

# Gibbs paradox: Mixing and non mixing potentials

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## Abstract

Entropy of mixing leading to Gibbs paradox is studied for different physical systems with and without potentials. The effect of potentials on the mixing and non mixing character of physical systems is discussed. We hope this article will encourage students to search for new problems which will help them understand statistical mechanics better.

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## 1 Introduction

Statistical mechanics is the study of macroscopic properties of a system from its microscopic description. In the ensemble formalism introduced by Gibbs[1] there are three ensembles-micro canonical, canonical and grand canonical ensemble. Since we are not interested in discussing quantum statistics we will use the canonical ensemble for introducing our ideas. To study the thermody-

namics of any system (which is the main aim of statistical mechanics) we need to calculate the canonical partition function, and then obtain macro properties like internal energy, entropy, chemical potential, specific heat, etc. of the system from the partition function. In this article we make use of the canonical ensemble formalism to study the extensive character of entropy and then to calculate the entropy of mixing. It is then used to explain the Gibbs paradox. Most text books

[2, 3, 4, 5, 6, 7, 8, 9] discuss Gibbs paradox considering only the case of the classical ideal gas, but here we analyze different physical systems with and without potentials. The study of Gibbs paradox is very fundamental as pointed out by Erwin Schrödinger- “It has always been believed that Gibbs paradox embodied profound thought. That it was intimately linked up with something so important and entirely new could hardly have been foreseen.”

## 2 Gibbs paradox

When entropy of an ideal gas was calculated using ensemble theory, it was found to be not extensive.

$$S = N k \left[ \ln \left( \frac{V}{\lambda^3} \right) + \frac{3}{2} \right].$$

The entropy of mixing for two ideal gases is the difference between the total entropy after mixing and that of individual systems before mixing. For the same particle density, the entropy of mixing is given by

$$\Delta S = k \left[ N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right].$$

If we find  $\Delta S$  for two different ideal gases it is found that there is a finite entropy of mixing, but a paradoxical situation is there for similar ones - instead of getting  $\Delta S = 0$  there is a finite entropy of mixing. Thus the non extensive character of the entropy equation causes the Gibbs paradox when there is mixing. This paradox is resolved in an ad hoc way by Gibbs. He put a correction factor  $N!$

in the denominator of the partition function. The corrected  $N$  particle partition function is

$$Q_N = \frac{Q_1^N}{N!},$$

where  $Q_1$  is the single particle partition function.

With this correction the entropy become extensive which resolves the paradox.

$$S = N k \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right].$$

The entropy of mixing then turns out to be

$$\begin{aligned} \Delta S = k & \left[ (N_1 + N_2) \ln \frac{V_1 + V_2}{N_1 + N_2} \right] \\ & - k \left[ N_1 \ln \frac{V_1}{N_1} + N_2 \ln \frac{V_2}{N_2} \right]. \end{aligned}$$

If the initial particle densities of two similar mixing systems are equal, this equation gives  $\Delta S = 0$ . The recipe of Gibbs corrects the enumeration of micro states as necessitated by the indistinguishability of identical particles [3].

## 3 Thermodynamics in the canonical ensemble

In the canonical ensemble the bridging equation to find the thermodynamics is

$$A = -kT \ln Q_N,$$

where  $A$  is the Helmholtz free energy,  $k$  is Boltzmann's constant and  $T$  is the absolute

temperature. To circumvent Gibbs paradox the above equation is modified as

$$A = -kT \ln \frac{Q_N}{N!}.$$

Using Stirling's approximation,  $\ln N! = N \ln N - N$ ,

$$A = -kT (\ln Q_N - N \ln N + N).$$

With the inclusion of Gibbs' correction factor  $A$  contains new terms which are  $T$  and  $N$  dependent. So the entropy ( $S$ ) given by the equation

$$S = - \left( \frac{\partial A}{\partial T} \right)_{V,N}$$

needs to be modified. In the coming sections we will consider different systems with and without potentials which can be grouped into mixing and non mixing systems as relevant to the Gibbs paradox. The systems are classified as

1. Free classical particles
2. Particles in a potential without Gibbs paradox
3. Particles in a potential with Gibbs paradox

In these sections we will connect the effect of potentials on entropy of mixing by finding the extensive nature of entropy for different physical systems.

