

Review

Thermodynamics of the System of Distinguishable Particles

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Abstract: The issue of the thermodynamics of a system of distinguishable particles is discussed in this paper. In constructing the statistical mechanics of distinguishable particles from the definition of Boltzmann entropy, it is found that the entropy is not extensive. The inextensivity leads to the so-called Gibbs paradox in which the mixing entropy of two identical classical gases increases. Lots of literature from different points of view were created to resolve the paradox. In this paper, starting from the Boltzmann entropy, we present the thermodynamics of the system of distinguishable particles. A straightforward way to get the corrected Boltzmann counting is shown. The corrected Boltzmann counting factor can be justified in classical statistical mechanics.

Keywords: entropy; Gibbs paradox; distinguishable particles

1. Introduction

The concepts of distinguishable and indistinguishable particles is important in Statistical Mechanics as their corresponding entropies are different. The entropy in statistical mechanics is defined in terms of the logarithm of the number of the accessible microstates in the phase space. The definition of the entropy is called Boltzmann entropy in which it is adopted in popular textbooks [1–4]. The microstates numbers for distinguishable and indistinguishable particles are certainly different and then their corresponding Boltzmann entropies are different, too. However, it is not trivial to know whether the distinguishability property may lead to different physical results. For example, the Gibbs paradox [6–31] presents one of the cases.

In its simplest case of the Gibbs paradox, the entropy of two identical volume of (distinguishable) ideal gas increases after mixture in which it violates our intuition. Consider two subsystems of equal

volumes V and particle numbers N are separated by a wall, the Boltzmann entropy of one system is

$$S = k \ln V^N \quad (1)$$

Hence the total entropy S_i of two systems is double,

$$S_i = 2k \ln V^N \quad (2)$$

in which the additivity of the Boltzmann entropy is assumed. Now the wall is removed, the gases of two systems mix. The entropy S_f is

$$S_f = k \ln(2V)^{2N} \quad (3)$$

Thus the mixing entropy reads

$$\begin{aligned} \Delta S &= S_f - S_i \\ &= 2Nk \ln 2 \end{aligned} \quad (4)$$

which is positive meaning that the mixing process is irreversible according to the second law of thermodynamics. Here we also assume the Boltzmann entropy is equivalent to the usual thermodynamical entropy (that is, the entropy identified in thermal properties).

The essence of the paradox is in fact that the entropy of the distinguishable particles is not extensive. The entropy of the mixture is not equal to the sum of their partition. To resolve the Gibbs paradox, one introduces the indistinguishable particles in which a permutation factor $1/N!$ (N is the total particle number) is included in the total microstate number to overcome the overcounting [6]. Hence, the entropy before mixing in Eq.(2) should be modified as

$$S_i = 2k \ln \left(\frac{V^N}{N!} \right) \quad (5)$$

and similarly, the entropy after mixing in Eq.(3) reads

$$S_f = k \ln \left(\frac{(2V)^{2N}}{(2N)!} \right) \quad (6)$$

The mixing entropy is

$$\begin{aligned} \Delta S &= 2Nk \ln 2 - k \ln \frac{(2N)!}{(N!)^2} \\ &= O(\ln N) \end{aligned} \quad (7)$$

In the thermodynamical limit $N \rightarrow \infty$, the mixing entropy per particle vanishes, and hence the Gibbs paradox is resolved.

The concept of indistinguishable particles is trivial in Quantum Mechanics. The identical particles in Quantum Mechanics are indistinguishable particles. Strictly speaking, one cannot distinguish two identical particles after their collision. At equilibrium, the number of microstates of the whole system is described in terms of the number representation (or the second quantized representation). The resolution of the Gibbs paradox is then straightforward in views of the quantum nature of identical particles.

However, we have also similar case in Classical Mechanics, for example, colloids. The colloidal particles (giant molecules) of size up to microns are distinguishable since its behavior should be governed by classical mechanics. In such a classical system, the entropy is certainly not extensive [2, 3] and the Gibbs paradox appears. Traditionally, to avoid the Gibbs paradox, colloidal particles are treated as indistinguishable particles [34] without any explicit reason. There is still a puzzle even though this kind of treatment turns out to be correct.

In this paper, we present the thermodynamics of the system of distinguishable particles, starting from the definition of entropy for the distinguishable particles. The presentation can easily show how the “reduced” entropy [32] instead of the original entropy determines the thermodynamical behaviors.

Before introducing our treatment for distinguishable particles, we classify the system of particles into three categories,

1. Distinguishable particles of the same species
2. Indistinguishable particles (certainly of the same species)
3. Particles of different species (certainly distinguishable)

by their phase spaces. Suppose we call the phase space of the system of N distinguishable particles of the same species (the first category) be Γ_N . The phase space of N indistinguishable particles (the second category) is then Γ_N/S_N with the permutation group S_N . The permutation group S_N is used to eliminate the overcounting microstate numbers from Γ_N .

