

## A quantum solution to Gibbs paradox with few particles

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We present a fully quantum solution to the Gibbs paradox (GP) with an illustration based on a gedanken experiment with two particles trapped in an infinite potential well. The well is divided into two cells by a solid wall, which could be removed for mixing the particles. For the initial thermal state with correct two-particle wavefunction according to their quantum statistics, the exact calculations show the entropy changes are the same for boson, fermion and non-identical particles. With the observation that the initial unmixed state of identical particles in the conventional presentations actually is not of a thermal equilibrium, our analysis reveals the quantum origin of the paradox, and confirms Jaynes' observation that entropy increase in Gibbs mixing is only due to the including more observables. To further show up the subtle role of the quantum mechanism in the GP, we study the different finite size effect on the entropy change and show the work performed in the mixing process is different for various types of particles.

**Gibbs paradox, identical particles, mixing entropy**

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### 1 Introduction

More than one century ago, Gibbs [1] pointed out that, if the entropy were not extensive due to the neglect of indistinguishability of particles, there would be an entropy increase after two ideal gases from two containers at thermal equilibrium are mixed. On the contrary, the inverse process would bring the system back to its original state and cause the entropy decrease for the closed system. This apparently violates the Second Law of Thermodynamics (SLT). However, for distinguishable particles, this inverse process would not bring the system to the original initial state, and not violate the SLT.

In many textbooks, e.g., ref. [2], the Gibbs paradox (GP) is claimed to be solved by considering the indistinguishability of particle in the view of quantum theory, and adding correction to the expression of entropy. This mixing process will

bring no entropy change for identical particles, while additional increase for non-identical ones. However, this pedagogic explanation includes neither the internal properties of particle nor a quantum peculiarity of the problem (e.g., non-commutativity). On this aspect, we still do not understand how the entropy changes disappear only when two gases are the same, even though they can be arbitrary similar. In the classical thermodynamic, it is always able to assumed the substances empirically distinguished, however without defining how small their difference is. Thus, it is expected the perfect resolution of the GP should be referred to the quantum mechanics with intrinsic consideration of indistinguishability, even with internal variables of particles. This point was considered by some authors [3, 4] by introducing the internal state phenomenologically, and the discontinues of entropy change is avoided by utilizing another thermodynamic quantity-work.

Another resolution was based on the recognition that the knowledge of difference in particle types serves as information, which enables extracting more work to compensate the

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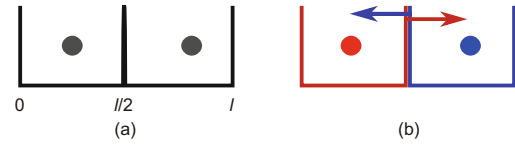
entropy increase [5]. However how the internal state involve in the mixing process is still unknown. On this sense, a fully consistent quantum description of the GP, to our best knowledge, is still lack, especially on the indistinguishability of the particles based on the standard quantum theory, such as the second quantization approach with symmetrizing wave functions. Fortunately, the quantum thermodynamics (QT) [6–8] has enlighten solutions to some paradoxes in thermodynamics [9, 10], e.g, the Maxwell’s demon (MD) paradox [10–12] with quantum Szilard engine. The QT may only concern the few-particle system, which sometimes is efficient to reveal the underlying principles and intrinsic mechanism.

In this work, we give a fully quantum solution to the GP involving the symmetrization of wave function of identical particles. We consider the mixing process of two particles confined in an infinite square potential well, which is divided into two sub-cells by a solid wall. Using the exact expression of the density matrix, we demonstrate explicitly that the initial un-mixing systems in the conventional presentation of GP are not in thermal equilibrium with respect to the whole well. For the identical particles, we follow the standard approach of second quantization and correctly write down the thermal equilibrium state of a un-mixing whole system by including internal variables and symmetrizing wave-function. This doing surprisingly restores the original version of GP for both non- and identical particles (Boltzman particles, and bosons/fermions) and solves the GP by showing the same entropy changes. The detailed comparisons with the case ignoring internal state is made to explicitly explain the origin of the paradox. For the cases with more particles, we also demonstrate almost the same result except for a little difference between boson and fermion, due to the finite size effect.

## 2 GP with an infinite potential well

In thermal equilibrium, the most probable state of many particles in a container with two sub-cells of equal volume usually is the situation with each cell containing the equal number of particles. Thus, to show up the essence of the GP, we firstly consider the two particle case, similar to the single molecule case [13] for the Szilard heat engine in resolving the MD paradox.

