Necessary Conditions for the Extensivity of Entropy

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Abstract

The resolution of the Gibbs paradox is traditionally attributed to the inclusion of the Gibbs Correction Factor (GCF), which involves dividing the number of microstates or the partition function by $N!$ to account for the indistinguishability of classical particles. While this combinatorial adjustment ensures the extensivity of entropy in many treatments, it is not sufficient in isolation. In this study, we argue that genuine extensivity of entropy in classical gases demands not only the GCF but also the fulfillment of the Classical Statistical Mechanics Condition (CSMC), $n\lambda^3 \ll 1$. This condition, which guarantees the suppression of quantum statistical effects, is essential to uphold the validity of classical approximations. By systematically analyzing this dual requirement, we present a more complete framework for understanding entropy in classical systems and offer a refined perspective on the resolution of the Gibbs paradox.

1 Introduction

Consider a gas of N non relativistic classical particles each with energy $E = \frac{p^2}{2m}$. In micro canonical ensemble, the number of micro states for classical particles is [1]

$$\Omega = \frac{\left(\frac{V}{h^3}\right)^N (2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \qquad (1)$$

where V is the volume, h is Planck's constant, m is the mass of the particle and N is the number of particles. Substituting $E = \frac{3}{2}NkT$,which represents the thermal energy of a classical ideal gas (where k is the Boltzmann constant and T is the absolute temperature), and then taking the logarithm on both sides while applying Stirling's approximation, we obtain:

$$\ln\Omega \simeq N\ln\left(\frac{V(2\pi mkT)^{\frac{3}{2}}}{h^3}\right) + \frac{3N}{2} \qquad (2)$$

Taking de Broglie wavelength $\lambda = \frac{h}{\sqrt{2\pi mkT}}$ and using Boltzmann relation $S = k\ln\Omega$, entropy [2]

$$S = k\ln\Omega \simeq Nk\ln\frac{V}{\lambda^3} + \frac{3}{2}kN \tag{3}$$

Entropy is an extensive thermodynamic quantity, but the given equation is not extensive. To restore extensivity, Gibbs, in an ad hoc manner, divided Ω by $N!$, leading to the extensive form of entropy [3, 4, 5, 6, 7, 8, 9]

$$S = k\ln\Omega \simeq Nk\left(\ln\frac{V/N}{\lambda^3}\right) + \frac{5Nk}{2} \tag{4}$$

This equation is assumed to be extensive based on the conclusion that the quantity within the bracket is non extensive, so that the equation becomes

$$S = N \times \text{Constant}$$

at constant temperature and volume. This means that S is having a linear dependence on the variable N.

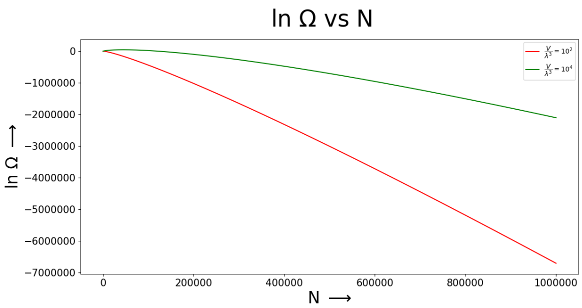

Figure 1: $\ln\Omega$ vs N for $\frac{l^3}{\lambda^3} = 10^2\&10^4$

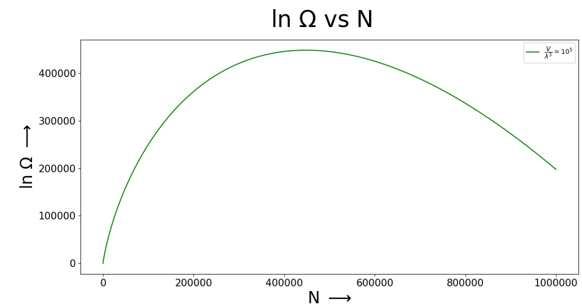

Figure 2: $\ln\Omega$ vs N for $\frac{l^3}{\lambda^3} = 10^5$

2 Influence of the term $\ln\frac{V/N}{\lambda^3}$ on extensivity

$\frac{V}{N}$ is the volume available for a particle to occupy in the given system. Let

$$V/N = l^3$$

Using this Equation (5) becomes

$$S = Nk\ln\frac{l^3}{\lambda^3} + \frac{5Nk}{2} \tag{5}$$

We took different values of $\frac{l^3}{\lambda^3}$ and plotted $\ln\Omega$ vs N graph. The maximum value of N is taken as 10^6. In Figure 1 and Figure 2 we had taken $\frac{l^3}{\lambda^3} = 10^2, 10^4$ and 10^5. We see that when $\frac{l^3}{\lambda^3} \ll N$ the graph will not be linear which means we cannot get a constant entropy or extensive entropy which depends only on N . In Figure 3 we took $\frac{l^3}{\lambda^3} = 10^8$ to 10^{18} for $N = 10^6$ and we got a linear graph. Thus entropy is only dependent on N which means extensive only when $l^3 \gg \lambda^3$ which is the CSMC. This is not a surprising result because we always say that GCF is used for classical ideal systems(which will be obeying CSM condition).

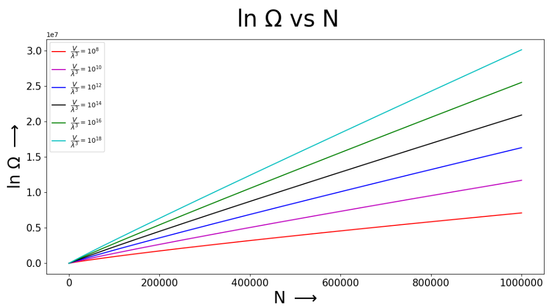

Figure 3: $\ln \Omega$ vs N for $\frac{l^3}{\lambda^3} = 10^8$ to 10^{18}

3 Conclusion

This work reinforces that the standard combinatorial resolution of the Gibbs paradox—dividing the number of microstates by $N!$—though essential, does not by itself guarantee the extensivity of entropy in classical systems. We have demonstrated that this resolution is valid only when the Classical Statistical Mechanics Condition (CSMC), $n\lambda^3 \ll 1$, is simultaneously satisfied. This condition ensures that quantum effects remain negligible and that the system can be meaningfully described by classical statistics. Importantly, this requirement is often left implicit or unacknowledged in traditional expositions. Our analysis clarifies that the proper reconciliation of thermodynamic and statistical mechanical entropy requires both the consideration of indistinguishability and the enforcement of the dilute limit. This dual perspective not only strengthens the conceptual basis of classical statistical mechanics but also sharpens its pedagogical value.

References

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