

Einstein's Quantum Theory of the Monatomic Ideal Gas: Non-statistical Arguments for a New Statistics¹

Eric Pérez and Tilman Sauer

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Outline

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- 5 A rightfully forgotten paper?

Einstein Quantum Theory of the Monatomic Ideal Gas

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4 June 1924	Bose writes to Einstein
c. 2 July 1924	Bose's paper (translated by AE) received by ZPh
10 July 1924	Einstein's first paper presented to the PA
20 September 1924	Einstein's first paper published
December 1924	Einstein's second paper signed
	Bose's paper published
8 January 1925	Einstein's second paper presented to PA
29 January 1925	Einstein's third paper presented to PA
9 February 1925	Einstein's second paper published
5 March 1925	Einstein's third paper published

Bose's contribution

- Bose's (timely) contribution. Quantization of the phase-space of lightquanta.

Density of states factor: $\frac{8\pi\nu^2}{c^3} V d\nu$ for Planck radiation law:

$$r(\nu, T) d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} d\nu$$

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“The Indian Bose gave a beautiful derivation of Planck's law including its constant on the basis of the loose light quanta. [*...auf Grund der losen Lichtquanten*] Derivation elegant, but essence remains obscure.”

(Einstein to Ehrenfest, 12 July 1924)

The Two Statistical Papers

- **Einstein's first paper**

- Quantization of the phase-space of molecules. Energy density:

$$2\pi \frac{V}{h^3} (2m)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

- Bose's statistics

- Equation of state $p = \frac{2}{3} \frac{\bar{E}}{V}$

- Classical limit $\frac{\bar{E}}{N} = \frac{3}{2} \kappa T \left[1 - 0.1768 h^3 \frac{N}{V} (2\pi m \kappa T)^{-\frac{3}{2}} \right]$

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- **Einstein's second paper**

- Condensation below a critical T
- Nernst's principle and extensivity of entropy satisfied
- de Broglie's thesis
- Predictions related to viscosity and electronic contribution to specific heat
- Loss of statistical independence of the particles

Ehrenfest's Objection

“Mr. Ehrenfest and other colleagues have raised the criticism that in Bose's theory of radiation and in my analogous theory of ideal gases the quanta or molecules are not treated as statistically independent entities without explicit mentioning of this feature in our respective papers. This is entirely correct. If the quanta are treated as statistically independent regarding their localization, one obtains Wien's law of radiation; if one treats the gas molecules in an analogous way, one arrives at the classical equation of state, even if one proceeds in exactly the same way as Bose and I have done.”

(“Zur Quantentheorie des einatomigen idealen Gases. Zweite Abhandlung”, p. 5)

The Statistical Dependence of Light Quanta

- Einstein knew this probably since 1909 (paper on fluctuations of radiation)
- Ehrenfest knew it probably since 1911 (paper on the necessity of quantization). He surely knew it since 1914 (combinatorics paper with Kamerlingh-Onnes)
- Who are the “other colleagues”?
 - Viktor R. Bursian, Iuri A. Krutkow
 - Otto Halpern

The “Other Colleagues”

Ehrenfest to Joffé, beginning of October 1924:

“My dear friend!

Precisely now Einstein is with us. 1. We coincide fully with him that **Bose's disgusting work** by no means can be understood in the sense that Planck's radiation law agrees with light atoms moving independently (if they move *independently* one of each other, the entropy of radiation would depend on the volume *not* as in Planck, but as in W. Wien, i.e. in the following way: $\kappa \log V^{E/h}$).

No, light atoms placed in the same cell of the phase space must depend one on the other in such a way that Planck's formula is obtained. Now we will clarify this question in a *polemic* manner. I, Krutkow and Bursian will publish in the next number of Z. Physik a few considerations against, and simultaneously Einstein will give them answer in the same issue.”

The "Other Colleagues"

Einstein to Halpern, September 1924:

- "1) All distributions of the individual quanta over the "cells" are equally probable (Wien's law).
2) All different quantum-distribution-pictures over the "cells" are equally probable (Planck's law) (...)

