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SHORT COMMUNICATIONS

Solution of the Gibbs Paradox in the Framework of Classical Mechanics (Statistical Physics) and Crystallization of the Gas C_{60}

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1. INTRODUCTION[1]

Each scientist who refutes a century old theory runs the risk of being accused of incompetence and of irritating those scientists who absorbed the old theory “with their mother’s milk". And if this is a scientist who has achieved a good deal in his area of knowledge, he also runs the risk of losing his hard-earned authority. This is borne out by the history of new discoveries in physics. Thus, the great physicist Boltzmann, virulently attacked by his contemporaries, committed suicide by throwing himself down the well of a staircase.

In 1900, Planck proposed his famous formula describing black body radiation, which gave results coinciding with experiments, but which he had not rigorously established. The mathematician Bose from India noticed that, in order to derive the formula, one must use a new statistic instead of the old one, the so-called Boltzmann statistic. It is possible that Planck was also aware of this statistic, but was afraid of being criticized or did not really believe in his own result. Bose, just like Boltzmann, was the object of virulent criticism, until Einstein gave his approval to the proposed statistic, which was also justified by the philosophical concepts of Ernst Mach. At first, physicists were bewildered and could not understand the Bose statistic, because they could not imagine how moving particles can exchange positions without using up any energy.

These two statistics may be illustrated by a simple financial example. Suppose we want to deposit two kopecks in two different banks; then we can say that there are three possibilities: (1) put both kopecks into one of the banks; (2) put both kopecks into the other bank; (3) one kopeck in one bank, the other, in the other one. Here it is of no consequence which of the two coins we deposit in the first bank and what is its year of issue. Now imagine a situation in which we are depositing two different diamonds instead of two kopecks. In that case, we have four options rather than three, because it is significant which diamond we placed in what bank, and so the variant in which the diamonds are placed in different banks yields two different options: (a) diamond 1 to bank 1 and diamond 2 to bank 2; (b) diamond 1 to bank 2 and diamond 2 to bank 1.

The reply to the bewilderment of physicists was given by Mach’s philosophical conception, claiming that the basic notions of classical physics (space, time, motion) are subjective in origin, and the external world is merely the sum of our feelings, and the goal of science is to describe these feelings. Therefore, if we are unable to distinguish particles in our subjective perception, then they are undistinguishable.

I propose a completely different philosophy. We can regard particles as distinguishable as well as undistinguishable. This only depends on the aspect of the system of particles that we are interested in, i.e., depends on the question we are seeking an answer to. Thus, returning to the money example, people

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[1] *Editor’s note.* This introduction was written by the author especially for the English version of his article.

are interested in the denominations of the bank notes they own, not in their serial numbers (unless of course they believe in “lucky numbers").

The situation in physics is similar. Suppose we have a receptacle filled with gas consisting of numerous moving particles. If we take a slow snapshot of the gas, the moving particles will display “tails" whose lengths depend on the velocity of the particle: the faster the motion, the longer the tail. Using such a photograph, we can determine the number of particles that move within a given interval of velocities. And we don’t care where which individual particle is located and which particular particle has the given velocity.

I have derived formulas which show how the number of particles is distributed with respect to velocity, for example, they show for what number (numerical interval) it is most probable to meet a particle moving with a velocity in that interval.

These formulas lead to a surprising mathematical fact: there exists a certain maximal number of particles after which the formulas must be drastically modified. If the number of particles is much less than this maximal number, the formulas coincide with the Gibbs distribution up to multiplication by a constant. Nevertheless, this is essential, because the corrected Gibbs formula thus obtained no longer leads to the Gibbs paradox.

The paradox now bearing his name was stated by Gibbs in his paper “On the equilibrium of heterogenous matter", published in several installments in 1876–1879, and resulted in great interest on the part of physicists, mathematicians, and philosophers. This problem was studied by H. Poincaré, G. Lorentz, J. Van-der-Waals, V. Nernst, M. Planck, E. Fermi, A. Einstein, J. von Neumann, E. Schrödinger, I. E. Tamm, P. V. Bridgeman, L. Brillouin, A. Landé and others, among them nine Nobel Prize laureates.

From my point of view, the solution of the Gibbs paradox can be obtained once we realize that the Gibbs formula in its classical form is invalid and we modify it in the way that I have indicated. This modification was previously interpreted as a consequence of quantum theory, but this is erroneous from the mathematical point of view, since the passage from quantum mechanics to classical mechanics cannot change symmetry and therefore cannot change the statistics.

