Quantum coherence, crucial to current investigations of quantum information, quantum computation [1–3], and quantum simulations [4, 5], is also capable of producing surprising effects in thermodynamics and statistical mechanics [6, 7]. For example, a heat engine, powered by an ensemble of trapped atoms with quantum coherence, could surpass the Carnot efficiency [7, 8], yet with no violation of the Second Law of Thermodynamics [8, 9]. Importantly, recent progresses in cold atom physics have allowed real experimental demonstrations of many quantum thermodynamic phenomena [10–14], at a region where the size of the trap is comparable with the thermal de Broglie wavelength [15]. Within these trapped atomic systems [10, 13], we will show that the quantum coherence, originally absent in classical thermodynamics, will in turn improve our understanding towards classical thermodynamics in a particular example of entropy increasing.

The entropy of an isolated system is believed to monotonically increase due to the irreversible process [16]. However, a completely isolated system with no interaction with other degrees of freedoms would follow a unitary evolution [17]. Such unitary evolution results in a constant entropy of the system, namely $S(t) = S(0)$ where $S(t) = -k_B \text{Tr}[\rho(t) \ln \rho(t)]$ and $\rho(t) = U(t) \rho(0) U^\dagger(t)$. This observation simply implies that the “isolated” system in classical thermodynamics is not completely isolated. The underlying question is, to what extent, the system is isolated to retain the statement of entropy increase in classical thermodynamics, while consistent with other assumptions.

One of the mostly referred models for entropy increase is the free expansion (FE) of ideal gas in a box, known as the Joule expansion [18, 19]. During FE, the internal energy is kept constant, while entropy would increase with $\Delta S = Nk_B \ln V_A/V_B$, where $V_B$ and $V_A$ are the volume of gas before and after expansion respectively [18]. The increase of the entropy is attributed to an irreversible process, whose physical correspondence, to our best knowledge, remains vague. In this letter, we show that such irreversible process could be a pure dephasing process, by which the quantum coherence are essentially removed after expansion.

To simplify the discussion, we consider a widely used model with a single atom (mass $M$) trapped in a 1D square potential [20–22] at temperature $T$, illustrated in Fig. 1(a). We include a quantum dephasing effect, which conserves the energy in order to match Joule’s statement of no energy exchange during FE in classical thermodynamics. With this dephasing process, the entropy change...
during FE, is shown as a function of the ratio between the trap size \(L\) and the thermal de Broglie wavelength \(\lambda_T = h(2\pi M k_B T)^{-1/2}\) with the orange curve in Fig. 1(b). For comparison, we also plot the entropy change of an isothermal expansion (IsoE), where the atom, in contact with a thermal bath, has a constant temperature. At the classic region \((L/\lambda_T \gg 1)\), the entropy changes for both processes match the well-known classical result \(\Delta S_c = k_B \ln 2\), when the trap size doubles. Apart from the classic region, e.g. \(L/\lambda_T < 1\), the entropy change after FE deviates from the classical one \(\Delta S_c\). At the limit \(L/\lambda_T = 0\), the entropy changes for two processes are different: it approaches a constant \(1.035k_B\) for FE, while reaches zero for IsoE. In the IsoE process, the atom is frozen to the ground state with both entropy and total energy constantly reduced as the temperature decreases.

**Theoretical framework** - Before expansion, the atom is trapped on the left side by a half-size square potential \(V_b(x)\),

\[
V_b(x) = \begin{cases} 
0 & -L/2 < x < 0 \\
\infty & \text{otherwise}
\end{cases},
\]

as shown in Fig. 1(a). For the single-atom Hamiltonian \(H_b = p^2/2M + V_b(x)\), the eigen-wavefunction is denoted as \(\phi_n^L\) with the corresponding energy \(E_n^L = 4n^2\alpha\), where \(\alpha = \pi^2\hbar^2/2ML^2\). In the region \(-L/2 < x < 0\), the probability amplitude of the atom is \((x \mid \phi_n^L) = \sqrt{L/\sin(2\pi nx/L)}\). We assume the atom is initially in a thermal equilibrium state with inverse temperature \(\beta = 1/(k_B T)\),

