Physical Chemistry
ISSN: 0974-7524

Physical Chemistry: An Indian Journal

Research | Vol 11 Iss 2

Explanation of the Gibbs paradox in statistical mechanics

Igor A. Stepanov[*]

Institute of Science and Innovative Technologies, Liepaja University, Liela 14, LV□3401, Liepaja, Latvia

[*]**Corresponding author:** Igor A. Stepanov, Liepaja University, Liela 14, LV□3401, Liepaja, Latvia.
E-mail: istepanov2001@gmail.com

Abstract

Previously, it was found that the internal energy of a system can be described by two functions which depend on the process. In the present paper, it is shown that in some processes the system must be considered in the phase space and in other processes it must be considered in the momentum subspace. Consequently, the Gibbs paradox in statistical mechanics can be explained. Entropy in thermodynamics and statistical mechanics is always extensive. Like internal energy, it is described by two functions, one of which depends purely on temperature, whereas the other depends on volume and pressure.

Keywords: Gibbs paradox; Ideal gas; Real gas; Equation of state; Internal energy; Mathematical definition of function.

Introduction

The Gibbs paradox was discovered at the end of the 19th century and has still not been solved [1–22]. It goes as follows: consider an adiabatic box containing ideal gas divided by a very thin impenetrable membrane in two equal parts, A and B (Figure 1). The temperature of the gas is T, the volumes of each compartment are V, and there are N atoms in each part. The entropies of the halves A and B are S. When one removes the partition, then, according to thermodynamics, the total entropy of the box becomes $2S$. However, in statistical physics, the entropy of one half is:

$$S = kN\left(\ln V + \frac{3}{2}\ln\frac{U}{N} + X\right), \tag{1}$$

where k is the Boltzmann constant, U is the internal energy, and X is a constant [6,11]. The entropy of the whole system is twice that value. After removing the membrane, the total entropy becomes:

$$S_2 = 2kN\left(\ln 2V + \frac{3}{2}\ln\frac{U}{N} + X\right). \tag{2}$$

Citation: Stepanov Igor A (2016) Explanation of the Gibbs paradox in statistical mechanics, Physical Chemistry: An Indian Journal, 11.

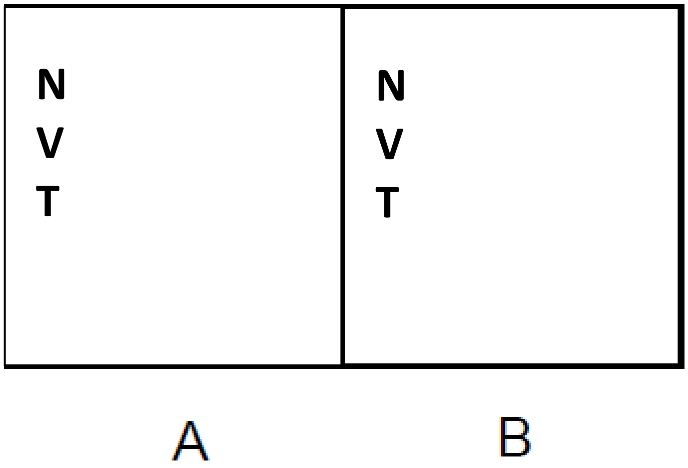

Figure 1: Gas boxes A and B used in the consideration of the Gibbs paradox. *N*, *V*, and *T* are the quantity of atoms, the volume of each box, and temperature, respectively.

The change in entropy is then:

$$S_2 - 2S = 2kN \ln 2 \,. \tag{3}$$

If one restores the partition, the total entropy again becomes 2*S*. Thus, entropy is not extensive in statistical physics. No increase or decrease in entropy should occur because no change in the state of the gas takes place as the membrane is removed or restored.