Let us model the whole container as an infinite high square potential well  $V(x, l)$  ( $= 0$  for  $x \in (0, l)$  and  $\infty$  elsewhere) to trap two particles (see Figure 1(a)). The well is initially separated by the infinite high  $\delta$ -potential, namely  $v\delta(x - l/2)$  with  $v \rightarrow \infty$ . With the single particle eigen-wavefunctions  $|\varphi_n^L\rangle$  ( $|\varphi_n^R\rangle$ ) on left (right) cell corresponding eigen-energies  $E_n^L$  ( $E_n^R$ )  $= 2\hbar^2 n^2 \pi^2 / Ml^2$ , the eigen-wavefunctions of two distinguishable particle system read as  $|\Phi_{nm}^{uv}\rangle = |\varphi_n^u\rangle_1 \otimes |\varphi_m^v\rangle_2$  corresponding to eigen-energies  $E_{nm}^{uv} = E_n^u + E_m^v$ , for  $u, v = R, L$ . With the explicit expressions of eigen-wavefunctions given in the Supplementary Materials (SM),  $\varphi_n^L(x) = \langle x | \varphi_n^L \rangle$  and  $\varphi_n^R(x)$  are supported over the whole domain  $(-\infty, \infty)$  including  $(0, l)$ . This observation seems trivial, however can serves



**Figure 1** GP modeling with two particles trapped in a one-dimensional square potential well of infinite depth with width  $l$ . (a) The ordinary potential. The box is separated by a central  $\delta$ -potential. (b) Different potentials trap different colored particles where the colors characterize their internal states. The mixing is realized by isothermally moving the barrier of each potential.

as the key point to resolve the GP as well as the MD paradox [10, 12].

To show this, we write down the thermal equilibrium state

$$\rho_T = \sum_{n,m} \sum_{u,v} \frac{1}{Z_T} e^{-\beta E_{nm}^{uv}} |\Phi_{nm}^{uv}\rangle \langle \Phi_{nm}^{uv}| \quad (1)$$

of two Boltzman particles with inverse temperature  $\beta$  and partition function  $Z_T$ . It includes not only the terms with  $|\Phi_{nm}^{RL}\rangle$  and  $|\Phi_{nm}^{LR}\rangle$  for two particles in the different sub-cells shown in Figure 1(a), but also the terms with  $|\Phi_{nm}^{RR}\rangle$  and  $|\Phi_{nm}^{LL}\rangle$  for two particles in the same sub-cells. If the later terms were ignored as in the conventional description of GP, the initial un-mixing state used here would not be in thermal equilibrium, and thus could not correctly address the very problem in GP correctly. For non-identical particles, we can actually assert that one specified atom in the right sub-cell and another in the left. As emphasized by Jaynes, the specified assertion to distinguishable particles actually reduces the system’s entropy. Such difference between non- and identical particles is the very root of the GP. Based on this observation, we solve the GP by introducing internal state to the identical particles to restore the original GP in the next section.

## 3 Quantum description

In order to resolve the GP, we would make the situation with equal number of particles in the both sub-cells be the thermal state by referring certain prior information. It is possible for non-identical particles since they could be subject to different potentials. With the similar method, we can prepare the initial thermal state for identical particles with internal variable. Using the “colors” to label the internal degenerate states, the blue  $|b\rangle$  and the red ones  $|r\rangle$ . Let the blue and red particles be trapped respectively in the left and right sub-cells with the Hamiltonian

$$H = p^2/2M + |b\rangle \langle b| V(x, l/2) + |r\rangle \langle r| V(x - l/2, l/2), \quad (2)$$

where the potential is shown in Figure 1(b). We assume that the internal state of the two identical particle are different. Obviously, this assumption assigns one bit information, which brings the identical particle with the same initial un-mixing state as non-identical one. Therefore, the Gibbs mixing could causes entropy increase for both non- and identical particles.

The single particle eigen-wavefunctions of the present system are  $|b\varphi_n^L\rangle \equiv |b\rangle \otimes |\varphi_n^L\rangle$  and  $|r\varphi_n^R\rangle \equiv |r\rangle \otimes |\varphi_n^R\rangle$  with corresponding eigen-energy  $E_n^L$  and  $E_n^R$ . Associating with their quantum statistics properties, the two-particle wavefunctions before the Gibbs mixing are symmetrized or anti-symmetrized as:

$$|\Psi_{nm}^{U-B(F)}\rangle = \frac{1}{\sqrt{2}} (|b\varphi_n^L\rangle_1 |r\varphi_m^R\rangle_2 \pm |r\varphi_m^R\rangle_1 |b\varphi_n^L\rangle_2) \quad (3)$$

with the same eigen-energy  $E_{nm}^{U-B(F)} = E_n^L + E_m^R$ . Here, the sign plus/minus corresponds the boson/fermion case. These eigen-functions determine the density matrix of this system  $\rho_{U-B(F)}$  (for the explicit form see the SM), similar to eq. (1) with the partition function  $Z_{U-B(F)} = \sum_{n,m} \exp(-\beta E_{nm}^{U-B(F)})$ .

