On the Interrelation between Gibbs Hypothesis and Symmetry Postulate

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Abstract: The question of the origin of the Gibbs-factorials is reconsidered. It is argued, using the example of the Brownian-motion, that their appearance in classical statistical calculations cannot in general be traced back to the symmetry postulate of quantum mechanics as often assumed.

In this note I propose to consider a problem of interpretation with no immediate practical consequence. It seems, nevertheless, worth of clarification.

In classical mechanics of pointlike particles dynamical states are associated with points of the phase-space. Though in general different points in phase-space correspond to different dynamical states of the system, Gibbs proposed[1] to make an important exception to this rule: phase points which differ only by *permutations* of identical particles are to be taken to represent the same dynamical state and, therefore, must be counted only once in probability distributions over phase-space. At the same time Gibbs suggests that since integrals over these distributions are much easier to handle without the above restriction, an equivalent but simpler procedure would consist in dividing the unconstrained integrals by the number of equivalent phase-space points. This last quantity is easy to compute: it is given by a simple product each term of which is equal to the factorial of the number of particles of a given type. The factorials in this product are the *Gibbs-factorials* and the whole procedure will be called below *Gibbs hypothesis*.

The necessity of this strange statistics was recognized by Gibbs in connection with the mixing of gases and liquids. It follows from thermodynamics that mixing of different substances is accompanied by an entropy increase related to the work extractable from the mixing process. However, the statistical description of the process reproduces this increase of the entropy

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only if Gibbs-factorials are properly taken into account; otherwise the theory would make no distinction between mixing of different or identical gases and would give no entropy change in either case. This argument of Gibbs may also be expressed in a somewhat more general form by saying that methods of statistical thermodynamics lead to an additive (extensive) entropy only if Gibbs-factorials are introduced[2].

Though the necessity of using Gibbs-factorials in calculations had been quickly accepted, sharp controversy as to the deeper sense of this procedure arose in the first quarter of the century[3]. However, with the birth of modern quantum mechanics this debate came to a sudden end, since the *symmetry postulate* of quantum theory seemed to settle the problem once for all. This fundamental principle requires that under permutation of identical particles the state vector changes at most by a phase factor which leads to no change at all in the physical state of the system. Therefore, whenever symmetry postulate is applicable it provides firm and transparent basis for Gibbs' procedure indeed. This conclusion is corroborated by the theories of ideal Bose and Fermi gases which in high temperature limit go over to the classical statistical description of ideal gases with the Gibbs-factorial automatically included[4].

According to the general opinion, the symmetry postulate of quantum mechanics fully elucidates the origin of Gibbs hypothesis and, therefore, serves as the *general explanation* of it. In order to illustrate this point of view I quote two examples. The first one is from the Part 6.6 of[5]: "It is not possible to understand classically why we must divide $\sum(E)$ by $N!$ to obtain the correct counting of states. The reason is inherently quantum mechanical..." The second is from the Chapter 16 of the standard text by T.L.Terrel referred to above: "The new factor $1/N! \cdots$ has arisen from our consideration of the symmetry of wave functions. In turn, the quantum mechanical postulate on symmetry of wave functions has its origin in the experimental indistinguishability of identical particles. Gibbs had the intuitive forsight, before the advent of quantum mechanics, to insert this factor $1/N!$."

A closer reflection, however, reveals that derivability of the Gibbs-factorials from the symmetry postulate is in itself insufficient to provide an explanation of Gibbs hypothesis in the general case. It certainly ensures that quantum mechanics of *identical particles* automatically obey this hypothesis but tells nothing of systems, consisting of *similar* (i.e. practically indistinguishable but not truly identical) *particles* as e.g. colloid particles

in a suspension. Systems, consisting of such constituents, fall outside the scope of the symmetry postulate but, nevertheless, require Gibbs-factorials for their correct description in the framework of statistical thermodynamics.

Gibbs-factorials enter into the working formulae of colloid physics somewhat implicitely. They are hidden within the relations taken over from the theory of dilute molecular solution whose properties are closely related to those of dilute suspensions. In order to expound the significance of Gibbs-factorials for colloids as systems, consisting of similar but certainly not identical particles, let us consider the widely known example of the equilibrium of Brownian-particles in the gravitational field of the Earth which was the object of J.Perrin's famous experiments. The treatment of this phenomenon in colloid physics[6] is based on the formula

$$RT\, d\ln a' + gv'(\rho' - \rho)\, dh = 0, \tag{1}$$

in which a', v' and ρ' are the activity, molar volume and weight-volume density of the dissolved substance, ρ is the density of the solvent and h is the height above some reference plane. For ideal solutions of constant density this equation may be integrated to obtain the barometric formula for the particle density C'

$$C' = C'_0 \exp\left[-\frac{gv'(\rho' - \rho)}{RT} \cdot h\right], \tag{2}$$

which was used by Perrin to calculate the Avogadro's number.

