

# What is the Gibbs Paradox

and do we need Quantum mechanics to resolve it?

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June 29, 2010

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# 1. Introduction

- ▶ The Gibbs paradox involves the contrast between mixing two quantities of (ideal) gases of a different kind and that of mixing two quantities of the same gas.
- ▶ In the case of different gases, mixing is accompanied by an entropy increase  $\Delta S = 2R \log 2$ ; in the case of same gases there is no entropy change:  $\Delta S = 0$ .
- ▶ This paradox is a useful probe for inter-theory relations:

*Thermodynamics vs Statistical Mechanics*

*Thermodynamics vs. Quantum Mechanics Statistical*

*Mechanics vs. Quantum Mechanics*

## Main claims:

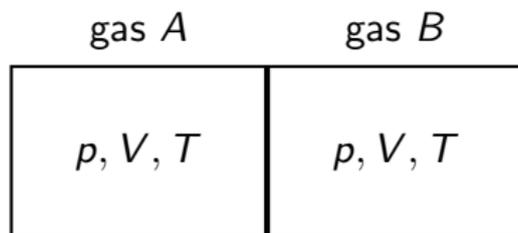
- ▶ What is understood by “the Gibbs paradox” is not the same in these different contexts.

Before  $\pm 1900$ : How can  $\Delta S$  change discontinuously when gases become more and more similar?

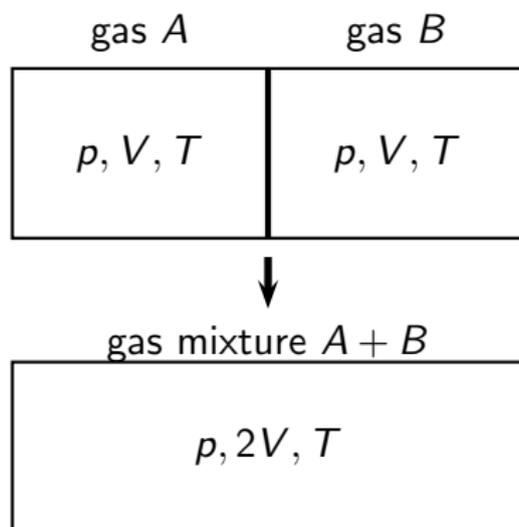
After  $\pm 1920$ : Why should the partition function be divided by  $N!$ ?

**Main Question:** how did this reconceptualization relate to the birth of quantum statistics?

# The Gibbs paradox in thermodynamics



# The Gibbs paradox in thermodynamics



Entropy change:

$$\Delta S := S_{A+B} - (S_A + S_B) = 2R \log 2$$

But if A is identical to B then  $\Delta S = 0$

## Gibbs 1876

*It is noticeable that the value of this expression does not depend on the kinds of gases considered, except that they must be of different kinds. If we should bring into contact two masses of the same gas, they would also mix, but there would be no increase of entropy. [ . . . ]*

*But if such considerations explain why the mixture of gases of the same kind stands on a different footing from the mixture of gases of different kinds, the fact is no less significant that the increase of entropy [ . . . ] is independent of the nature of the gases.*

*Now we may without violence to the general laws of gases suppose other gases to exist than such as actually do exist and there does not appear to be any limit to the resemblance which there might be between two such kinds of gas. But the entropy of mixing would be independent of the degree of similarity or dissimilarity. [ . . . ]*

*In such respects, entropy stands strongly contrasted with energy.*

What assumptions are being used?

- ideal gases
- Dalton's law
- additivity of entropy
- extensivity of entropy

A naive derivation:

$$\begin{aligned}S_A(V, T) &= c_V^A \log T + R \log V \\S_B(V, T) &= c_V^B \log T + R \log V \\S_{A+B}(V, T) &= (c_V^A + c_V^B) \log T + 2R \log 2V \\ \Delta S &:= S_{A+B} - (S_A + S_B) = 2R \log 2\end{aligned}\quad (1)$$

But if  $A \equiv B$

$$S_{A+A} = S_A(2V, T) = 2S_A(V, T)$$

Hence  $\Delta S = 0$

Gibbs sent out offprints to many colleagues. His work became known in France through a treatment of Duhem and Germany through Ostwald's translation.