The mixing process is carried out by moving the right side of left potential to the position  $x = l$  and the left side of the right potential to the position  $x = 0$  isothermally, illustrated in Figure 1(b). After the mixing process, two particles are constrained in the larger domain ( $0 < x < l$ ). The single-particle wavefunctions of this system then become  $|\phi_n^s\rangle \equiv |s, \phi_n(x, l)\rangle$  (degenerate for  $s = b, r$ ) with the same eigen-energy  $E_n = n^2\pi^2\hbar^2/2Ml^2$ . The two-particle wavefunctions after mixing  $|\Psi_{nm}^{M-B(F)}\rangle \sim |\phi_n^b\rangle_1 |\phi_m^r\rangle_2 \pm |\phi_n^r\rangle_2 |\phi_m^b\rangle_1$  corresponds to eigen-energy  $E_{nm}^{M-B(F)} = E_n + E_m$ , which gives the density matrix  $\rho_{M-B(F)}$  with partition function  $Z_{M-B(F)}$ . The entropy change in the mixing process is simply calculated by using von Neuman entropy as  $\Delta S_{B(F)} = \text{Tr}[\rho_{U-B(F)} \ln \rho_{M-B(F)}] - \text{Tr}[\rho_{M-B(F)} \ln \rho_{M-B(F)}]$ .

We notice that the calculations about entropy change concern only the eigen-energies, rather than the concrete form of the wavefunction. However, the symmetry type of the wavefunction determines the counts of states to the partition function. For two non-identical particles with un-symmetrized eigen-wavefunctions  $|\Psi_{nm}^{U-N}\rangle = |b\varphi_n^L\rangle_1 \otimes |r\varphi_m^R\rangle_2$ , the corresponding eigen-energy simply is  $E_{nm}^{U-N} = E_n^L + E_m^R$ . Then, using the wavefunctions after mixing  $|\Psi_{nm}^{M-N}\rangle = |b\phi_n\rangle_1 \otimes |r\phi_m\rangle_2$  with the eigen-energies  $E_{nm}^{M-N} = E_n + E_m$ , we obtain the same expression of the entropy increase  $\Delta S_N$ . Therefore, it is concluded that the entropy changes in the process of mixing two Bosonic, Fermionic and non-identical particle are the same, namely

$$\Delta S_B = \Delta S_F = \Delta S_N. \quad (4)$$

On this sense, GP is resolved.

It is also meaningful to compare the present results with that without considering the internal state for Bosonic and Fermionic particles. In our consideration, the initial un-mixing state is a thermal state with all the three situations in eq. (1). The mixing process is completed by removing the central potential isothermally. The entropy change  $\Delta S'_X$  and work  $W'_X = k_B T [\ln Z'_{U-X} - \ln Z'_{M-X}]$  are calculated by using the partition functions of un-mixing and mixed particles  $Z'_{U-X}$  and  $Z'_{M-X}$  with  $X = B, F, N$ . Here, we deal with the usual setup in the conversional presentation of GP for non-identical atoms, which is the same as that with internal

state. We refer the detailed analysis for different species to Supplement Materials. One prominent feature is that both entropy changes and work done for different species are different, while these are the same in the process above with the correct considerations about internal state. We show these differences in Figure 2. In Figures 2(a) and (b), the entropy changes of identical particle approaches zero, while that of non-identical particles is  $2 \ln 2$ . The discrepancy just recovers the discontinuousness of entropy changes in conventional presentation of GP. The similar difference in work extraction is illustrated in Figures 2(c) and (d). In the present model, no internal freedom is probed and no prior information is added for identical particles. In comparison with the previous presentation of GP with internal freedom, we can conclude that the discontinuousness is caused by the different start-point between identical and non-identical particles.

To understand the above result, we recall the conventional presentation of GP that the initial state of the identical particles is formally different from the non-identical ones, which results in no entropy change for mixing identical particles. To our understanding, the same entropy changes are restored, solely by restoring the GP problem with the same start points for the different types of particles. With this observation, we conclude that the GP is rooted in the initial difference of un-mixing state rather than the character of indistinguishability of particles. It is also noticeable that we only utilize the quantum definition of entropy, the von Neuman entropy, other than any phenomenological presentations.