## 4 Free classical particles

Free particles can be

1. Non-relativistic free particles
2. Massive particles with a relativistic formulation
3. Ultra relativistic

### 4.1 Non-relativistic

For a single non-relativistic particle, the energy is

$$E = \frac{p^2}{2m}$$

and the  $N$  particle partition function is

$$Q_N = \left( \frac{V}{\lambda^3} \right)^N,$$

where  $V$  is the volume and  $\lambda$  is the de Broglie thermal wavelength given by

$$\lambda = \frac{h}{(2\pi m kT)^{\frac{1}{2}}}.$$

The entropy is

$$S = N k \left[ \ln \left( \frac{V}{\lambda^3} \right) + \frac{3}{2} \right]$$

which is not extensive. Introducing the Gibbs correction factor  $\frac{1}{N!}$  in the  $N$  particle partition function we get

$$Q_N = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N$$

and entropy becomes

$$S = N k \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right] \quad (1)$$

which is extensive.

## 4.2 Massive particles with a relativistic formulation

For relativistic particles the energy is

$$\epsilon_p = \sqrt{p^2 c^2 + m^2 c^4}$$

For massive particles  $mc^2 \gg pc$  and the partition function is

$$Q_N = \left[ \frac{V}{\lambda^3} e^{-\beta m c^2} \right]^N,$$

where  $\beta = \frac{1}{kT}$ , and the entropy is

$$S = Nk \ln \left[ \frac{V}{\lambda^3} e^{-\beta m c^2} \right] + \frac{3}{2} Nk + \frac{N}{T} m c^2$$

which is not extensive. With the Gibbs correction factor the entropy becomes

$$S = Nk \left[ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right]$$

which is same as in Eq.(1).

## 4.3 Ultra relativistic

Here  $pc \gg mc^2$  and the partition function is

$$Q_N = \left[ \frac{8\pi V}{h^3} \left( \frac{kT}{c} \right)^3 \right]^N.$$

The de Broglie thermal wavelength is

$$\lambda_r = \frac{hc}{2\pi^{\frac{1}{3}} kT}.$$

So

$$Q_N = \left[ \frac{V}{\lambda_r^3} \right]^N.$$

Using this partition function if we calculate the entropy we will get it as not extensive but intensive. Introducing the Gibbs correction factor the entropy becomes

$$S = Nk \left[ \ln \left( \frac{V}{N \lambda_r^3} \right) + 4 \right].$$

which is clearly extensive.

The above calculations show that all types of free particles exhibit the Gibbs paradox if the Gibbs correction factor is not used.

## 5 Particles in a potential

In the coming two sections we will check what will be the effect of potentials in the system to the extensive character of entropy and thereby to the Gibbs paradox.

### 5.1 Particles in a potential without Gibbs paradox

#### 1. Particles in a harmonic potential

Consider an array of equally spaced  $N$  harmonic oscillators along a finite length  $L$  with one particle per harmonic oscillator site. The Hamiltonian for a single particle is

$$H = \frac{p^2}{2m} + \frac{1}{2} K x^2$$

where  $K$  is the spring constant given by  $K = m\omega^2$ , where  $m$  is the mass of the particles and  $\omega$  its angular frequency.

The single particle partition function is

$$Q_1 = \frac{1}{h} \int_{-\infty}^{\infty} e^{-\beta \frac{p_x^2}{2m}} dp_x \int_{-L/2}^{L/2} e^{-\beta \frac{Kx^2}{2}} dx$$

$$= \frac{kT}{\hbar\omega} \text{Erf} \left( \sqrt{\frac{\beta K L^2}{8}} \right)$$

In the thermodynamic limit  $N, L \rightarrow \infty$  and  $N/L$  is finite, the  $\text{Erf}(\infty) = 1$ , so for the infinite length the single particle partition function reduces to

$$Q_1 = \frac{kT}{\hbar\omega}$$

and then

$$Q_N = (Q_1)^N.$$

So the entropy is

$$S = Nk \left[ 1 + \ln \frac{kT}{\hbar\omega} \right],$$

which is extensive even without Gibbs correction factor. So there is no entropy of mixing, and in this case the entropy is simply additive. The harmonic potential bounds the particles in the system. When two such systems are in contact no particle flow happens from system to the other. Thus the harmonic potential makes the system non mixing.