Theory

There is a paradox in the theory of ideal gas [23–27]. The gas law for monatomic gas is:

$$PV = RT \,, \tag{4}$$

where P is pressure, V is volume, R is the universal gas constant, and T is temperature. Two variables are necessary to determine a thermodynamic state of a gas, such as its internal energy. From kinetic theory and experiments on free expansion, the internal energy of ideal gas is [23–27]:

$$U(T) = \frac{3}{2}RT \tag{5}$$

The paradox is that the energy in this equation depends on only one variable, yet must depend on two. From Eqs. (4) and (5) it follows that:

$$U(P,V) = \frac{3}{2}PV \,. \tag{6}$$

Here the energy depends on two variables. The author of [23–25] stated that the characterization of gas using Eq. (5) was a wrong approach because the physical quantity *internal energy* must depend on two variables (not on one). It must also depend on volume. He argued that equations of state with two variables must be used instead which show that the internal energy of gases, in each situation, is expressed only as a function of volume and pressure.

This paradox is also valid for real gases because in a wide range of temperatures and pressures their properties very minimally differ from those of ideal gas. For example, at T = 273.15 K and atmospheric pressure, the molar volumes of argon, helium, hydrogen, nitrogen, oxygen, and methane deviate at about 0.1 percent from that of ideal gas ($22.414 \cdot 10^{-3}$ m^3) and even less for higher temperatures and lower pressures. For argon, the difference between the experimental and theoretical heat capacity is less than 0.1 percent [23-25,28].

This paradox was explained in [27]. In [26], based on the results from [29], it was mathematically proven that the internal energy U can be represented as two different functions, $U_1(T)$ or $U_2(P,V)$; the first depending on temperature only and the second depending on pressure and volume only. One can notice that the internal energy function depends on the process performed on the system (although both functions are quantitatively equal). For some processes, the internal energy depends on the volume and for some it does not. Consider two volumes, V_1 and V_2 ($V_2 > V_1$), each containing a mole of ideal gas. The energies of the gas in both volumes are equal and given by Eq. (5). If one introduces a quantity of heat, δQ, into each of the volumes, the energies of gas again become equal and defined by Eq. (5), but with a higher temperature. These are correct results and there are no mistakes in Eq. (5). If, however, one compresses the volumes, then the process must be defined by Eq. (6). There are thus two types of processes. In the first, the volume of the system is changed (but not by compression, either positive or negative) and, in the second, the system is compressed or expanded by mechanical work. Both types are characterized by different internal energy functions. There is no universal internal energy function. Quantitatively both internal energy functions are identical, that is, $U(T)$ given by Eq. (5) is identically equal to $U(P,V)$ given by Eq. (6).

According to the rigorous mathematical definition of function [29], internal energy must be constituted of two different functions which depend on different variables [26]. Let us cite [26] rewriting internal energy equations with one independent variable, T, as a function of additional variables is not a trivial mathematical manipulation. Doing so reveals that the rigorous mathematical definition of the word ‘function’ necessitates U being dependent on other variables as well. Why is it so important to adhere to this mathematical definition? Because it is a building block in the foundation upon which calculus, an indispensable tool in thermodynamics, is based.

One can explain the Gibbs paradox in statistical mechanics in the same way. In Helmholtz free energy:

$$F = U - TS \, , \tag{7}$$

internal energy, U, depends on the process. The entropy can be obtained from Eq. (7) by the equation:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \, , \tag{8}$$

and therefore there are two different entropy functions which depend on the process.

Let us perform a simplified derivation of Helmholtz free energy for monatomic ideal gas [30]. It can be obtained through the partition function, Z:

$$F = -kT \ln Z \, , \tag{9}$$

where Z is:

$$Z = \int \exp\left(-\frac{U}{kT}\right) \mathrm{d}\Gamma , \qquad (10)$$

and where dΓ is an element of the phase space. Here, the integration is performed over the whole phase space. The energy, U, equals the sum of the kinetic energies of the atoms:

$$U = \sum_{i=1}^{N} \frac{p_i^2}{2m} . \qquad (11)$$

Here, p_i is the momentum of the i-th atom. Introducing Eq. (11) into Eq. (10), one obtains a $6N$-dimensional integral:

$$Z = \int \ldots \int \exp\left(-\sum_{i=1}^{N} \frac{p_{i=1}^2}{2mkT}\right) \mathrm{d}\Gamma_1 \ldots \mathrm{d}\Gamma_N . \qquad (12)$$

Some authors explain the Gibbs paradox by introducing the factor $1/N!$ into the right-hand side of Eq. (12), but this is to apply a quantum approach to what is a classical problem. Many authors have recognized that quantum theory has no bearing on the matter [2,7,8,14,18–22].