For the third category, each particle belongs to its particular species. The corresponding phase space of N particles of different species is $\Gamma_1 \otimes \Gamma_1 \otimes \dots \otimes \Gamma_1$ (total N direct products).

The thermodynamics for the second and third categories were already well discussed in the textbook [2].

2. Thermodynamics of Distinguishable Particles

To study the thermodynamical variables of the distinguishable particle system, we consider two subsystems of particle number N_1, N_2 , volumes V_1, V_2 , energies E_1, E_2 , respectively, in which their particles, volumes, and energies are allowed to be exchanged.

Before two subsystems in contact, the phase space is $\Gamma_{N_1} \otimes \Gamma_{N_2}$. After contact, the phase space becomes $\Gamma_{N_1+N_2}$ which is larger than $\Gamma_{N_1} \otimes \Gamma_{N_2}$ by $(N_1 + N_2)!/(N_1!N_2!)$ times. This number is the number of way to select N_1 particles and N_2 particles from the total $N_1 + N_2$ particles. That is,

$$\Gamma_{N_1+N_2} = (\Gamma_{N_1} \otimes \Gamma_{N_2}) \oplus (\Gamma_{N_1} \otimes \Gamma_{N_2}) \oplus \dots \quad (8)$$

in which there are total $(N_1 + N_2)!/(N_1!N_2!)$ copies (or configurational degeneracy). This degeneracy was pointed out by Penrose [5].

The total entropy as a whole becomes

$$S = S_1(N_1, V_1, E_1) + S_2(N_2, V_2, E_2) + k \ln \frac{(N_1 + N_2)!}{N_1!N_2!} \quad (9)$$

S_1 and S_2 are the entropies of the subsystems separately. The last term arises from the configurational degeneracy. The existence of the additional term is due to the nonextensive property of the system. The

distinguishability implies nonextensivity of the entropy [3] in which the total system entropy is not the naive addition of the subsystem entropies. Similar cases are also well known in other physical system [33].

Because of that, it is easily seen that the Gibbs paradox usually mentioned in the textbook [2] vanishes when we look at the phase space of the system of distinguishable particles carefully.

When two subsystems are in equilibrium, the total entropy attains its maximum, then we have

$$S = S_1(N_1, V_1, E_1) + S_2(N_2, V_2, E_2) + S_0(N_1, N_2) \tag{10}$$

with $S_0 = k \ln((N_1 + N_2)!/(N_1!N_2!))$ from Eq. (9). Under the constraint of energy $E_1 + E_2 = E$, volume $V_1 + V_2 = V$, and particle number $N_1 + N_2 = N$, the equilibrium attains when the entropy becomes extremum such that

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0 \tag{11}$$

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0 \tag{12}$$

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} + \frac{\partial S_0}{\partial N_1} = 0 \tag{13}$$

We can then obtain, for the system of distinguishable particles, the expression of the temperature T as

$$\frac{1}{T} = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} = \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \tag{14}$$

the pressure P as

$$\frac{P}{T} = \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} = \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} \tag{15}$$

By noticing that

$$\frac{\partial S_0}{\partial N_1} = -\frac{\partial}{\partial N_1}(k \ln N_1!) + \frac{\partial}{\partial N_2}(k \ln N_2!) \tag{16}$$

we can express the chemical potential μ as

$$\frac{\mu}{T} = - \left. \frac{\partial(S_1 - k \ln N_1!)}{\partial N_1} \right|_{E_1, V_1} = - \left. \frac{\partial(S_2 - k \ln N_2!)}{\partial N_2} \right|_{E_2, V_2} \tag{17}$$

Now we introduce the “reduced” entropy [32]

$$S^{\text{red}} = S - k \ln N! \tag{18}$$

such that the above expressions for thermodynamical variables

$$\frac{1}{T} = \left(\frac{\partial S^{\text{red}}}{\partial E} \right)_{V, N} \tag{19}$$

$$\frac{P}{T} = \left(\frac{\partial S^{\text{red}}}{\partial V} \right)_{E, N} \tag{20}$$

$$\frac{\mu}{T} = - \left(\frac{\partial S^{\text{red}}}{\partial N} \right)_{E, V} \tag{21}$$

are re-written in the usual way of thermodynamics for indistinguishable particles. For the system of distinguishable particles, the “reduced” entropy S^{red} instead of the original entropy S defines the thermodynamical variables of the system. Our presentation is somehow a straightforward way to justify the “reduced” entropy adopted for the classical (distinguishable) systems in condensed matter physics [34].