In this situation, the following phenomenon, rather strange from the mathematical point of view, arises. If the number of particles is greater than the maximal number indicated above, then the “superfluous" particles, as we already explained, do not fit into the obtained distribution and the velocity of these particles turns out to be much less than the mean velocity of particles in the gas. This effect differs from the Bose–Einstein condensate phenomenon from quantum theory, because in quantum theory these particles are at the very lowest energy level, they have the lowest speed, i.e., roughly speaking, they stop.

Further, I try to give a physical interpretation to the obtained rigorous mathematical formulas. I interpret the maximal number of particles mentioned above as oversaturated vapor; the superfluous particles are then regarded as nuclei around which droplets begin to grow if the gas has a liquid phase, or, if it doesn’t, crystallization occurs. As a result, this can explain the so-called phase transition of the first kind, in which, as the result of the system achieving equilibrium, the number of particles changes from that number for an oversaturated gas to that for a saturated one. Indeed, it is only those particles which move at speeds greater than the speed of the “superfluous" particles that can be doubtlessly regarded as particles of the “pure" gas (vapor), while the others have condensed or have mixed with the condensed particles.

As the prominent experimenters R. Strey and H. Reiss write, present-day experiments in the homogeneous formation of droplets in argon display a substantial (“dramatic") discrepancy between the experimental data and the theoretical prediction based on the widely used old classical theory. I hope that the approach that I propose here will eradicate this discrepancy.

2. MAIN RESULTS

In my paper [1, p. 68], I cited an example from economics, similar to the one above, that supports exchangeability theory (instead of the “independence condition”). In my opinion, we must revise, in this vein, the “Gibbs conjecture on thermodynamic equilibrium,” which is based (see [2]) on the property of independence leading to the theorem on the multiplication of probabilities. It is this conjecture that leads to the Gibbs distribution, which is refuted by the Gibbs paradox, i.e., in essence, by the mathematical counterexample to this conjecture, as mentioned above in the Introduction.

From the mathematical point of view, the point is whether we consider an ordered or unordered sample [3]. Kozlov showed [2] that the ergodicity conjecture, on which attempts to prove the Gibbs distribution are based, is also invalid. He found a remarkable class, the Poincaré set. Apparently, this set can be used to justify "dynamical convergence" to the distribution given below.

Suppose that E_0 is the energy related to the mean translational velocity of the molecules in a liquid in the equilibrium state "gas— liquid".[2] This velocity is much less than the mean velocity of the molecules of the gas. We cannot say that these velocities and, accordingly, the energy of the "condensate" are zero.

Let us consider a model of the equilibrium of two phases, namely, of "gas—liquid" (without impurities!) in which we take into account only the translational velocity of the molecules in the "condensate" (the liquid) and normalize the integrals over p and q to the phase volume bounded by the energy level specified by the mean velocity of the molecules in the condensate (the liquid). The energy level increases, of course, as the temperature rises.

Now let us pass to the derivation of the distribution of Bose—Einstein type in classical mechanics.

Suppose that N is the number of free particles with Hamiltonian $p^2/2m$ in the volume Ω, let $p=(p_x,p_y,p_z)$, and suppose that the energy of N particles is bounded by the constant $\mathscr{E}_N \gg 1$, i.e., $\mathscr{E}_N/E_0 \to \infty$. Let us evaluate b from the relation

$$\int \frac{p^2}{2m}(e^{b\cdot p^2/2m}-1)^{-1}\,dp=\mathscr{E}_N, b\to 0 \qquad \text{as} \quad \mathscr{E}_N\to\infty.$$

By

$$\mathscr{N}=\frac{1}{(mE_0)^{3/2}}\int (e^{b\cdot p^2/2m}-1)^{-1}\,dp$$

we define the number of particles "saturating" the volume Ω, with $N \geq \mathscr{N}$.

Let us split the space of momenta p into a finite number of regions

$$E_l \leq \frac{p^2}{2m} \leq E_{l+1}, \ \ l=0,\dots,s-1, \quad E_0>0, \quad E_s=E; \qquad p\in\mathbb{R}^3. \tag{1}$$

Let us carry out an unordered sampling with replacement of N_l out of N particles (balls) to the "box"

$$E_l \leq \frac{p^2}{2m} \leq E_{l+1}$$

under the condition

$$\sum_{i=1}^{s} N_i \frac{p_i^2}{2m} \leq \mathscr{E}_N. \tag{2}$$

Suppose that ρ_{E_l} is the density of the number of particles in an interval less than or equal to E_l:

$$\rho_{E_l}=\sum_{j=1}^{l}\frac{N_i}{\mathscr{N}}\,.$$

In the theorem that follows, P is the Lebesgue measure of the phase volume defined in parentheses in (3) with respect to the whole volume (2).