This integral equals:

$$Z = \left[\int \exp\left(-\frac{p_1^2}{2mkT}\right) \mathrm{d}\Gamma_1\right]^N = \left[\int \exp\left(-\frac{p_1^2}{2mkT}\right) \mathrm{d}\mathbf{p_1}\right]^N \left[\int \mathrm{d}\mathbf{r_1}\right]^N = \left(2\pi mkT\right)^{3N/2} V^N . \qquad (13)$$

Here d$\mathbf{p_1}$ and d$\mathbf{r_1}$ are the elements of the momentum space and position space, respectively, of the first particle. Therefore, from Eq. (9):

$$F = -kTN\left[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\left(2\pi mk\right)\right]. \qquad (14)$$

Now, taking the derivative of this free energy with respect to temperature, Eq. (8), one obtains the entropy of ideal gas:

$$S = kN\left[\ln V + \frac{3}{2}\ln T + \ln\left(2\pi mk\mathrm{e}\right)^{3/2}\right]. \qquad (15)$$

In the Gibbs paradox, the volume of the system changes not by compression or straining. Therefore, the internal energy does not depend on the volume. This is possible only when the system is described by the momentum space. Performing the derivation of Helmholtz energy and entropy of ideal gas in the momentum space, one obtains:

$$F = -kTN\left[\frac{3}{2}\ln T + \frac{3}{2}\ln\left(2\pi mk\right)\right], \qquad (16)$$

and

$$S = kN\left[\frac{3}{2}\ln T + \ln\left(2\pi mk\mathrm{e}\right)^{3/2}\right]. \qquad (17)$$

One can see that this entropy is additive.

Discussion

The internal energy can be obtained through the partition function:

$$U = kT^2 \frac{\partial}{\partial T} \ln Z . \qquad (18)$$

It is interesting to note that the energy of ideal gas obtained introducing Eq. (13) into the above equation coincides with that in Eq. (5), that is, it does not depend on the volume. The change in the entropy of the process described by Eq. (5) does not depend on the volume either:

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} . \tag{19}$$

The expression for entropy, Eq. (17), being introduced into Eq. (19), gives the correct result but Eq. (15) produces an incorrect result. Eq. (15), though, correctly characterizes the process with volume change:

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{P\mathrm{d}V}{T} . \tag{20}$$

Conclusions

According to the mathematical definition of the word function, the internal energy function of a system can be of two different types. The first one depends on a single variable: temperature; the second depends on two variables: pressure and volume. The internal energy function depends on the process performed on the system (nevertheless, both types of the function are quantitatively identical). The energy function which depends only on temperature is used in processes where the volume of the system is changed not by compression or stretching; and the energy function which depends on the volume and pressure is used in processes where the volume of the system is changed by positive or negative compression. In the Gibbs paradox, the former case is used and the energy function of the first type must be applied. It was shown that in the former case, the system must be described by the momentum space. In the latter case, the system must be described by the traditional phase space. This explains the Gibbs paradox in statistical mechanics. The entropy is always extensive. It also can be described by two different functions which depend on the process performed on the system. The first function depends only on temperature, and the second depends on volume as well.