The first to express misgivings were

C. Neumann (1891):

*Trotz alledem heftet sich an den Satz ein gewisses Misstrauen, in folge der Umstandes dass derselbe ungültig wiurd sobald A und B zwei Quantitäten desselben Gases sind. Sehe z.B. Gibbs durch welche aber in meinen Augen die hier vorhandene Dunkelheit nicht ganz beseitigt wird.*

Wiedeburg 1894 *Das Gibbs'sche Paradoxon*. But there were earlier pertinent discussions on related issues between Duhem (1882) and Poincaré (1892).

## Views on the Gibbs paradox in TD

**conventionalism** Entropies in thermodynamics are really only defined up to a (conventional) constant. So, (taking  $c_V^A = c_V^B = c$

$$S_A(V, T) = c \log T + R \log V + K_A$$

$$S_B(V, T) = c \log T + R \log V + K_B$$

$$S_{A+B}(V, T) = 2c \log T + 2R \log 2V + K_{A+B}$$

$$\Delta S = 2R \log 2 + K_{A+B} - K_A - K_B$$

Duhem (1882) makes the assumption that  $K_{A+B} = K_A + K_B$  but he is criticized by Poincaré: If we express entropy as a function of  $(V, p)$  instead we obtain

$$S_A(V, p) = c \log p + (R + c) \log V + K'_A$$

etc., which leads to  $\Delta S = 2(R + c) \log 2 + K'_{A+B} - K'_A - K'_B$

Assuming

$$K'_{A+B} = K'_A + K'_B$$

yields an entirely different  $\Delta S$  But why is one more obvious than the other?

# Views on the Gibbs paradox in TD

- ▶ (Operationalism) Wiedeburg 1894:  
Changes in entropy two states are only defined when there exists a quasistatic process between these states. From the mixed state of different gases  $A$  and  $B$  we can quasistatically go to the unmixed states by assuming the existence semi-permeable membranes.  
But if  $A = B$ , the existence of a semipermeable membrane is self-contradictory. That explains the paradox.  
Cf: Bridgman(1941):  
To say that two gases are different **means** there is no way to separate them. Conversely, to say that gases are the same **means** there is no way to separate them.
- ▶ The discontinuity is explained through a corresponding discontinuity in the 'universe of operations'.

- ▶ Observer-dependence (Maxwell 1878, Grad 1961, Van Kampen 1984, Jaynes 1992): There is no real matter of fact about whether gases are really “the same”, but rather as conventional choice: Any observer who regards different gases as the same may consistently use an entropy assignment in which  $\Delta S = 0$ .

# The Gibbs paradox in statistical mechanics

Gibbs 1902:

- ▶ consider a classical ideal gas of  $N$  'entirely similar' particles, i.e., its Hamiltonian  $H(\vec{q}_1, \vec{p}_1; \dots; \vec{q}_N, \vec{p}_N)$  is permutation invariant.
- ▶ Should the phase points  $x = (\vec{q}_1, \vec{p}_1; \dots, \vec{q}_N, \vec{p}_N)$  and  $x' = \Pi x$  be identified or not? (with  $\Pi$  any permutation of  $\{1, \dots, N\}$ ).
- ▶ Gibbs distinguishes two points of view, but does not choose sides:
  - ▶ Generic: Yes,  $x$  is the same state as  $x'$ .
  - ▶ Specific No,  $x$  and  $x'$  are different.