#### 4 Mixing entropy and work of two particle systems

As for the quantum effect in our approach for GP, the finite size of the well induces many interesting phenomenon. To explicitly demonstrate the effect, we take the Bosonic case for example. In terms of the Theta function  $\theta_3(0, q) = 1 + 2 \sum_n q^{n^2}$ , the partition functions before and after the Gibbs mixing are expressed[ see Appendix ] as  $Z_{U-B} = [\theta_3(0, q) - 1]^2/4$  and  $Z_{M-B} = [\theta_3(0, q^{1/4}) - 1]^2/4$  respectively with the parameters  $q = \exp(-2\beta\pi^2\hbar^2/ml^2)$ . The straightforward calculation explicitly gives the entropy increase during the mixing process as:

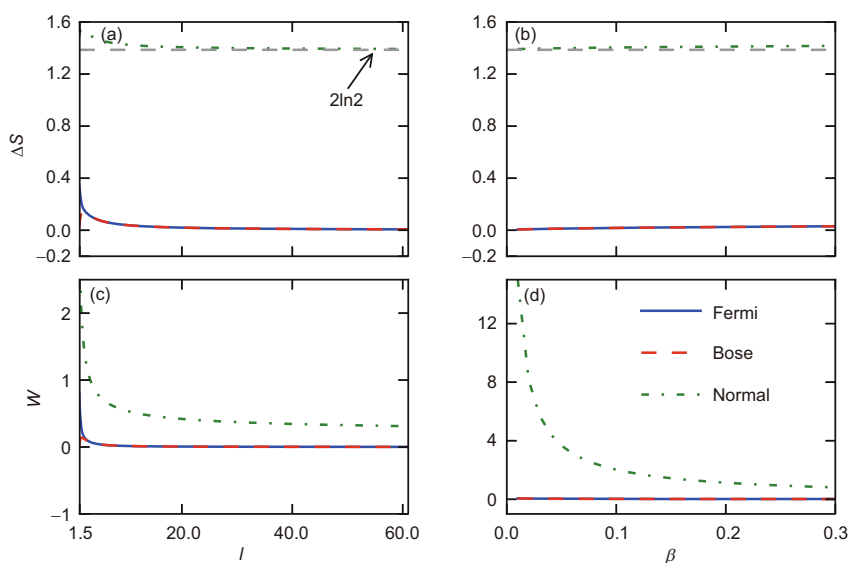
$$\Delta S_B = 2(\beta\partial_\beta - 1) \ln \frac{\theta_3(0, q) - 1}{\theta_3(0, q^{1/4}) - 1}. \quad (5)$$

Using the duality of the Theta-function  $(-\ln q/\pi)^{1/2} \theta_3(0, q) = \theta_3(0, \exp(\pi^2/\ln q))$ , we prove that  $\theta_3(0, q) \rightarrow 1/\sqrt{-\ln q/\pi}$  in the high temperature limit  $T \rightarrow \infty$  or in the classical limit  $L \rightarrow \infty$ . With this observation, the classical result is recovered as  $\lim_{L \rightarrow \infty} \Delta S_B = 2 \ln 2 = \Delta S_{\text{classical}}$ .

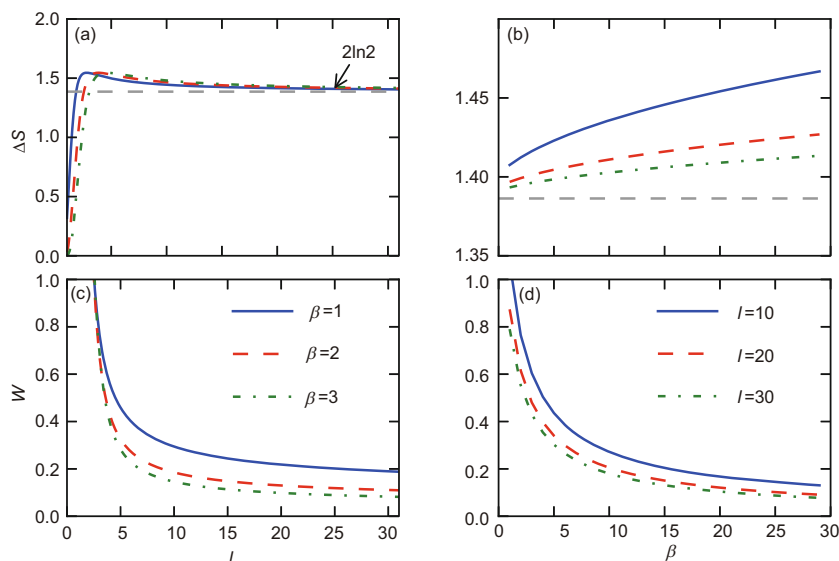
Very quantum nature is the dependence of entropy change on size of the trap and also on the temperature, illustrated in Figure 3(a). The entropy change  $\Delta S_{\text{classical}}$  in the classical case is marked as gray-dashed line in Figures 3(a) and (b). The entropy changes tends to the classical one  $\Delta S_{\text{classical}}$

as the trap size approaches infinite, presented in Figure 3(a). This confirms our theoretical analysis given above. We also show its dependence on the inverse temperature  $\beta$  in Figure 3(b). The entropy also tends to the classical case as the inverse temperature approaches zero ( $\beta \rightarrow 0$ ), since the thermal fluctuation compares well the discreteness of the energy levels in the well. Finally, starting with the correct uses of the eigen-vectors and -energies, we consider work done in the mixing process as refs. [4, 5]. The mixing process is performed isothermally, and the work just compensates the

free energy change, namely,  $W_B = k_B T [\ln Z_{U-B} - \ln Z_{M-B}]$ , which is the same for different species. This seemingly-trivial observation also solves GP. We show in Figures 3(c) and (d) the work done as function of trap size  $l$  and inverse temperature  $\beta$  respectively. With larger trap size, the work approaches zero. However, it is not zero as temperature increase. Similar behavior has also been observed in the insertion process of SHE [10]. Theoretically, the work diverges as  $\sqrt{T}$  as  $T \rightarrow \infty$ . The detailed derivation is presented in supplement materials.