Reference

1. Paglietti A (2012) Ideal gas interaction with thermal radiation in classical thermodynamics and Gibb’s paradox. Continuum Mech Therm 24: 201-210.
2. Dieks A (2011) The Gibbs paradox revisited. In: Dieks D, Gonzalo W, Uebel T, Hartmann S, Weber M (eds) Explanation, Prediction, and Confirmation. The Philosophy of Science in a European Perspective, Springer, Netherlands, 2: 367.
3. Maslov VP (2011) Mixture of new ideal gases and the solution of the Gibbs and Einstein paradoxes. Russ J Math Phys 18: 83-101.
4. Cheng CH (2009) Thermodynamics of the System of distinguishable particles. Entropy 11: 326-333.
5. Kozlov VV (2009) Kinetics of collisionless gas: Equalization of temperature, growth of the coarse-grained entropy and the Gibbs paradox. Regul Chaotic Dyn 14: 535-540.
6. Swendsen RH (2008) Gibbs’ paradox and the definition of entropy. Entropy 10: 15-18.
7. Maslov VP (2008) Solution of the Gibbs Paradox in the Framework of Classical Mechanics (Statistical Physics) and Chrystalizations of the Gas C60. Math Notes 83: 716-722.

8. Uffink J (2007) Compendium of the foundations of classical statistical physics. In: Butterfield J and Earman J (eds) Handbook for Philsophy of Physics. Elsevier, Amsterdam p. 924.
9. Naim AB (2007) On the So-Called Gibbs Paradox, and on the Real Paradox. Entropy 9: 132-136.
10. Nagle JF (2004) Regarding the Entropy of Distinguishable Particles. J Stat Phys 117: 1047-1062.
11. Swendsen RH (2002) Statistical Mechanics of Classical Systems with Distinguishable Particles. J Stat Phys 107: 1143-1166.
12. Tseng CY, Caticha A (2002) Yet another resolution of the Gibbs paradox: an information theory approach. In: AIP Conference Proceedings, 617: 331.
13. Scherer LGC (2001) La paradoja de Gibbs. J Mexican Chem Soc 45: 145-148.
14. Warren PB (1998) Combinatorial Entropy and the Statistical Mechanics of Polydispersity. Phys Rev Let 80: p. 1369.
15. Lin SK (1996) Gibbs paradox of entropy of mixing: experimental facts, its rejection and the theoretical consequences. Electronic J Theor Chem 1: 135-150.
16. Richardson IW (1989) The Gibbs paradox and unidirectional fluxes. Eur Biophys J 17: 281-286.
17. Lin SK, Ziran Zazhi. (1989) 12(5), 376. In Chinese.
18. Rosen R (1964) The Gibbs' Paradox and the Distinguishability of Physical Systems. Philos Sci 31: 232-236.
19. Urusov VS (2007) Gibbs paradox and symmetrization of a multicomponent system. Dokl. Physical Chemistry 417: 337-341.
20. Dieks D, Dijk VV (1988) Another look at the quantum mechanical entropy of mixing. Am J Phys 56: 430.
21. Jaynes ET (1992) The gibbs paradox. In: Erickson G, Neudorfer P, Smith CR (eds) Maximum-Entropy and Bayesian Methods. Kluwer, Netherlands.1.
22. Navarro L (1998) Gibbs, Einstein and the Foundations of Statistical Mechanics. Arch Hist Exact Sci 53: 147-180.
23. Guy AG, JOM (1995) 47(9), 3.
24. Guy AG (1993/95). Mater. Sci. (Wroclaw), 19(104), 61.
25. Guy AG (1997) More on ideal gas. JOM 49: 4-5.
26. Stracher GB, Guy AG (1998) The Internal Energy of a PV = RT Gas: A Univariable or Multivariable Function. Math Geol 30: 251-258.
27. Stepanov IA (2014) Physical Chemistry: An Indian J 9(4) 151.
28. Robinson JJ, Trumble KP, Gaskell DR (1997) More on the ideal gas law. JOM 49: 3.
29. Dick TP, Patton CM (1995) Calculus PWS Publ. Co., Boston.
30. Vasiljev AM, Vvedenie V (1980) Statisticheskuju Fiziku, Vysshaja shkola, Moscow.