Mixing indistinguishable systems leads to a quantum Gibbs paradox

Full technical version: arXiv:2006.12482

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Introduction

As is often the case in physics, important conceptual breakthroughs about the connection between information and thermodynamics were stimulated by a number of famous paradoxes. Maxwell's demon is one notable example; another is the Gibbs paradox [1]. Gibbs devised a deceptively simple thought experiment in which two ideal gases are initially on the left- and right-hand sides of a partitioned box (with equal volumes and particle numbers n). The partition is removed so that the gases expand to fill the box and mix. For a single gas, the doubling in volume comes with an entropy increase of $nk_B \ln 2$. For two different gases, the entropy therefore increases by $2nk_B \ln 2$, while for identical gases effectively nothing has changed and so the entropy remains the same. The paradox comes when we imagine different gases that are similar enough to be indistinguishable by some observer: is there an entropy change, or not?

Historically, the paradox was seen as problem in correctly counting microstates such that the entropy becomes extensive, involving accounting for indistinguishability of particles [2, 3]. As Gibbs himself understood – more recently clarified by Jaynes [4] – the paradox has a clear operational resolution. The entropy change is indeed observer-dependent, as it corresponds to the amount of work an experimenter with specific capabilities can extract from the mixing process. An *ignorant observer*, who has no device in their lab to distinguish the gases, cannot extract work and thus deduces no entropy change. An *informed observer* can in principle extract $2nk_BT \ln 2$ of work by using two semi-permeable pistons to interact separately with the gases and letting them expand independently. To quote Jaynes [4]: 'the number of fish that you can catch is an "objective experimental fact"; yet it depends on how much "subjective" information you have about the behavior of fish.'

There have been several discussions of how quantum mechanics affects the Gibbs paradox [3, 5–7]. In this work [8], we model the thought experiment to take seriously the many-body quantum character of identical particles (bosons and fermions). For an ignorant observer, we find a counter-intuitive and striking distinction from the classical case that survives even in the macroscopic limit.

Model

We consider a toy model of a non-interacting gas of identical bosons or fermions. Each particle has "space" and "spin" degrees of freedom, respectively labelled x, s. The box is divided into $d/2$ "cells" on the left and right (d being even), comprising the spatial degree of freedom. The spin s is a qubit whose orthogonal basis states $|\uparrow\rangle, |\downarrow\rangle$ are used as the distinguishing label for the two gases. We take a vanishing Hamiltonian $H = 0$ – which at first glance seems unrealistic, however even classically this assumption reproduces the correct entropy for an ideal gas [3].

The initial state is with n spin-$\uparrow$ particles fully thermalised (i.e., maximally mixed) over the left $d/2$ cells, and similarly the right-hand n particles are chosen as either spin-$\uparrow$ or -$\downarrow$ corresponding to the cases of identical or different gases. The ignorant observer is unable to access the spin (the gases hence appearing indistinguishable); the informed observer is permitted to engineer spin-dependent dynamics [9].

We let work be extracted via a globally energy-conserving interaction with a heath bath B at some temperature T and a work battery b (which need not be explicitly modelled here). The optimum extractable work W in going from an initial state ρ to final state ρ' is taken as the difference in free energy F, where $F(\rho) = \mathrm{Tr}(H\rho) - k_B T S(\rho)$, and $S(\rho) = -\mathrm{Tr}\,\rho \ln \rho$ is the von Neumann entropy [10, 11]. Due to the vanishing Hamiltonian this reduces to $W = k_B T[S(\rho') - S(\rho)] =: k_B T \Delta S$. This is typically an over-simplification, for instance in a resource-theoretic context in which different varieties of free energy must be considered [12, 13]. However, W turns out to be interpretable as a mean work value, whose fluctuations we later characterise.

Formalism

Our analysis hinges on a careful study of the first-quantised Hilbert space $\mathcal{H}_N$ of N particles. This is obtained by taking the (anti-)symmetric part of $\mathcal{H}_x^{\otimes N} \otimes \mathcal{H}_s^{\otimes N}$ for bosons (fermions), representing N copies of the single-particle Hilbert spaces $\mathcal{H}_x$, $\mathcal{H}_s$ for space and spin. In particular, we need to describe the state space seen by the ignorant observer, by tracing out the spin part. To do this, we use a decomposition [14] resulting from Schur-Weyl duality [15]:

$$\mathcal{H}_N = \bigoplus_{J=0}^{N/2} \mathcal{H}_x^J \otimes \mathcal{H}_s^J \tag{1}$$

(note that $N = 2n$ is even). Here, J can be interpreted as the usual total spin magnitude quantum number, and it simultaneously labels $\mathcal{H}_s^J$ as irreps of $SU(2)$ and $\mathcal{H}_x^J$ as irreps of $SU(d)$. Formula (1) essentially says that the permutation symmetry properties of the space and spin parts have to combine together to give overall (anti-)symmetry. It generalises the well-known case of $N = 2$, where $J = 0, 1$ correspond to the singlet and triplet subspaces. For two bosons, a spatial singlet pairs with a spin singlet, and the same for triplets. For two fermions, the symmetries pair oppositely.