For the case of indistinguishable particles defined in the phase space Γ_N/S_N , its entropy is simply equivalent to the “reduced” entropy mentioned above. Although the original entropies for both the distinguishable and indistinguishable particles are different, the entropies governing their corresponding thermodynamics are still the same. Thermodynamics cannot tell the distinguishability of the system.

Suppose our system is N_1, V_1, E_1 in contact with the reservoir of N_2, V_2, E_2 in which $N_1 \ll N_2, V_1 \ll V_2, E_1 \ll E_2$, the entropy of the reservoir can be expanded into Taylor’s series around N, V, E such that

$$\begin{aligned} S &= S_1(N_1, V_1, E_1) + S_2(N_2, V_2, E_2) + S_0(N_1, N_2) \\ &= S_1^{\text{red}}(N_1, V_1, E_1) + S_2^{\text{red}}(N_2, V_2, E_2) + k \ln N! \\ &\simeq S_2^{\text{red}}(N_2, V_2, E_2) + k \ln N! \end{aligned} \tag{22}$$

in which the system entropy S_1 is neglected assuming $S_1 \ll S_2$. The reduced entropy S_2^{red} can be analyzed by Taylor’s series expansion around N, V, E up to first order, that is,

$$\begin{aligned} &S_2^{\text{red}}(N_2, V_2, E_2) \\ &= S_2^{\text{red}}(N - N_1, V - V_1, E - E_1) \\ &= S_2^{\text{red}}(N, V, E) - N_1 \left(\frac{\partial S_2^{\text{red}}}{\partial N_2} \right)_{E, V, N_2=N} - V_1 \left(\frac{\partial S_2^{\text{red}}}{\partial V_2} \right)_{E, N, V_2=V} - E_1 \left(\frac{\partial S_2^{\text{red}}}{\partial E_2} \right)_{E_2=E} \\ &= S_2^{\text{red}}(N, V, E) - \frac{1}{T}(-\mu N_1 + E_1 + V_1 P) \end{aligned} \tag{23}$$

with the temperature of the reservoir T .

The total entropy becomes

$$\begin{aligned} S &= S_2^{\text{red}}(N, V, E) - \frac{1}{T}(-\mu N_1 + E_1 + V_1 P) + k \ln N! \\ &= -\frac{1}{T}(-\mu N_1 + E_1 + PV_1) + C \end{aligned} \tag{24}$$

where C is a constant independent of N_1, E_1, V_1 . The probability $p(N_1, V_1, E_1)$ of the system is proportional to the corresponding phase space volume. The phase space we are now considering is $\Gamma_{N_1+N_2}$, and hence from Eq. (8) there are exactly $N!/(N_1!N_2!)$ copies of the state characterized by N_1, V_1, E_1 . We have

$$\begin{aligned} p(N_1, V_1, E_1) &\propto \frac{N!}{N_1!N_2!} \Omega_1(N_1, V_1, E_1) \\ &\propto \frac{1}{N_1!} \Omega_1(N_1, V_1, E_1) \\ &\propto \frac{1}{N_1!} \exp\left(\frac{\mu N_1 - E_1 - PV_1}{kT}\right) \end{aligned} \tag{25}$$

under the condition that $N_1 \ll N_2$.

The probability distribution allows us to formulate the Grand Canonical ensemble in which our system interacts with a particle-energy reservoir. The grand partition function

$$\begin{aligned}\Xi(\mu, V, T) &= \sum_{N_r=0}^{\infty} \sum_s \frac{1}{N_r!} e^{\mu N_r/kT} e^{-E_s/kT} \\ &= \sum_{N_r=0}^{\infty} e^{\mu N_r/kT} \mathcal{Z}_{N_r}(V, T)\end{aligned}\quad (26)$$

with the partition function

$$\mathcal{Z}_{N_r}(V, T) = \frac{1}{N_r!} \sum_s e^{-E_s/kT} \quad (27)$$

of the corrected Boltzmann counting due to the factor $1/N_r!$.

3. Conclusion

In summary, although the phase spaces of the system of distinguishable particles is different from that of indistinguishable one, their thermodynamics are in fact equivalent. It also implies that the corrected Boltzmann counting factor can be justified in classical statistical mechanics.

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32. The "reduced entropy" is $S - k \ln N!$ in which S is the original entropy and N is the number of particles in the system. We adopted the terminology because it is the same as the entropy of the system assuming that the particles in the system are indistinguishable. "Reduced" here means the reduction of the distinguishability degrees of freedom.
33. For example, if we consider the surface energy of the system, then the energy of the system is not proportional to its mass (nonextensive). When two subsystems are in contact, their total energy are

not equal to the sum of the original two energies. Another example is the system with long-ranged electrostatic interaction.

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