Theorem 1. *The following relation holds*:

$$\mathsf{P}\left(\left|\rho_{E_l}-\int_{p^2/2m\leq E_l}(e^{b\cdot p^2/2m}-1)^{-1}\,dp \Big/ \int (e^{b\cdot p^2/2m}-1)^{-1}\,dp\right| \geq N^{-1/3+\varepsilon}\right)=O(\mathscr{N}^{-k}), \tag{3}$$

where k is any integer and $\varepsilon>0$ is arbitrarily small.

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[2] This model is given for clarity. The situation in which there is no liquid phase, such as in the case of C_{60}, but there is an equilibrium state "gas—solid body" is more realostic.

All $N-\mathscr{N}$ particles lie on the levels not higher than E_0 if $N-\mathscr{N} > \mathscr{N}^{2/3+\varepsilon}$.

Proof. The theorem follows from a general theorem on the Bose distribution [1]. The refinement of the estimates was given in [4], [5]. Choose a partition so that $E_{l+1}-E_l = E_0$ and $(E_{l+1}-E_l)/E > \mathscr{N}^{-1/4}$. Then

$$E_l = E_0(l+1). \tag{4}$$

Suppose that N_l is an unordered sample with replacement to the cell $E_{l+1}-E_l$. In other words, the *unordered sampling* with replacement of

$$\dim\Omega\int_{E_l}^{E_{l+1}}\frac{p^2}{2m}\,dp = \frac{4\pi}{5}(2m)^{3/2}(E_{l+1}^{5/2}-E_l^{5/2})\dim\Omega$$

out of N balls to the cells ("energy boxes") *leads to the relation*

$$\sum_l N_l E_l q_l \le \mathscr{E}_N, \qquad q_l \cong C[l^{1/2}], \tag{5}$$

where C is a constant.

This implies that, for "multiplicities of the form $[l^{1/2}]$" for the "occupation numbers" N_l, Theorem 1 from [5] holds, namely, the following is valid.

Set $\Delta N = \mathscr{N}^{2/3+\varepsilon}$, where ε is a sufficiently small positive number. There exist constants C_k, $k=1,2,\dots$, such that, for any $l\in\mathbb{Z}_+$, the following estimate holds:

$$P\left(\left|\sum_{l=1}^{s}(N_l-\overline{N}_l)\right| > \Delta N\right) \le C_k\mathscr{N}^{-k}, \tag{6}$$

where

$$\overline{N}_l = \frac{q_l}{e^{bl}-1}, \qquad l=1,2,\dots$$

(in our case, q_l is equal to $q_l=[l^{1/2}]$).

Since $\rho_{E_l} = \sum_{j=1}^{l}N_j/\mathscr{N}$, this implies that, on applying the Euler–Maclaurin formulas to the series

$$\sum_{l=l_0}^{s}\overline{N}_j = \sum_{l=l_0}^{s}q_l\frac{1}{e^{bl}-1},$$

we find

$$\sum_{l=l_0}^{s}q_l\frac{1}{e^{bl}-1} \sim \int_{l_0}^{s}\frac{x^{1/2}}{e^{bx}-1}\,dx. \tag{7}$$

Hence, replacing $x=p^2/2m$ and dividing (5) by $\mathscr{N}$, we obtain the assertion of the theorem. □

To distinguish the classical case from the quantum one, we shall replace the term "condensate precipitation" by the term "clusterization". For $N>\mathscr{N}$, the particles seem to cluster, to "paste together," and now the clusters are in motion with energy E_0, and if they are in the gravitational field, then they "fall to the bottom" (see below).

Now consider the case $N<\mathscr{N}$, i.e., the number of particles is less than the saturation number. In this case, the exponential is preceded by the factor $c>1+\varepsilon$, where ε is an arbitrarily small positive number independent of b.

Suppose that, for prescribed $\mathscr{E}_N$ and N, the constants b and c are calculated from the conditions

$$\int\frac{p^2}{2m}(ce^{b\cdot p^2/2m}-1)^{-1}\,dp = \mathscr{E}_N, \tag{8}$$

$$\int(ce^{b\cdot p^2/2m}-1)^{-1}\,dp = N. \tag{9}$$

The following theorem is valid.