For the ignorant observer, crucially, the subspaces $\mathcal{H}_x^J$ are fully distinguishable. J is a conserved quantity – however, any operation is permitted within each J block. This lets us find the final state of maximal entropy subject to the conservation of J. A certain amount of work W_J may be deterministically extracted for each J occurring with probability p_J, and on average we obtain $\sum_J p_J W_J = k_B T \Delta S$. The initial spin configuration thus leaves its imprint on the extractable work through the distribution p_J.

Results

In the case of identical gases, the entropy changes for the two observers $\Delta S_{\mathrm{info}}, \Delta S_{\mathrm{igno}}$ are exactly as obtained classically. With different spins, the same is true for the informed observer. However, the situation for the ignorant observer with orthogonal spins is fundamentally different. Of course, they can never perform better than the informed observer, so $\Delta S_{\mathrm{igno}} \leq \Delta S_{\mathrm{info}}$. However, in many cases, ΔS_{igno} is greater than what is classically possible – see Fig. 1. Then *different gases are of use even if they cannot be distinguished.*

Something remarkable happens in what we term the low-density limit – when d is much larger than n. This may be thought of as the box approaching a continuum. Here, we find that the gap between the two observers tends to a constant, namely the Shannon entropy of the distribution p_J:

$$\Delta S_{\mathrm{info}} - \Delta S_{\mathrm{igno}} \xrightarrow{d\to\infty} H(\mathbf{p}) = -\sum_J p_J \ln p_J. \tag{2}$$

Even more remarkably, if we then consider a macroscopic limit where n is large, it turns out that $H(\mathbf{p}) = \mathcal{O}(\ln n)$ and thus is negligible, so

$$\Delta S_{\text{info}} \approx \Delta S_{\text{igno}} \approx 2n \ln 2 \quad (n \gg 1 \text{ and } d \gg n^2). \tag{3}$$

Let us emphasise that this is the *complete opposite to the classical ideal gas*, despite being in the same continuum macroscopic limit.

We also compute the work fluctuations in these limits, finding them to be $\mathcal{O}(1)$ and so negligible. Moreover, we generalise to the case of non-orthogonal spins, obtaining a smooth interpolation between identical and different gases.

Discussion

The underlying mechanism is a generalisation of the Hong-Ou-Mandel effect from quantum optics, wherein an unmeasured degree of freedom (e.g. polarisation) affects the interference properties of photons. Unlike classical particles, for which the space and spin degrees of freedom can be decoupled, with quantum particles, overall symmetrisation means that relational information about the spins "leaks" into the spatial part. In the macroscopic, low-density limit, this information is sufficient to completely overcome the limitations of the ignorant observer.

Of course, this power comes a cost. In order to achieve the full quantum advantage, the ignorant observer has to couple their apparatus to the system via a highly many-body entangled basis (determined by the decomposition (1)). In a sense, the complexity of such an operation is comparable with the quantum Fourier transform [16] – explaining why the effect is not observed classically.

Our results demonstrate a fundamental difference in the roles of information and control between classical and quantum thermodynamics. This involves rethinking the way that microstates are counted in standard semi-classical analyses of quantum gases. With a sufficient degree of quantum control, the quantum-classical divergence survives – even maximising – in the macroscopic limit. Therefore it provides a counterexample to the naïve expectation that classical thermodynamics is recovered in a simple macroscopic limit. In showing the profound impact of quantum information upon one of the most important thermodynamical thought experiments, we hope that this work will inspire the exploration of more ways that genuinely quantum features can be exploited in thermodynamics.

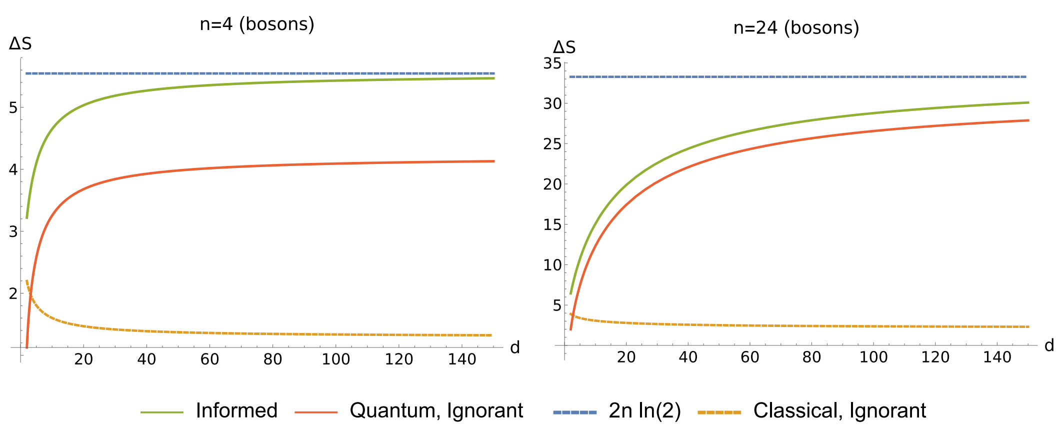

FIG. 1. Plots of the mixing entropy change as a function of total cell number d, as described by informed and ignorant observers in both the classical and quantum cases. The classical ideal gas limit $2n\ln(2)$ is shown for reference.

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[9] Subject to the caveat of not being able to change the number of each spin type, or else we would have to consider the spin as its own entropy-containing system, which is not in keeping with the spirit of the Gibbs mixing setting.
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