## 2. Quartic oscillator

For a quartic oscillator the Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2} K q^4.$$

The  $N$  particle partition function is

$$Q_N = \left[ \Gamma \left( \frac{1}{4} \right) \frac{\sqrt{\pi m}}{2 h K^{\frac{1}{4}}} (2kT)^{\frac{3}{4}} \right]^N.$$

The entropy is

$$S = Nk \left[ \frac{3}{4} + \ln \Gamma \left( \frac{1}{4} \right) \frac{\sqrt{\pi m}}{2 h K^{\frac{1}{4}}} (2kT)^{\frac{3}{4}} \right]$$

which is extensive.

## 3. Anharmonic oscillator

For an anharmonic oscillator the Hamiltonian is

$$H = \frac{p^2}{2m} + Cq^2 - gq^3 - fq^4$$

where  $C, g$  and  $f$  are positive constants but their values are very small. The  $N$  particle partition function is

$$Q_N = \left[ \left( \frac{2m}{C} \right)^{\frac{1}{2}} \frac{\pi kT}{h} (X) \right]^N,$$

where

$$X = \left[ 1 + \frac{3kT}{4} \left( \frac{f}{C^2} + \frac{5g^2}{4C^3} \right) + \dots \right].$$

The entropy is

$$S = Nk \left[ 1 + \ln \left[ \left( \frac{2m}{C} \right)^{\frac{1}{2}} \frac{\pi kT}{h} \right] \right] + Y,$$

where

$$Y = Nk \left[ \frac{3}{2} kT \left( \frac{f}{C^2} + \frac{5g^2}{4C^3} \right) + \dots \right].$$

The entropy is extensive.

#### 4. Electron in a magnetic field

Consider a system of localized particles of spin half with magnetic moment  $\mu_B$ , in the presence of an external magnetic field of strength  $B$ . The  $N$  particle partition function is given by

$$Q_N = [2 \cosh(\beta\mu_B B)]^N.$$

The entropy

$$S = Nk \ln [2 \cosh(\beta\mu_B B)] - Nk [\beta\mu_B B \tanh(\beta\mu_B B)]$$

is extensive.

In all the above calculations we have taken particles which are localized by some potentials which makes the system non mixing so that there is no Gibbs paradox. There is another way to differentiate between mixing and non mixing systems or extensive and non extensive systems. The technique is to draw the single particle phase space trajectories. We can see in Figure 1 that the phase space diagrams of the above localized systems have closed trajectories. This then implies that the systems are non mixing (but the converse is not true as, for example, in chaotic systems).

### 5.2 Particles in a potential with Gibbs paradox

#### 1. Non-relativistic free particles in a gravitational field

Consider a collection of  $N$  particles of mass  $m$  enclosed in a vertical cylinder of

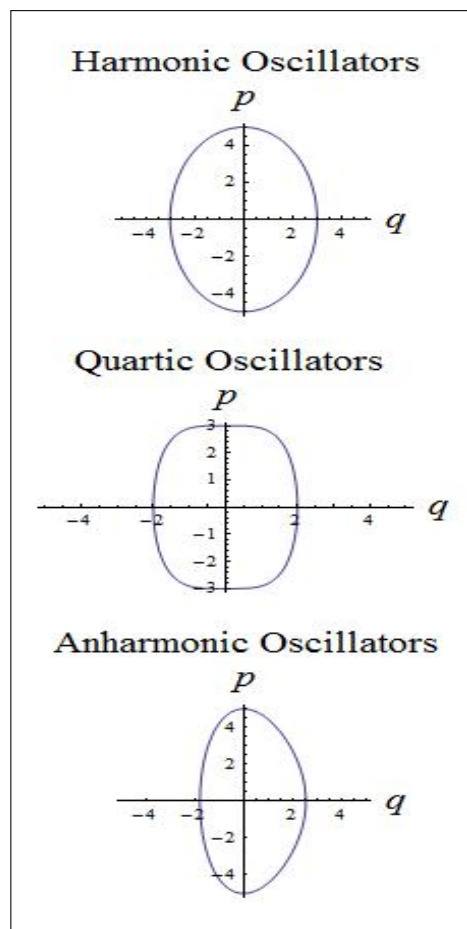


Figure 1: Single particle phase space diagrams

height  $L$  in a uniform gravitational field. The total energy of the system is

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz,$$

where  $mgz$  is the gravitational potential energy with  $z$  as the height of the particle. The  $N$  particle partition function is