\[
\rho(t_0) = \sum_{n=1}^{\infty} \frac{\exp[-\beta E_n^L]}{Z} \mid \phi_n^L \rangle \langle \phi_n^L |,
\]

where \(Z = \sum_{n=1}^{\infty} \exp[-\beta E_n^L] = \sum_{n=1}^{\infty} \exp[-qn^2]\) is the partition function with \(q = 4\alpha\beta\). The dimensionless parameter \(q\) is rewritten in terms of the trap size \(L\) and the thermal wavelength \(\lambda_T\) as \(q = 2\pi(\lambda_T/L)^2\). The partition function is simplified with Theta-function as \(Z = [\theta_3(0,e^{-q})]^{-1}/2\). The internal energy of atom is \(\langle H_b \rangle = -\partial \ln Z / \partial \beta\), which approaches \(k_B T/2\) at high temperature limit [23], matching the equipartition theorem in classical thermodynamics [16].

After a sudden moving of the right wall, we have a new trap potential \(V_n(x)\) with twice the size \(L\). The corresponding eigen wavefunction for the new Hamiltonian \(H_n = p^2/2m + V_n(x)\) is denoted as \(\mid \psi_n \rangle\) with energy \(E_n = n^2\alpha\). The initial state of atom can be rewritten with this new basis \(\{\mid \psi_n \rangle\}\),

\[
\rho(t_0) = \sum_m D_m \mid \psi_m \rangle \langle \psi_m \rangle + \sum_{m_1 \neq m_2} F_{m_1 m_2} \mid \psi_{m_1} \rangle \langle \psi_{m_2} \rangle ,
\]

where \(D_m = \sum_{n=1}^{\infty} \langle \psi_m \mid \phi_n^L \rangle \langle \phi_n^L \mid \psi_m \rangle \exp[-qn^2]/Z\) is the diagonal term, and \(F_{m_1 m_2} = \sum_{n=1}^{\infty} \langle \psi_{m_1} \mid \phi_n^L \rangle \langle \phi_n^L \mid \psi_{m_2} \rangle \exp[-qn^2]/Z\) is the off-diagonal element, corresponding to the quantum coherence.

Clearly, the off-diagonal term is relevant in counting the entropy at least for the initial state, namely, \(\text{Tr} [\rho_0 \ln \rho_0] \neq \sum D_m \ln D_m\). If the atom is completely isolated with no interaction with any other degrees of freedom, this non-vanishing coherence term would contribute to entropy, resulting in no entropy change. With this observation, we remark here that a dephasing mechanism would be necessary for demolishing the coherence in order to recover the general statement of entropy increase in thermodynamics.

The immediate question is whether dephasing solely is sufficient to recover the classical result of entropy increase. The answer is yes. Supposing only dephasing is involved to demolish all off-diagonal elements, we obtain a completely mixed state \(\rho_t = \sum_m D_m \mid \psi_m \rangle \langle \psi_m \rangle\). In the following discussion, we will concentrate on the discussion on the effect of quantum dephasing, while delay the corresponding dynamics to next section.

Let’s first calculate the diagonal terms \(D_m\). The probabilities for even and odd quantum numbers are

\[
D_m = \begin{cases} 
\frac{\exp[-qm^2/4]}{2Z} & m = 2k \\
\sum_{n=1}^{\infty} \frac{32n^2 \exp[-qm^2]}{Z(m^2-k^2)^2\pi^2} & m = 2k - 1
\end{cases}
\]

with \(k = 1, 2, 3,...\) We remark that the summation in \(D_m\) can be analytically performed for even number, yet not for odd number. The analytic simplicity for even number is a direct result of the double size after expansion. The
nodes of wavefunctions after expansion match the boundary of the wall position before expansion. One interesting result is the odd and even portions have equal total contributions, namely, $\sum_{k=1}^{\infty} D_{2k} = \sum_{k=0}^{\infty} D_{2k+1} = 1/2$.

