mean thermal wavelength of the particles, *h* is the Planck constant, *k* is the Boltzmann constant, *m* is the rest mass of a particle, *T* is the gas temperature, *N* is the total number of particles, *N*₀ is the number of particles in the ground state, *V* is the volume of the gas, $z = \exp(\mu/kT)$ is the fugacity of the gas, μ is the chemical potential of the gas, $g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{z^{-1} e^z - 1} = \sum_{j=1}^\infty z^j/j^n$ is called the Bose function and $\Gamma(n)$ is the Gamma function.

When $T \ge T_c$, the particle number of the ground state is macroscopically negligible compared to the total particle number of the ideal Bose gas system [1, 2, 12], where T_c is the critical temperature of BEC of the system. Using equations (1) and (2), one can find that the internal energy, entropy and enthalpy of an ideal Bose gas system are, respectively, given by [12]

$$U = \frac{3}{2}PV = \begin{cases} \frac{3}{2}NkTg_{5/2}(z)/g_{3/2}(z) & T \ge T_{\rm c} \\ \frac{3}{2}(N-N_0)kT\frac{\zeta(5/2)}{\zeta(3/2)} = \frac{3}{2}\frac{\zeta(5/2)}{\zeta(3/2)}NkT\left(\frac{T}{T_{\rm c}}\right)^{3/2} & T < T_{\rm c} \end{cases}$$
(3)

$$S = \begin{cases} \frac{5}{2}Nk\frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z & T \ge T_{\rm c} \\ \frac{5}{2}(N - N_0)k\frac{\zeta(5/2)}{\zeta(3/2)} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)}Nk\left(\frac{T}{T_{\rm c}}\right)^{3/2} & T < T_{\rm c} \end{cases}$$
(4)

$$H = U + PV = \begin{cases} \frac{5}{2}NkT\frac{g_{5/2}(z)}{g_{3/2}(z)} & T \ge T_{\rm c} \\ \frac{5}{2}(N - N_0)kT\frac{\zeta(5/2)}{\zeta(3/2)} = \frac{5}{2}N\frac{\lambda_{\rm c}^3}{\zeta(3/2)}P & T < T_{\rm c} \end{cases}$$
(5)

where

$$\zeta(5/2) = 1.341 \qquad \qquad \zeta(3/2) = 2.612 \qquad N - N_0 = N(T/T_c)^{3/2} \\ \lambda_c = h/(2\pi m k T_c)^{1/2} \qquad T_c = \frac{h^2}{2\pi m k} \left[\frac{N}{V_c \zeta(3/2)}\right]^{2/3} = \frac{1}{k} \left[\frac{h^3 P_c}{(2\pi m)^{3/2} \zeta(5/2)}\right]^{2/5}$$



Figure 1. The curves of the heat capacities at constant volume and at constant pressure varying with temperature, where T_c is the critical temperature of Bose–Einstein condensation of an ideal Bose gas system.

and V_c and P_c are the volume and pressure of the Bose system respectively, when BEC occurs.

From equations (3) and (5), one can prove that the heat capacities at constant volume and constant pressure are, respectively, given by [12]

$$C_{V} = \begin{cases} \frac{15}{4} Nk \left[\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{5} \frac{g_{3/2}(z)}{g_{1/2}(z)} \right] & T \ge T_{c} \\ \frac{15}{4} Nk \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_{c}} \right)^{3/2} & T < T_{c} \end{cases}$$
(6)

and (a detailed derivation is given in appendix A)

$$C_P = \begin{cases} \frac{25}{4} Nk \left[\frac{g_{1/2}(z)g_{5/2}^2(z)}{g_{3/2}^3(z)} - \frac{3}{5} \frac{g_{5/2}(z)}{g_{3/2}(z)} \right] & T \ge T_{\rm c} \\ 0 & T < T_{\rm c}. \end{cases}$$
(7)

It is clearly seen from equations (6) and (7) that when $T \rightarrow 0$, $C_V \rightarrow 0$ and $C_P \rightarrow 0$. This shows that equations (6) and (7) do not contradict the Nernst theorem.

With the help of the above results, we can discuss the low-temperature behaviour of the Bose system and the influence of quantum degeneracy on the performance of some typical thermodynamic processes.