**Figure 2** Entropy change in the process of mixing two atoms as a function of trap size  $l$  (a) with different inverse temperature  $\beta = 0.5$  and inverse temperature  $\beta$  (b) with different  $l = 10$  for different species: Fermi (blue-solid), Bose (red-dashed) and non-identical (green-dash dotted). Work done as function of trap size (c) and inverse temperature (d). The classical case of entropy change  $\Delta S_{\text{classical}}$  is also marked as gray-dashed line in (a) and (b).



**Figure 3** Entropy change in the process of mixing two atoms as a function of trap size  $l$  (a) with different inverse temperature  $\beta = 1$  (blue-solid), 2 (red-dashed) and 3 (green-dash dotted) and inverse temperature  $\beta$  (b) with different  $l = 10$  (blue-solid), 20 (red-dashed) and 30 (green-dash dotted). Work done as function of trap size (c) and inverse temperature (d). The classical case of entropy change is marked as gray-dashed line in (a) and (b).

## 5 Mixing entropy of 4 particle systems

To give prominence to the properties of quantum statistics, we consider the mixing process of four particles. Initially, there are two particles in each sub-cell. The internal states of the particles in the right/left side are all blue/red. Its partition function in thermal equilibrium is initially (see Appendix):

$$Z_{U-B(F)}(N=4) = [Z_2^{U-B(F)}(q)]^2,$$

where  $Z_2^{B(F)}(q) = \frac{1}{2} [(Z_1(q^4))^2 \pm Z_1(q^8)]$  denotes the partition function of a two-particle system confined in a square potential well with width  $l/2$ . For  $Z_1(q) = [\theta_3(0, q) - 1]/2$ , there exist two limit results: in the quantum limit with low temperature  $\beta/l^2 \rightarrow \infty$ , we have  $Z_1(q) \sim 2q$ ; and in the classical limit  $\beta/l^2 \rightarrow 0$ , we have  $Z_1(q) \sim 1/2 \sqrt{-\ln q/\pi} - 1/2$ . Together with the partition function (see Appendix)  $Z_{M-B(F)}(N=4) = (Z_2^{B(F)}(q^{1/4}))^2$  after mixing, we calculate the entropy change as:

$$\Delta S_{B(F)}(N=4) = 2(1 - \beta\delta\beta) \ln \frac{Z_2^{B(F)}(q)}{Z_2^{B(F)}(q^{1/4})}. \quad (6)$$

In the classical limit, we have  $\lim_{l \rightarrow \infty} \Delta S_{B(F)}(N=4) = 4 \ln 2$ . Indeed, when deviating from the classical limit or the lower temperature, the entropy change displays the obvious differences between boson and fermion.

If we mix identical particles without considering the internal state, one must start from an equilibrium state with partition function (see Appendix)  $Z'_{U-B(F)}(N=4) = \sum_{n=0}^N Z_n^{B(F)}(q) Z_{4-n}^{B(F)}(q)$ , and that  $Z'_{M-B(F)}(N=4) = Z_4^{B(F)}(q^{1/4})$  after mixing. In the classical limit, we obtain the entropy change as  $\lim_{l \rightarrow \infty} \Delta S'_{B(F)}(N=4) = 0$ . The results obtained here can be directly generated for the arbitrary atom number  $N$ .

## 6 Summary

We have resolved the GP in a fully quantum framework with the correct presentations of the initial thermal states of the working substances consisting of the particles with different quantum statistical properties. Here, we utilize a standard quantum description, the wave function symmetrization from the second quantization of the particles with internal variable. The key point is our finding that the problem in the paradox are rooted in the different uses (somehow misuses) of the initial thermal state for identical and non-identical particles. We use examples with two and four particles to illustrate our comprehensive understanding for GP. We show that the entropy change of identical and non-identical particles are the same for two particle system, but the deference could only be found as the finite size effect in the low temperature, or in the cases with more than two particles.

## Appendix

In this appendix, we provide the detailed calculations of the article.