$$Q_N = \left[ \frac{\mathcal{A}kT}{mg\lambda^3} (1 - e^{-\beta mgL}) \right]^N,$$

where  $\mathcal{A}$  is the area of cross section of the cylinder. In the limit when  $L \rightarrow \infty$  the partition function becomes

$$Q_N = \left[ \frac{\mathcal{A}kT}{mg\lambda^3} \right]^N.$$

The entropy is

$$S = Nk \left[ \ln \left( \frac{\mathcal{A}kT}{mg\lambda^3} \right) + \frac{5}{2} \right]$$

which is not extensive. With the Gibbs correction factor the entropy is changed to

$$S = Nk \left[ \ln \left( \frac{\mathcal{A}kT}{Nmg\lambda^3} \right) + \frac{7}{2} \right]$$

which is now extensive. If the potential energy is very large the particles will drop to the ground and will become stationary.

## 2. Diatomic molecule with inter-particle potential

Here we consider a system of diatomic molecules with the 2-particle Hamiltonian given by

$$H = \frac{p_1^2 + p_2^2}{2m} + \varepsilon|r_{12} - r_0|$$

where  $\varepsilon$  and  $r_0$  are positive constants and  $r_{12} = |\vec{r}_1 - \vec{r}_2|$  is the distance between the two particles.

$$Q_1 = \left( \frac{2\pi m}{\beta} \right)^3 V 4\pi X$$

where

$$X = \left[ \frac{2r_0^2}{\beta\varepsilon} + \frac{4}{(\beta\varepsilon)^3} - \frac{2e^{-\beta\varepsilon r_0}}{(\beta\varepsilon)^3} \right].$$

$$A = -NkT \ln \left[ \left( \frac{2\pi m}{\beta} \right)^3 V 4\pi X \right]$$

and the entropy

$$S = Nk \left[ \frac{3}{2} + \frac{Y}{X} \right] + Nk \ln \left[ \left( \frac{2\pi m}{\beta} \right)^3 V 4\pi X \right],$$

where

$$Y = \frac{2k(r_0)^2 T}{\varepsilon} + \frac{12kT^3}{\varepsilon} - e^{-\beta\varepsilon r_0} \left( \frac{6kT^3}{\varepsilon} + \frac{2k^2 T^2 r_0}{\varepsilon^2} \right).$$

$S$  is not extensive. With the Gibbs correction factor the entropy is

$$S = Nk \left[ \frac{5}{2} + \frac{Y}{X} \right] + Nk \ln \left[ \left( \frac{2\pi m}{\beta} \right)^3 \frac{V}{N} 4\pi X \right].$$

We now get an extensive entropy.

## 3. Diatomic dipoles in external electric field

Consider a system of diatomic molecules with electric dipole moment  $\mu$  and moment of inertia  $I$  placed in external electric field of strength  $E$ . The energy of a molecule is given by

$$E = \frac{p^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} - \mu E \cos \theta.$$

The  $N$ particle partition function is

$$Q_N = \left[ \frac{V}{\lambda^3} \left( \frac{I}{\beta \hbar^2} \frac{2 \sinh(\beta \mu E)}{\beta \mu E} \right) \right]^N$$

and the entropy

$$S = Nk \ln \left[ \frac{8\pi^2 k^2 T^2 IV}{\mu E \lambda^3} \sinh(\beta \mu E) \right] - \frac{N\mu E}{T} \coth(\beta \mu E) + \frac{7}{2} Nk$$

is not extensive. With the Gibbs correction factor the entropy is

$$S = Nk \ln \left[ \frac{8\pi^2 k^2 T^2 IV}{\mu E N \lambda^3} \sinh(\beta \mu E) \right] - \frac{N\mu E}{T} \coth(\beta \mu E) + \frac{9}{2} Nk$$

which is now extensive.