Theorem 2. *The following relation holds*:

$$\mathsf{P}\left(\left|\rho_{E_l} - \int_{p^2/2m \le E_l} (ce^{b\cdot p^2/2m} - 1)^{-1}\,dp \Big/ \int (ce^{b\cdot p^2/2m} - 1)^{-1}\,dp\right| \ge \sqrt{\frac{\ln N}{N}}\,\psi(N)\right) = O(N^{-k}), \tag{10}$$

where k is an arbitrary integer.

Proof. The proof is similar to that of Theorem 1. ☐

Hence

$$\frac{N}{\mathcal{N}} = \frac{\int x^{1/2}/(ce^x - 1)\,dx}{\int x^{1/2}/(e^x - 1)\,dx}, \tag{11}$$

and, as $N/\mathcal{N} \to 0$, we have $c \to \infty$, which leads to the Maxwell distribution. Moreover, the factor in this distribution is such that the Gibbs paradox cannot occur. This, incidentally, was obvious from the initial setting.

For the classical ideal gas, i.e., in the case $\mathcal{N}/N \gg 1$, the following relation holds:

$$\frac{P}{n\theta} = 1, \tag{12}$$

where P is the pressure of the gas, $n = N/V$ is the concentration, θ is the temperature in energy units, $\theta = kT$, where k is the Boltzmannn constant, and T is the absolute temperature (in Kelvins). Equation (12) is the equation of state of an ideal classical gas.

For $\mathcal{N}/N > 1$, we obtain

$$\frac{P}{n\theta} = \frac{\zeta(5/2)}{\zeta(3/2)} \approx \frac{1.341}{2.612} \approx 0.523,$$

where ζ is the Riemann function.

However, it is difficult to attain the state $\mathcal{N}/N > 1$ experimentally, because the presence of impurities (such as aerosols in water vapor) will lead to relation (12). Therefore, we can only assert that it is impossible to realize the relation

$$\frac{P}{n\theta} < \frac{\zeta(5/2)}{\zeta(3/2)} \tag{13}$$

in an experiment, no matter how pure the gas, if the repulsive potential is not taken into account (see the remark at the end of the paper; compare with the notion of phase transition of zeroth kind [6]). In this sense, we can say that the state

$$1 > \frac{P}{n\theta} \ge 0.523 \tag{14}$$

is metastable and, for $P/n\theta < 0.523$, is unstable. Note that the superfluid state is also metastable.

The applicability of distributions of Bose–Einstein type and the existence of clusterization for a classical gas could be verified in the following experiment. It is necessary to create an supersaturated fullerene gas not containing impurities. For the fullerenes not to be deposited on the vessel walls, they should be covered with grafene (preferably, spanned over a hard substrate). [3] When a piece of cloth, aluminum, or plastic is introduced into the vessel, the excess of fullerene molecules precipitates on the material, i.e., condensation occurs, so that an equilibrium is established between the fullerene in solid phase and that in gas phase. The quantity of the deposited fullerene depends on the degree of supersaturation of the fullerene gas. Experimental data can be compared with the quantity that can be predicted on the basis of the formula obtained here for the number of particles needed to saturate the volume and the number of particles in the condensate . If the atomic-force microscope (AFM) can distinguish smaller clusters, then the energy of these clusters can be greater than E_0.

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[3] If the gas precipitates on the walls, then it is necessary to pump up the missing particles.

Suppose that T is the saturation temperature in the volume Ω. Lower the temperature down to T_0 so that

$$\frac{R(T-T_0)}{E_0} = c\left(\frac{RT_0}{E_0}\right)^s,$$

where $1/4 < s \le 1/2$ and c is a constant. Then a condensate appears at

$$E_1 \cong cE_0\left(\frac{RT_0}{E_0}\right)^{2-4s}.$$

Hence the number of particles of the supersaturated "vapor" at the temperature T_0 is

$$N_0 = \int_0^\infty \frac{1}{e^{\beta_0\cdot p^2/2m}-1}\,dp,$$

where $\beta_0 = (RT_0)^{-1}$, and the number of *superfluous* (added) particles is