Where does formula (1) come from? It comes from the formula for the chemical potential of the solute in a *molecular* solution applied to colloid particles in a suspension. Such a borrowing conforms with the basic hypothesis of Einstein's famous 1905 paper [7] to the effect that Brownian-particles are nothing but molecules of visible size.

The second term in (1) is the change in the gravitational potential energy of the dissolved matter corrected for the hydrostatic lifting force. What concerns the logarithmic term, in textbooks on physical chemistry [8] it is related through equilibrium condition $\mu'(l) = \mu'(g)$ to the logarithmic term in the chemical potential of an ideal gas.

Though these considerations constitute a true explanation of (1), an alternative approach[9] reveals that the logarithmic term bears in fact its origin from the Gibbs-factorial $n'!$ of the solute particles. The starting point of this

latter approach is the general expression of the free enthalpy G of a dilute solution (in the limit $n' \longrightarrow 0$) which obeys all the basic physical requirements known to be satisfied by free enthalpy.

If at $n' = 0$ G were a smooth function of n' it could be expanded in powers of n' and to lowest nontrivial order the simple expression

$$G = G^* + n' \cdot \alpha \tag{3}$$

would be obtained in which G^* is the free enthalpy of the pure solvent and α is independent of n'. But G is in fact a singular function of n' at $n' = 0$ and cannot be expanded in a Taylor-series around this point. The origin of the singularity is the Gibbs-factorial $n'!$ in the denominator of the statistical sum Z. Since $G = -kT \ln Z$ the free enthalpy does contain a term $+kT \cdot \ln n'!$ which can be written also in the form $kT \cdot n'(\ln n' - 1)$. It is this term which cannot be expanded around $n' = 0$ and so must be explicitely included into (3). Hence, we have at $n' \longrightarrow 0$ the expression

$$G = G^* + n' \cdot \alpha + kT \cdot n'(\ln n' - 1). \tag{4}$$

However, this formula is still in flaw. G must be a first order homogeneous function of n and n', the number of molecules in the solvent and the solute respectively. Since the term $\ln n'$ spoils homogeneity, G necessarily contains another logarithmic term too wich combine with $\ln n'$ into $\ln(n'/n)$. The general lowest order form of the free enthalpy is, therefore,

$$G = G^* + n' \cdot \alpha + kT \cdot n' \left[\ln \left(\frac{n'}{n} \right) - 1 \right]. \tag{5}$$

From this formula one can calculate the chemical potentials per mole of both the solvent and the solute:

$$\mu = N_A \frac{\partial G}{\partial n} = \mu^* - RT \frac{n'}{n}$$
$$\mu' = N_A \frac{\partial G}{\partial n'} = N_A \alpha + RT \ln \left(\frac{n'}{n} \right).$$

In calculating μ we put $\dfrac{\partial \alpha}{\partial n} = 0$ since, owing to homogeneity, the independence of α on n' implies its independence on n too.

In the gravitational field of the Earth these equations are modified to

$$\mu = \mu^* - RT\frac{n'}{n} + gv\rho h \tag{6}$$

$$\mu' = N_A\alpha + RT\,\ln\left(\frac{n'}{n}\right) + gv'\rho' h. \tag{7}$$

The constancy of the chemical potentials along the vertical direction leads to the equations

$$\frac{\partial\mu^*}{\partial P}\frac{dP}{dh} - RT\frac{d}{dh}\left(\frac{n'}{n}\right) + gv\rho = 0 \tag{8}$$

$$N_A\frac{\partial\alpha}{\partial P}\frac{dP}{dh} + RT\frac{d}{dh}\ln\left(\frac{n'}{n}\right) + gv'\rho' = 0. \tag{9}$$

For the pure solvent $\mu^* = N_A G^*/n$, hence

$$\frac{\partial\mu^*}{\partial P} = \frac{N_A}{n}\frac{\partial G^*}{\partial P} = \frac{N_A}{n}V = v.$$

On the other hand, from (5) we have

$$N_A\frac{\partial\alpha}{\partial P} = \frac{N_A}{n'}\left(\frac{\partial G}{\partial P} - \frac{\partial G^*}{\partial P}\right) = \frac{N_A}{n'}V' = v'.$$