#### 4. Particles with a potential of the form $\frac{1}{2} C |r_2 - r_1|^2$

Consider a system with Hamiltonian

$$H = \frac{p_1^2 + p_2^2}{2m} + \frac{1}{2} C |r_2 - r_1|^2$$

This Hamiltonian approximates a non interacting diatomic molecule. The  $N$  particle partition function is

$$Q_N = \left[ \left( \frac{2\pi m}{h\beta} \right)^3 V \left( \frac{2\pi}{\beta C} \right)^{\frac{3}{2}} \right]^N$$

The entropy

$$S = Nk \ln \left[ \left( \frac{2\pi mk}{h} \right)^3 V T^{\frac{9}{2}} \left( \frac{2\pi k}{C} \right)^{\frac{3}{2}} \right] + \frac{9}{2} Nk$$

is not extensive. Introducing the Gibbs correction factor the entropy becomes

$$S = Nk \ln \left[ \left( \frac{2\pi mk}{h} \right)^3 \frac{V}{N} T^{\frac{9}{2}} \left( \frac{2\pi k}{C} \right)^{\frac{3}{2}} \right] + \frac{11}{2} Nk$$

which is now extensive.

#### 5. Free electrons in a magnetic field

Free electrons in a uniform magnetic field  $\vec{B}$  follow a helical path with an axis parallel to the field direction, say, the  $z$  axis. The projection on the  $x, y$  plane is a circle. The energy associated with the circular motion is quantized in units of  $\frac{e\hbar B}{mc}$  and the energy associated with the linear motion along the  $z$  axis is taken as continuous. The total energy of such particles is

$$E = \frac{e\hbar B}{2mc} \left( j + \frac{1}{2} \right) + \frac{p_z^2}{2m}$$

where  $j = 0, 1, 2, 3, \dots$ . The  $N$  particle partition function is

$$Q_N = \left[ \frac{V}{\lambda^3} \frac{\beta \mu_{eff} B}{\sinh(\beta \mu_{eff} B)} \right]^N$$

where  $\mu_{eff} = e\hbar/2mc$  and the entropy is

$$S = Nk \left[ \ln \left( \frac{V}{\lambda^3} \right) \frac{\beta \mu_{eff} B}{\sinh(\beta \mu_{eff} B)} \right] + Nk \left[ \beta \mu_{eff} B \coth(\beta \mu_{eff} B) + \frac{1}{2} \right]$$

The entropy is not extensive. By introducing the Gibbs correction factor for



the  $N$  particle partition function the entropy becomes

$$S = Nk \left[ \ln \left( \frac{V}{N\lambda^3} \right) \frac{\beta\mu_{eff}B}{\sinh(\beta\mu_{eff}B)} \right] + Nk \left[ \beta\mu_{eff}B \coth(\beta\mu_{eff}B) + \frac{3}{2} \right]$$

which is extensive. The above system is the Landau diamagnetic system in which electrons circulate in a helical path and collide with the walls, and bounce to and fro and behave as free particles.

From the above examples we find that even though these systems are under certain potentials they are non localized and such systems shows the Gibbs paradox.

## Conclusions

We have attempted to find the dependence of potentials and their effect on the Gibbs paradox by studying the extensive nature of entropy. It is found that there are potentials which do not allow mixing and for such systems there is no need of the Gibbs correction factor in the  $N$  particle partition function. There are some potentials which allow mixing and hence there is a necessity of the Gibbs correction term for the entropy to be extensive. We found that if the equation for the partition function is volume and temperature dependent it can be written as

$$Q_N \propto V\phi(T)$$

for systems which shows the Gibbs paradox, and for systems which do not show the Gibbs paradox

$$Q_N \propto V^0\phi(T)$$

indicating the volume independence and only temperature dependence. In our analysis we found that in the case of free particles, the Gibbs correction is essential to overcome the Gibbs paradox. In the cases of particles confined in a potential like harmonic, quartic, anharmonic potentials, and static electrons in a magnetic field we found that confinement makes the system localized and does not allow particles to flow and so there is no Gibbs paradox. For the systems like free electrons in a magnetic field, non-relativistic free particles in gravitational field and diatomic dipoles in an external electric potential, even if there is a potential there is no confinement, and the system is non localized which allows flow of particles.

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