### Appendix A Wavefunctions

The un-mixing single particle wave-function is listed as:

$$\langle x|\varphi_n^L\rangle = \begin{cases} \sqrt{\frac{4}{l}} \sin(2n\pi x/l), & 0 < x < l/2, \\ 0, & \text{otherwise,} \end{cases} \quad (a1)$$

$$\langle x|\varphi_n^R\rangle = \begin{cases} \sqrt{\frac{4}{l}} \sin[2n\pi(x-l/2)/l], & l/2 < x < l, \\ 0, & \text{otherwise,} \end{cases} \quad (a2)$$

with the same eigen-energy  $E_n^L = E_n^R = 2n^2\pi^2\hbar^2/MI^2$ . After the removing the central potential, the atoms can stay in the whole area. The wavefunction is

$$\langle x|\phi_n\rangle = \begin{cases} \sqrt{\frac{2}{l}} \sin(n\pi x/l), & 0 < x < l, \\ 0, & \text{otherwise,} \end{cases} \quad (a3)$$

with energy  $E_n = n^2\pi^2\hbar^2/(2MI^2)$ .

### Appendix B Mixing process of 2 atoms

(1) With internal freedom

The Hamiltonian for the atoms with internal freedom is written as:

$$H = |b\rangle\langle b| \otimes H_b + |r\rangle\langle r| \otimes H_r, \quad (b1)$$

where  $H_i = p^2/2m + V_i$  ( $i = b, r$ ) is the corresponding Hamiltonian of the atom with internal state  $i = b, r$ . For this model, the mixing is done by moving the right boundary of the left potential to the right ( $x = l$ ) and the left boundary of the right potential to the left ( $x = 0$ ). For the Bosonic case, the partition function of unmixing two atoms is

$$\begin{aligned} Z_{U-B} &= \sum_{n,m=1}^{\infty} \exp[-2\beta\pi^2\hbar^2(n^2 + m^2)/MI^2] \\ &= \left( \sum_{n=1}^{\infty} q^{4n^2} \right) \left( \sum_{m=1}^{\infty} q^{4m^2} \right) \\ &= Z_1(q^4)^2, \end{aligned} \quad (b2)$$

where  $q = \exp(-\beta\pi^2\hbar^2/2MI^2)$  and  $Z_1(\tau) = \sum_{n=1}^{\infty} \tau^{n^2}$  is the one-particle partition function and it can be related to the Theta function by

$$Z_1(\tau) = [\theta_3(0, \tau) - 1]/2.$$

The partition function of mixed atoms is obtained similarly as:

$$Z_{M-B} = Z_1(q)^2. \quad (b3)$$



The results for Fermionic and non-identical atoms is the same as that of Bosonic case. It is clear that  $q \in (0, 1)$  and approaches 1 as  $T \rightarrow \infty$  or  $l \rightarrow \infty$ . The Theta-function has a duality feature

$$\sqrt{-\ln(q)/\pi} \theta_3(0, q) = \theta_3\left(0, \exp\left(\frac{\pi^2}{\ln q}\right)\right). \quad (\text{b4})$$

With this equation, we explicitly get

$$\begin{aligned} \theta_3(0, q) &= \left(-\frac{\ln q}{\pi}\right)^{-1/2} \theta_3\left(0, \exp\left(\frac{\pi^2}{\ln q}\right)\right) \\ &= \left(-\frac{\ln q}{\pi}\right)^{-1/2} \left[1 + 2 \sum_{n=1}^{\infty} \exp\left(\frac{\pi^2 n^2}{\ln q}\right)\right]. \end{aligned} \quad (\text{b5})$$

The factor  $\exp(\pi^2/\ln q)$  is no more than 1 when  $T$  or  $l$  is sufficiently large, which leads to

$$1 \leq 1 + \sum_{n=1}^{\infty} \exp\left(\frac{\pi^2 n^2}{\ln q}\right) \leq 1 + \sum_{n=1}^{\infty} \exp\left(\frac{\pi^2 n}{\ln q}\right) = \frac{1}{1 - e^{\pi^2/\ln q}}. \quad (\text{b6})$$

Thus,  $\sum_{n=1}^{\infty} \exp\left(\frac{\pi^2 n}{\ln q}\right)$  approaches 0 as  $T \rightarrow \infty$  or  $l \rightarrow \infty$  and the asymptotic behavior of  $\theta_3(0, q)$  as  $T \rightarrow \infty$  or  $l \rightarrow \infty$  is

$$\theta_3(0, q) = \left(-\frac{\ln q}{\pi}\right)^{-1/2} [1 + o(1)]. \quad (\text{b7})$$

Using the above relationship, the classical limit can be obtained as:

$$\begin{aligned} \lim_{l \rightarrow \infty} \Delta S_B &= \lim_{L \rightarrow \infty} \left(\beta \frac{\partial}{\partial \beta} - 1\right) \ln \frac{\left(\sqrt{\frac{Ml^2}{2\beta\pi\hbar^2}} - 1\right)^2}{\left(\sqrt{\frac{2Ml^2}{\beta\pi\hbar^2}} - 1\right)^2} \\ &= 2 \ln 2. \end{aligned} \quad (\text{b8})$$

### (2) Without internal freedom

In this section, we will discuss the mixing process of two identical atoms without any internal freedom. In this situation, the two atoms has the probability to stay in the same side of the chamber.