Substituting these expressions into (8) and (9) we have (after replacing n'/n with the ratio of the particle densities)

$$v\frac{dP}{dh} - RT\frac{d}{dh}\left(\frac{C'}{C}\right) + gv\rho = 0 \tag{10}$$

$$v'\frac{dP}{dh} + RT\frac{d}{dh}\ln\left(\frac{C'}{C}\right) + gv'\rho' = 0. \tag{11}$$

Now, C is practically independent of h, hence

$$\frac{d}{dh}\left(\frac{C'}{C}\right) = \frac{1}{C}\frac{dC'}{dh} \quad \text{and} \quad \frac{d}{dh}\ln\left(\frac{C'}{C}\right) = \frac{1}{C'}\frac{dC'}{dh}.$$

The first of these expressions is C'/C-times smaller than the second and can be neglected. Then from (10) we have $\dfrac{dP}{dh} = -g\rho$. Substituting this into (11) we obtain the equation

$$RT\frac{d}{dh}\ln\left(\frac{C'}{C}\right) + g(\rho' - \rho)v' = 0, \tag{12}$$

which when solved leads again to the barometric formula (2).

In the second approach which has been now completed it is formula (12) which corresponds to (1). Since in the limit $n' \longrightarrow 0$ this last formula becomes identical to (12) it is plainly obvious that the logarithmic terms correspond to each other and both originate from the last term of (4) which in turn stems from the Gibbs-factorial $n'!$. If, therefore, one admits that the application of formulae of molecular physics to suspensions — the common practice in colloid physics — is justified, then one thereby accepts also that Gibbs-factorials must be applied to systems of both identical and similar particles. Since the latters are outside the domain of the symmetry postulate, quantum mechanics can not be claimed to provide the general basis for the explanation of Gibbs hypothesis in spite of the common belief.

The notion of similar particles involves obviously an element of subjectivity not shared by the concept of identity of particles. However, Gibbs-factorials appear always as ingredients of the entropy (or related thermodynamic functions), and the ambiguity in the distinction between similar particles and distinguishable ones leads to the same kind of uncertainty in it that has already been thoroughly discussed earlier in connection with the anthropomorphic notion of the entropy[10].

This latter concept is based on the information theoretic interpretation which identifies entropy with the measure of the lack of information about the system[11]. But information can be quantified only with respect to some set of a priori expectations and it is these expectations through which an unavoidable anthropomorphic element comes into play. A good example is provided by the existence of isotopes[12]. So far as the differences in their properties are beyond the capacity of experiments (as is the case in classical chemistry) no inconsistency is introduced by calculating the entropy of elements as if isotopes were indistinguishable, though from the point of view of the theory of isotope separation this would be a crude error.

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Notes

[1] J.W.Gibbs, *Elementary Principles in Statistical Mechanics,* (Yale University Press, New Haven, 1902), Chapter 15.

[2] C.Kittel, *Elementary Statistical Physics,* (New York, John Wiley& Sons), Chapter 9.

[3] Interesting details on the history of the Gibbs-factorial are found in M.J.Klein, "Ehrensfest's contributions to the Development of Quantum Statistics I. II.," Proc. Koninkl. Ned. akad. Wetensch. (Amsterdam), **62,** 41 (1958).

[4] T.L.Terrel, *Statistical Mechanics,* (New York, McGraw-Hill, 1956).

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[6] G.Scatchard, *Equilibrium in Solutions. Surface and Colloid Chemistry,* (Harvard University Press, Cambridge, 1976) p. 256.

[7] A.Einstein, *Investigations on the Theory of Brownian Movement,* (New-York, Dover, 1956)

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[9] L.D.Landau and E.M.Lifshitz, *Statistical Mechanics,* (Pergamon Press, London, 1981), Chapters 87 - 90.

[10]The anthropomorphic nature of the entropy has been stressed by E.T.Jaynes, "Gibbs vs Boltzmann Entropies," Am. J. Phys. **33,** 391 (1965). The opposite point of view is defended in K.G.Denbigh and J.S.Denbigh, *Entropy in Relation to Incomplete Knowledge,* (Cambridge University Press, 1985). For a critical review of this book see H.Price, Brit. J. Phil. Sci. **42,** 111 (1991).

[11]L.Brillouin, *Science and Information Theory,* (Academic Press, New York, 1956) Part 12.

[12]E.Schroedinger, "Isotopie und das Gibbs'sche Paradoxon," Zeitschrift für Physik **5,** 163 (1921).