3. Isobaric and adiabatic processes

Using equations (6) and (7), one can easily generate the curves of the heat capacities at constant volume and constant pressure varying with temperature, as shown in figure 1. It is clearly seen from figure 1 that the curve of the heat capacity at constant volume varying with temperature is continuous at the critical temperature T_c , while the curve of the heat capacity at constant pressure varying with temperature is discontinuous at the critical temperature T_c . When $T \rightarrow T_c^+$, $C_P \rightarrow \infty$; when $T < T_c$, $C_P = 0$. Thus, the heat capacity at constant pressure has an infinite jump at the critical temperature T_c . This point can also be directly seen from equation (7). When $T \rightarrow T_c^+$, z = 1 [13] and

$$g_l(1) = \sum_{i=1}^{\infty} \frac{1}{i^l} = \zeta(l)$$
(8)



Figure 2. The entropy-temperature and entropy-fugacity curves of an ideal Bose gas.

is the Riemann zeta function. Equation (8) shows that for $l \leq 1, \zeta(l)$ diverges. This implies that when $T \to T_c^+, g_{1/2}(1)$ in equation (7) tends to infinity, i.e., $g_{1/2}(1) \to \infty$ and $C_P \to \infty$. Consequently, a constant-pressure process from the region of $T > T_c$ to that of $T < T_c$ is forbidden. Thus, a constant-pressure process for an ideal Bose gas cannot be operated across the critical temperature of BEC of the Bose system.

From equation (4), we can plot the entropy-temperature and entropy-fugacity curves, as shown by the solid and dashed lines in figure 2, respectively. The curves in figure 2 show clearly that the entropy S is a monotonically increasing function of temperature T but is a monotonically decreasing function of fugacity z. When $T \leq T_c$, z = 1 is the maximum value of the fugacity, so the range of z is from 0 to 1. For a given Bose system, S and N are unchanged during an isentropic process, so that the value of the fugacity z also remains unchanged. The property can directly be seen from figure 2 or equation (4) and, in fact, has been expounded in textbooks [1]. For example, it has been described in [1] that the ratio of the entropy of the Bose system, S, to the total number of the particles, N, is a homogeneous function of order zero in μ and T, i.e., $S/N = \varphi(\mu/T)$. Because S and N are unchanged during an isentropic process, the values of μ/T and z also remain unchanged. Because of the cause, the process starting from the state of z < 1 cannot attain the state of z = 1 through an isentropic process. This implies the fact that such an isentropic process from the region of $T > T_c$ to that of $T < T_c$ is impossible.

4. Some forbidden thermodynamic cycles

It is well known that the Carnot cycle, Otto cycle, Brayton cycle, Ericsson cycle, Diesel cycle and Atkinson cycle are some important models of the typical thermodynamic cycles [14, 15]. These cycle models are often used in the investigation of thermodynamics. When these cycles working with the Bose gas are operated at low temperatures, BEC of the working gas must be considered. Because of the causes mentioned above, the Carnot cycle, Otto cycle, Brayton cycle, Ericsson cycle, Diesel cycle and Atkinson cycle consisting of the adiabatic and/or isobaric processes and other processes are forbidden to be operated across the critical temperature of BEC of the Bose system. It is very important to note this problem in the investigation related to quantum thermodynamic cycles.

Besides the thermodynamic cycles mentioned above, the Stirling cycle is also an important model of the typical thermodynamic cycles. However, unlike thermodynamic cycles

mentioned above, the Stirling cycle does not include the isobaric or adiabatic processes. It is seen from figure 1 or equation (6) that the heat capacity at constant volume is finite no matter whether temperature of the Bose gas is larger than, equal to or smaller than the critical temperature of BEC of the Bose system. This implies that an isometric process from the region of $T > T_c$ to that of $T < T_c$ can be carried out. Thus, the Stirling cycle consisting of two isochoric and two isothermal processes and working with an ideal Bose gas can be operated across the critical temperature of BEC of the Bose system and consequently it will have some novel characteristics which need to be studied.

5. Conclusions

For an ideal Bose gas system, an isentropic or isobaric process from the region of $T > T_c$ to that of $T < T_c$ is impossible. For any thermodynamic cycle consisting of adiabatic and/or isobaric processes and other processes, it cannot be operated across the critical temperature of BEC of the ideal Bose gas system. These cycles include the Carnot cycle, Otto cycle, Brayton cycle, Ericsson cycle, Diesel cycle, Atkinson cycle, etc.