**Bosonic Case** The eigen-functions before mixing are  $|\Theta_{nm}^{U-B}\rangle_{RR} = [|\varphi_n^R\rangle_1 |\varphi_m^R\rangle_2 + |\varphi_m^R\rangle_1 |\varphi_n^R\rangle_2] / \sqrt{2}$ ,  $|\Theta_{nm}^{U-B}\rangle_{RL} = [|\varphi_n^R\rangle_1 |\varphi_m^L\rangle_2 + |\varphi_m^L\rangle_1 |\varphi_n^R\rangle_2] / \sqrt{2}$  and  $|\Theta_{nm}^{U-B}\rangle_{LL} = [|\varphi_n^L\rangle_1 |\varphi_m^L\rangle_2 + |\varphi_m^L\rangle_1 |\varphi_n^L\rangle_2] / \sqrt{2}$  for  $n \neq m$  and when  $n = m$  the eigen-functions  $|\Theta_{nn}^{U-B}\rangle_{RR} = |\varphi_n^R\rangle_1 |\varphi_n^R\rangle_2$  and  $|\Theta_{nn}^{U-B}\rangle_{LL} = |\varphi_n^L\rangle_1 |\varphi_n^L\rangle_2$ . The partition function is then derived as:

$$\begin{aligned} Z'_{U-B} &= \sum_{n,m=1}^{\infty} (2 + \delta_{nm}) \exp[-2\beta\pi^2\hbar^2(n^2 + m^2)/(Ml^2)] \\ &= \frac{1}{2} [\theta_3(0, q^4) - 1]^2 + \frac{1}{2} [\theta_3(0, q^8) - 1]. \end{aligned} \quad (\text{b9})$$

After the mixing, the two-particle wavefunction are  $|\Theta_{nm}^{M-B}\rangle = [|\phi_n\rangle_1 |\phi_m\rangle_2 + |\phi_m\rangle_1 |\phi_n\rangle_2] / \sqrt{2}$  for  $n \neq m$  and when  $n = m$   $|\Theta_{nn}^{M-B}\rangle = |\phi_n\rangle_1 |\phi_n\rangle_2$ . The partition function is

$$\begin{aligned} Z'_{M-B} &= \sum_{n,m=1}^{\infty} \frac{1}{2} (1 + \delta_{nm}) \exp[-\beta\pi^2\hbar^2(n^2 + m^2)/(2Ml^2)] \\ &= \frac{1}{8} [\theta_3(0, q) - 1]^2 + \frac{1}{4} [\theta_3(0, q^2) - 1]. \end{aligned} \quad (\text{b10})$$

**Fermionic Case** The function before mixing should be anti-symmetrized as  $|\Theta_{nm}^{U-F}\rangle_{RR} = [|\varphi_n^R\rangle_1 |\varphi_m^R\rangle_2 - |\varphi_m^R\rangle_1 |\varphi_n^R\rangle_2] / \sqrt{2}$ ,  $|\Theta_{nm}^{U-F}\rangle_{LL} = [|\varphi_n^L\rangle_1 |\varphi_m^L\rangle_2 - |\varphi_m^L\rangle_1 |\varphi_n^L\rangle_2] / \sqrt{2}$  with  $n \neq m$  and  $|\Theta_{nm}^{U-F}\rangle_{RL} = [|\varphi_n^R\rangle_1 |\varphi_m^L\rangle_2 - |\varphi_m^L\rangle_1 |\varphi_n^R\rangle_2] / \sqrt{2}$ .

$$\begin{aligned} Z'_{U-F} &= \sum_{nm} (2 - \delta_{nm}) \exp[-2\beta\pi^2\hbar^2(n^2 + m^2)/(Ml^2)] \\ &= \frac{1}{2} [\theta_3(0, q^4) - 1]^2 - \frac{1}{2} [\theta_3(0, q^8) - 1]. \end{aligned} \quad (\text{b11})$$

After the mixing, the two-particle wavefunction are  $|\Theta_{nm}^{M-F}\rangle = [|\phi_n\rangle_1 |\phi_m\rangle_2 - |\phi_m\rangle_1 |\phi_n\rangle_2] / \sqrt{2}$  with  $n \neq m$ . The partition function is

$$\begin{aligned} Z'_{M-F} &= \sum_{nm} \frac{1}{2} (1 - \delta_{nm}) \exp[-\beta\pi^2\hbar^2(n^2 + m^2)/(2Ml^2)] \\ &= \frac{1}{8} [\theta_3(0, q) - 1]^2 - \frac{1}{4} [\theta_3(0, q^2) - 1]. \end{aligned} \quad (\text{b12})$$