*"the question is to be decided in accordance with the requirements of practical convenience of the problems with which we are engaged."*

	Specific	Generic
Phase space	$\Gamma$	$\tilde{\Gamma} = \Gamma / \{\Pi\}$
phase space volume	$dx$	$d\tilde{x} = dx / N!$
partition function	$Z = \int_{\Gamma} e^{-\beta H(x)} dx$	$\tilde{Z} = Z / N!$
expectations	$\langle A \rangle_s = \frac{1}{Z} \int_{\Gamma} A e^{-\beta H} dx$	$\langle A \rangle_g = \frac{1}{\tilde{Z}} \int_{\Gamma} A e^{-\beta H} d\tilde{x}$
Entropy	$S = \frac{\partial}{\partial T} (kT \log Z)$	$\tilde{S} = \frac{\partial}{\partial T} (kT \log \tilde{Z})$

Only difference between specific and generic view in canonical ensemble is in the entropy

$$\tilde{S} = S - \log N! \approx S - N \log N - N$$

(But since  $N$  is constant in the canonical ensemble, this term can be absorbed in in the arbitrary additive constant.)

There are no empirical differences between the specific and generic viewpoints with a fixed  $N$ .

But Gibbs prefers generic viewpoint.

for an ideal gas one gets (ignoring terms depending only on  $T$ )

$$S = \frac{3}{2}kN \log V \quad \text{not extensive}$$

$$\tilde{S} = \frac{3}{2}k \log V/N \quad \text{extensive}$$

For the entropy of mixing in the specific point of view

$$\Delta S = S(2V, 2N) - 2S(V, N) = 3kN \log 2 \quad \text{same gases}$$

$$\Delta S = 3kN \log 2 \quad \text{different gases}$$

In generic viewpoint

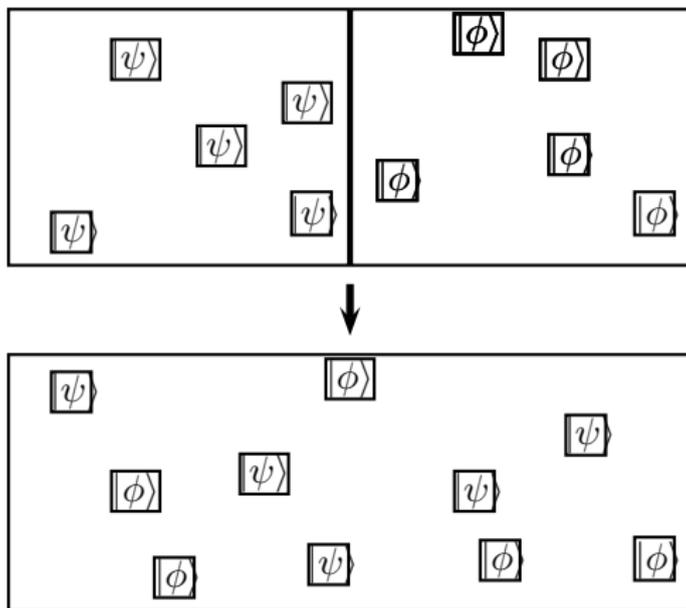
$$\Delta S = 0$$

$$\Delta S = 3kN \log 2$$

Hence, in the generic viewpoint we reproduce the Gibbs paradox of TD!

# QM to the rescue

Von Neumann (1933) discusses a gas of boxes, each containing a single quantum particle in state  $|\psi\rangle$



- ▶ Von Neumann assumes the entropy of the gas mixture is determined by the density operator  $W = \frac{1}{2}(|\psi\rangle\langle\psi| + |\phi\rangle\langle\phi|)$ .
- ▶ He argues that  $S = -Nk \text{Tr} W \log W$ , by considering two special cases:
  - if  $|\phi\rangle = |\psi\rangle$ :  $\Delta S = 0$
  - if  $|\psi\rangle \perp |\phi\rangle$ :  $\Delta S = Nk \log 2$ .
- ▶ He claims that the paradox (discontinuity) is solved since  $\Delta S$  will vary gradually between these two extremes, as a function of  $|\langle\psi|\phi\rangle|$ .

Schrödinger (1952, p.61)

*It was a famous paradox pointed out by W.Gibbs that the same entropy increase must not be taken into account when the molecules are of the same kind, although, according to the naive view, diffusion takes place then too, but unnoticeable to us.*

*The modern view solves this paradox by declaring that the second case is no real diffusion because exchange between like particles is not a real event.*