We show the probability $D_{in}$ in Eq. (3) for both even and odd numbers in Fig. 2 at $T = 1$ (Fig. 2a), $T = 100$ (Fig. 2b), and $T = 1000$ (Fig. 2c). Gray dashed lines mark the probabilities at thermal equilibrium with initial temperatures, except for a normalization factor $1/(2\pi)$. The distribution of even number states indeed follows that of thermal equilibrium at the initial temperature, as in Fig. 2, while the distribution for the odd-number state deviates from the thermal distribution at initial temperature. Therefore, the atom after FE is not on a thermal equilibrium. Such deviation from the thermal equilibrium is reduced at high temperature, illustrated in Fig. 2(c).

The FE process conserves the total energy of gas atom. The effect of conserving energy is directly reflected through an extreme case at zero temperature. At zero temperature, the initial state before expansion is the ground state $|\phi_{n=1}\rangle$ with energy $E_{ini} = 4\alpha$, which is four times of the energy of the ground state $|\psi_{n=1}\rangle$ of the gas after FE. Taking the limit, one directly gets $D_{2k} = 1/2\delta_{k,1}$ ($k = 1, 2, 3...$), which implies atom has half probability to go the even-number state with the same energy $E_{2} = E_{1}^2$. The other half of initial internal energy is redistribution into odd number states with the distribution $D_{2k-1} = 32/[(2k - 1)^2 - 4)]^2\pi^2]$. With the distribution above, the gas entropy after expansion is ready to be calculated via von Neumann-Shannon entropy definition

$$S_{f} = -k_{B}\text{Tr}[\rho_{f}\ln\rho_{f}],$$

while the entropy before expansion is $S_{i} = -k_{B}\text{Tr}[\rho_{i}\ln\rho_{i}]$. The entropy change after FE $\Delta S_{FE} = S_{f} - S_{i}$ is plotted vs the ratio $L/\lambda_{T}$, as blue line with circles in Fig. 1. In the calculation, we have used natural unit, $k_{B} = 1$ and $\hbar = 1$, and set the mass $M = 1$, the temperature $T = 1$. In the simulation, the ratio $L/\lambda_{T}$ is changed via varying the trap size $L$. The curve shows an asymptotic approaching to the classical case with entropy change $\Delta S_{c} = k_{B}\ln 2$ at the classical region $L/\lambda_{T} \gg 1$. This asymptotic behavior confirms that the well-know classical result of entropy increase is retained with solely considering dephasing. In this region, the entropy change during IsoE is close to that of FE, as shown in Fig. 1(c). However, the processes are different: (1) FE involves the dephasing mechanism as the irreversible process, while IsoE is reversible. (2) The atom’s internal energy during FE is kept constant, while decreases for IsoE process.

Notable difference at the region ($L/\lambda_{T} \sim 1$) is shown in Fig. 1. The entropy change during FE is larger than the classical result $k_{B}\ln 2$. The interesting case is at zero temperature, where the entropy of initial state is zero, namely, $S_{i} = 0$. A direct calculation of the entropy after FE gives $S_{f} = 1.035k_{B}$, as illustrated in Fig. 1. The constant 1.035 can be calculated via the probabilities at zero temperature. During IsoE, the atom is frozen to the ground state both initially and finally at zero temperature. Therefore, the entropy change is simple zero at zero temperature.

**Dephasing and Dynamics** – By including dephasing, we have shown the recovery of the classical result of entropy change, and more importantly the deviation apart from classical region. We now turn to the physical origin of the dephasing process, which can be a result of the fluctuation of the wall of the trap. Supposing the wall has small fluctuations, $L \rightarrow L + \delta L$, the eigen-energy of the single particle is changed to $E_{n}(L + \delta L) \approx E_{n}(L) + 2E_{n}(L)\delta L$. This coupling to the wall is similar to the coupling in cavity optomechanics, where the cavity wall has a small displacement. Following the similar procedure, we obtain an effective interaction between the trapped atom and the trap wall as

$$H_{int} = \sum_{n=1}^{\infty} g_{n}|\psi_{n}\rangle\langle\psi_{n}|(b + b^{\dagger}),$$

where $b(b^{\dagger})$ is the annihilation (creation) operator for fluctuation of the trap wall, and $g_{n} = 2\alpha n^{2}$. Multiple modes of the wall with interaction $H_{int} = \sum_{n}\sum_{\xi} g_{n}\xi|\psi_{n}\rangle\langle\psi_{n}|(b_{\xi} + b_{\xi}^{\dagger})$, result in dephasing to gas molecule in the square trap, namely,

$$\frac{\partial}{\partial t}\rho(t) = i[H, \rho(t)] + L[\rho(t)],$$

where $L[\rho(t)] = \sum_{mn} \gamma_{mn} (L_{m}^{\dagger}L_{n}\rho + \rho L_{m}^{\dagger}L_{n} - 2L_{m}^{\dagger}L_{n}\rho L_{n}^{\dagger})$ is the Liouville operator with $L_{n} = |\psi_{n}\rangle\langle\psi_{n}|$.