## Appendix C Mixing process of 4 atoms

### (1) With internal freedom

At beginning, there are two blue atoms (whose internal states are  $|b\rangle$ ) in the left compartment and two red atoms (whose internal states are  $|r\rangle$ ) in the right compartment. Thus, the initial partition function is

$$Z_{U-B(F)}(N=4) = (Z_2^{B(F)}(q))^2, \quad (\text{c1})$$

where  $Z_2^{B(F)}(q)$  denotes the cononical partition function of a two-particle system confined in a square potential well with width  $l/2$ . The explicit expression of  $Z_2^{B(F)}(q)$  is

$$Z_2^{B(F)}(q) = \frac{1}{2} \left( (Z_1(q^4))^2 \pm Z_1(q^8) \right). \quad (\text{c2})$$

The concrete form of the un-mixing gas is rewritten as:

$$\begin{aligned} Z_{U-B(F)}(N=4) &= \frac{1}{4} \left( (Z_1(q^4))^2 \pm Z_1(q^8) \right)^2 \\ &= \frac{1}{4} \left( \frac{(\theta_3(0, q^4) - 1)^2}{2} \pm \frac{\theta_3(0, q^8) - 1}{2} \right)^2. \end{aligned} \quad (\text{c3})$$

After mixing, these four atoms are confined in a infinity high square well with width  $l$ . The partition function is simply

$$\begin{aligned} Z_{M-B(F)}(N=4) &= (Z_2^{B(F)}(q^{1/4}))^2 \\ &= \frac{1}{4} \left( (Z_1(q))^2 \pm Z_1(q^2) \right)^2 \end{aligned}$$

$$= \frac{1}{4} \left( \left( \frac{\theta_3(0, q) - 1}{2} \right)^2 \pm \frac{\theta_3(0, q^2) - 1}{2} \right)^2. \quad (c4)$$

Therefore the entropy change is

$$\Delta S_{B(F)} = (1 - \beta\delta_\beta) \ln \frac{Z_{M-B(F)}(N=4)}{Z_{U-B(F)}(N=4)}. \quad (c5)$$

Using the property of Theta function, it is not difficult to show that under the classical limit ( $T \rightarrow \infty$  or  $l \rightarrow \infty$ ), the entropy change tends to be  $4 \ln 2$  for both Boson and Fermion systems.

(2) Without internal freedom

In this section, we discuss the mixing process which is the same as the one in the last section except that the atoms considered here do not contain internal freedom. In this circumstance, the initial state is a mixing of 5 situations, i.e., the  $n$ -th situation is that there are  $n$  atoms in the left compartment while the others are in the right compartment. Thus, the initial partition function is

$$Z'_{U-B(F)}(N=4) = \sum_{n=0}^4 Z_n^{B(F)}(q) Z_{4-n}(q), \quad (c6)$$

where  $Z_n^{B(F)}(q)$  denotes the cononical partition function of a  $n$ -particle system confined in a square potential well with width  $l/2$ . The relationship between  $Z_n^{B(F)}(q)$  and  $Z_1(q)$  can be found in Table 1.

After the mixing process, the system becomes a well containing four identity atoms and the partition function is

$$\begin{aligned} Z'_{U-B(F)}(N=4) &= Z_4(q^{1/4}) \\ &= \frac{1}{24} \left( \begin{array}{l} Z_1(q) + 3Z_1(q^2)^2 \pm 6Z_1(q^4) \\ \pm 6Z_1(q^2)Z_1(q)^2 + 8Z_1(q^3)Z_1(q) \end{array} \right). \end{aligned} \quad (c7)$$

This partion function can also be related to the Theta function by the ways mentioned above. The entropy change during this process is

$$\Delta S'_{B(F)}(N=4) = (1 - \beta\delta_\beta) \ln \frac{Z'_{M-B(F)}(N=4)}{Z'_{U-B(F)}(N=4)},$$

**Table 1** The relationship between  $Z_n^{B(F)}(q)$  and  $Z_1(q)$  for  $n = 2, 3, 4$

$n$	$Z_n^{B(F)}(q)$
2	$\frac{1}{2} (Z_1(q)^2 \pm Z_1(q^2))$
3	$\frac{1}{6} (Z_1(q)^3 \pm 3Z_1(q^2)Z_1(q) + 2Z_1(q^3))$
4	$\frac{1}{24} \left( \begin{array}{l} Z_1(q)^4 + 3Z_1(q^2)^2 \pm 6Z_1(q^4) \\ \pm 6Z_1(q^2)Z_1(q)^2 + 8Z_1(q^3)Z_1(q) \end{array} \right)$

which can also be proved that  $\lim_{L \rightarrow \infty} \Delta S'_{B(F)}(N=4) = 0$  by using the property of the Theta function.

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