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Appendix

According to the definition of the heat capacity at constant pressure and equation (5), one can obtain

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P} = \frac{5}{2}Nk \left[\frac{\partial}{\partial T} \left(T\frac{g_{5/2}(z)}{g_{3/2}(z)}\right)_P\right]_N.$$
 (A1)

When $T \ge T_c$, one can easily derive the following relations,

$$\left[\frac{\partial}{\partial T}g_{3/2}(z)\right]_V = -\frac{3}{2}\frac{N}{V}\frac{\lambda^3}{T} = -\frac{3}{2T}g_{3/2}(z)$$
(A2)

$$\left[\frac{\partial}{\partial V}g_{3/2}(z)\right]_T = -\frac{N}{V^2}\lambda^3 = -\frac{1}{V}g_{3/2}(z) \tag{A3}$$

and

$$V = \frac{NkT}{P} \frac{g_{5/2}(z)}{g_{3/2}(z)}$$
(A4)

from equations (1) and (2). Using equations (A2)-(A4) and the Bose function, we can prove

$$g_{n-1}(z) = z \frac{\partial}{\partial z} g_n(z) = \frac{\partial}{\partial (\ln z)} g_n(z)$$
(A5)

$$\left(\frac{\partial g_{5/2}(z)}{\partial T}\right)_{P} = \left(\frac{\partial g_{5/2}(z)}{\partial \ln z}\right)_{P} \left(\frac{\partial \ln z}{\partial z}\right)_{P} \left(\frac{\partial z}{\partial T}\right)_{P} = g_{3/2}(z)\frac{1}{z} \left(\frac{\partial z}{\partial T}\right)_{P}$$
(A6)

$$\left(\frac{\partial g_{3/2}(z)}{\partial T}\right)_{P} = \left(\frac{\partial g_{3/2}(z)}{\partial \ln z}\right)_{P} \left(\frac{\partial \ln z}{\partial z}\right)_{P} \left(\frac{\partial z}{\partial T}\right)_{P} = g_{1/2}(z)\frac{1}{z} \left(\frac{\partial z}{\partial T}\right)_{P}$$
(A7)

$$\left(\frac{\partial z}{\partial T}\right)_{V} = \left[\frac{\partial z}{\partial g_{3/2}(z)}\frac{\partial g_{3/2}(z)}{\partial T}\right]_{V} = -\frac{3z}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}$$
(A8)

and

$$\left(\frac{\partial z}{\partial V}\right)_T = \left[\frac{\partial z}{\partial g_{3/2}(z)}\frac{\partial g_{3/2}(z)}{\partial V}\right]_T = -\frac{z}{V}\frac{g_{3/2}(z)}{g_{1/2}(z)}.$$
(A9)

Using equations (A4) and (A6)–(A9) and the thermodynamic relation

$$\left(\frac{\partial z}{\partial T}\right)_{P} = \left(\frac{\partial z}{\partial T}\right)_{V} + \left(\frac{\partial z}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{P}$$
(A10)

we obtain

$$\left(\frac{\partial g_{5/2}(z)}{\partial T}\right)_P = -\frac{g_{3/2}^2(z)}{g_{1/2}(z)} \left[\frac{3}{2}\frac{1}{T} + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right].$$
(A11)

$$\left(\frac{\partial g_{3/2}(z)}{\partial T}\right)_{P} = -g_{3/2}(z) \left[\frac{3}{2}\frac{1}{T} + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P}\right]$$
(A12)

and

$$\left(\frac{\partial V}{\partial T}\right)_{p} = \frac{Nk}{P} \left[\frac{5}{2} \frac{g_{1/2}(z)g_{5/2}^{2}(z)}{g_{3/2}^{3}(z)} - \frac{3}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)}\right].$$
(A13)

Substituting equations (A11)–(A13) into equation (A1), one obtains the heat capacity at constant pressure as

$$C_P = \frac{25}{4} Nk \left[\frac{g_{1/2}(z)g_{5/2}^2(z)}{g_{3/2}^3(z)} - \frac{3}{5} \frac{g_{5/2}(z)}{g_{3/2}(z)} \right].$$
 (A14)

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