In cold atom experiments, the density profile of gas $p(x, t) = \langle x| \rho(t)|x \rangle$ in the square potential is a measurable quantity. We show the dynamical evolution of the
density profile for both short time and long time in Fig. 3(a) at low temperature $T = 1$. In the simulation, we set the same dephasing rate $\gamma_{nm} = \gamma$. The initial localized atom on the left ($-1/2 < x/L < 0$), flows to the right and then bounces between the two walls, see Fig. 3(a) at short time scale $t \in [0, 5]$. Meanwhile, the atom spreads into the whole square trap, illustrated by long-time behavior $t \in [35, 40]$ in Fig. 3(a), with lowering revival peak on each side as times of bouncing increases. The profile at the steady state is illustrated in Fig. 3(b) with the blue solid line, along with the profile of gas at equilibrium (the orange dashed line). The profile after FE shows a distinct feature of a dip, illustrated by the blue curve at middle of the square trap ($x/L = 0$), instead of a peak (orange line) for that at thermal equilibrium. The appearance of the dip is caused by the non-equilibrium distribution shown in Fig. 2(a). The evolution of density profile at higher temperature ($T = 100$) is shown in Fig. 3(c), with the steady distribution in Fig. 3(d). At high temperature, the discrepancy of steady-state profile from equilibrium one is significantly reduced, as illustrated in Fig. 3(d). The reduction of discrepancy from equilibrium one is the direct result of distribution above.

One important relation in trapped atoms is the dependence of entropy $S(T)$ on the internal energy $E(T)$, namely $S(T) \sim E(T)$ curve [24]. We have shown that the atom is at non-equilibrium state after free expansion. Such non-equilibrium system has an abnormal $S \sim E$ curve, illustrated as the orange line in Fig. 4. In the simulation, we increase the temperature ($T$) with the size ($L$) of trap fixed. Due to the thermal isolation, the internal energy for gas after free expansion is four times its ground state energy ($\pi^2 \hbar^2/(2mL^2)$) at absolute zero temperature, while it is the ground state energy for isothermal expansion. The resulting non-equilibrium distribution after free expansion, leads to the non-zero entropy $S_I(T \to 0) = 1.035k_B$, illustrated in Fig. 4 at zero temperature. The corresponding of entropy-energy for gas at equilibrium is illustrated as blue curve in Fig. 4. Different from the curve for atom after FE, this curve shows both zero entropy and exact ground state energy at zero temperature.

It’s worthy to check the current experimental accessibility [13] for later verification of our theoretical observations. In Ref. [13], a square trap is experimentally realized with size $70\mu m \times 50\mu m \times 35\mu m$, and a Rubidium 87 atom with $120$nm has a thermal wavelength $\lambda_T \sim 1\mu m$. The ratio between trap size and thermal wavelength is roughly $L/\lambda_T \sim 0.05$, which is marked as an arrow on Fig. 1. With these parameters, the difference from the classical result is merely seen. To reach the region with prominent difference, one needs to reduce the ratio by 10 times, by either reducing the trap size to roughly several $\mu m$ or the temperature around $1nk$. Such requirements are achievable, noticing the coldest atom ensemble has been created in a sub picokelvin region [25].

In conclusion, we have shown how the dephasing process in a quantum fashion can serve as the irreversible process, and further deepen our understanding of entropy increase in classical thermodynamics. Furthermore, the discrepancies from classical thermodynamics are also illustrated for the single atom in the square trap, far apart from the classical region. We prove that such discrepancies are mainly caused by the non-equilibrium state of the atom after FE, and can be experimentally tested via normal measurements of the density profile or energy-entropy relation.

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