$$\int_0^\infty \frac{1}{e^{\beta\cdot p^2/2m}-1}\,dp - N_0,$$

where $\beta = (RT)^{-1}$. However, the number of particles left after the final precipitation into the condensate, i.e., the number of particles outside the condensate (the number of particles of the *saturated* vapor) is

$$\int_{(RT_0)^{-s}}^\infty \frac{1}{e^{\beta_0\cdot p^2/2m}-1}\,dp,$$

and hence is less at the expense of the "superfluous particles." Thus, there occurs a jump in the number of particles, i.e., a phase transition of the first kind; this is in contrast to the transition to supersaturated vapor (a phase transition of the third kind). Hence the metastable state of an supersaturated vapor at the time when the nuclei of crystals begin to appear gradually passes into the stable state of a saturated pair with a jump in the number of particles and in the entropy.

The proposed experimental scheme can also be used to solve the technological problem of producing materials impregnated with fullerene molecules. The degree of material impregnation can be monitored by measuring the degree of supersaturation of the fullerene gas.

The proof of the following theorem is similar to that of Theorems 1 and 2.

Consider the Hamiltonian function $H(p,q) = p^2/2m + V(q)$, where $p,q \in \mathbb{R}^3$ and the inequality $V(q) \le |q|^6$ as $q \to \infty$; further, suppose that, for given $\mathscr{E}_N$ and N, the constants $b > 0$ and $c \ge 1$ are calculated from the conditions

$$\int \frac{p^2}{2m}(ce^{b(p^2/2m+V(q))}-1)^{-1}\,dp\,dq = \mathscr{E}_N, \tag{15}$$

$$\int (ce^{b(p^2/2m+V(q))}-1)^{-1}\,dp\,dq = N, \tag{16}$$

$$\int (e^{b(p^2/2m+V(q))}-1)^{-1}\,dp\,dq = \mathscr{N}. \tag{17}$$

Theorem 3. *The following relation holds*:

$$\mathsf{P}\left(\left|\rho_{E_l} - \int_{p^2/2m+V(q)\le E_l}(ce^{b(p^2/2m+V(q))}-1)^{-1}\,dp\,dq \Big/ \int(ce^{b(p^2/2m+V(q))}-1)^{-1}\,dp\,dq\right| \ge \frac{\ln N}{\sqrt{N}}\psi(N)\right) = O(N^{-k}), \tag{18}$$

where k is an arbitrary integer and $N \le \mathscr{N}$.

For $N > \mathscr{N}$, N in the inequality and estimate (18) should be replaced by $\mathscr{N}$. The difference $N - \mathscr{N}$ is clusterized and $c = 1$.

If there is an external field (such as the gravitational field) and the repulsive potential between the fullerene molecules has been calculated [7], then we can write the equation for the dressed potential depending on b (i.e., on the temperature) and obtain corrections of the form (15)–(17), where $V(q)$ depends on b in the same volume Ω.

For $c = 1$, the integral over p and q over the whole space provides a dependence of $\mathscr{N}$ on b and m refining (14), which can be verified in an experiment.

Let us present the integral equation for the dressed potential for the fullerene gas:

$$U(x,y,z) = -mgz + \varepsilon\beta^{-3/2}\int_{0.35\text{ nanometers}}^{\infty}\biggl[\biggl\{\biggl(\frac{d}{r}\biggr)^{43} - \biggl(\frac{d}{r}\biggr)^{9}\biggr\}F(\beta U(\xi,\eta,\zeta))\,d\xi\,d\eta\,d\zeta\biggr], \qquad (19)$$

g is the acceleration of gravity, $d = 0.96$ nm (nanometers), $\varepsilon/R = 6150$ K (Kelvins),

$$r = \sqrt{(x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2};$$

$F(\beta U)$ is a function of the form

$$F(\beta U) = \beta^{3/2}\int_{-\infty}^{\infty}\frac{dp_x\,dp_y\,dp_z}{e^{\beta U}e^{\beta\cdot|p|^2/2m} - 1} = 4\pi(2m)^{3/2}e^{-\beta U}\,\Phi\biggl(e^{-\beta U},\frac{3}{2},1\biggr),$$

where Φ is a special function defined by

$$\Phi(\alpha,\nu,\mu) = \sum_{n=0}^{\infty}(\mu+n)^{-\nu}\alpha^n,$$

m is the mass of C_{60} $\beta = 1/RT_0$, T_0 is the temperature in Kelvins, and R is the Boltzmannn constant; the radius of the fullerene molecule is equal to 0.35 nanometers.

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