Without experience one cannot decide between (1) and (2). The concept of independent atom-like quanta calls for (1), but experience demands (2). **Bose's derivation therefore cannot be regarded as a genuine theoretical justification of Planck's law, but only as a reduction of that law to a simple, but arbitrary statistical elementary hypothesis.(...)**

This therefore also entails the implicit presupposition of **certain statistical dependencies** between the states of the molecules, **a presupposition which the gas theory as such does not suggest**. It would therefore be all the more interesting to know whether real gases behave according to this theory."

On the Correctness of the Distribution Law

- Einstein to Kamerlingh-Onnes, 13 November 1924 (on experimental data)
- Einstein to Ehrenfest, 8 January 1925

"I will then completely convince you about the gas-degeneracy-equation, I found another sound if only not totally complete approach to it, **free of the incriminated statistics**. But how to set up a mechanics that leads to something like this? "

- Einstein to Schrödinger, 28 February 1925

"In Bose's statistics, which I use, the quanta or molecules are regarded as *not independent of each other*. [...] I failed to emphasize clearly the fact that here **a new kind of statistics is employed**, which for the time being is justified by nothing but its success (...)

In a third paper, which is currently in press, I lay out considerations that are **independent of statistics** and that are analogous to the derivation of Wien's displacement law. These latter results have convinced me completely of the correctness of the road to follow."

The Third, Non-statistical Paper

- 1 Analogy with radiation: closing the circle initiated in 1905. A displacement law for gases.
- 2 Dimensional analysis: a known resort for Einstein
- 3 An adiabatic transformation and a conservative field of force: where is the 'quantum influence'?

Analogy with Radiation: Closing the Circle initiated in 1905

“Here we plan to engage in considerations, in the field of gas theory, that are largely analogous, in method and outcome, to those that lead, in the field of radiation theory, to Wien's displacement law.” (Einstein, 1925)

(“Zur Quantentheorie des idealen Gases”, p. 18)

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(“Zur Quantentheorie des idealen Gases”, p. 18)

	Combinatorics	Thermodynamics- Statistical Distribution
Radiation	Bose	Planck's radiation law → Rayleigh-Jeans' (Wien's displacement law is always valid)
Gas	Bose-Einstein	Einstein's distribution law → Maxwell- Boltzmann's distribu- tion law

Dimensional Analysis: a Known Resort for Einstein

- The distribution function: $\rho = \rho(L, \kappa T, V, m)$

$$dn = \rho(L, \kappa T, V, m) \frac{V dp_1 dp_2 dp_3}{h^3}$$

(L kinetic energy, κ Boltzmann constant, T temperature, V volume, m mass of a molecule, h Planck constant, p_i Cartesian momenta).

- ρ is dimensionless + only two dimensionless monomials can be constructed:

$$\rho = \Psi \left(\frac{L}{\kappa T}, \frac{m \left(\frac{V}{N} \right)^{\frac{2}{3}} \kappa T}{h^2} \right)$$

- Possible to further reduce the number of arguments without introducing “questionable” assumptions.

Einstein's 1909 dimensional argument

Cavity filled with gas molecules, radiation, and ions, the quantities that should be included as arguments of the spectral density are:

RT/N : energy of a molecule (dimensionally speaking),

c : speed of light,

e : quantum of electricity,

ν : frequency.

The dimensions of the density of radiant energy r are $ML^{-1}T^{-1}$. r must have the form:

$$r = \frac{e^2}{c^4} \nu^3 \Psi \left(\frac{Ne^2 \nu}{Rc T} \right). \quad (1)$$

This is the only possible combination to establish a dimensionless relation for r with the quantities considered by Einstein. Comparing with Planck's radiation law,

$$r = \frac{\alpha \nu^2}{c^3} h \nu \frac{1}{e^{\frac{h\nu}{\kappa T}} - 1} \quad (2)$$

(α is a dimensionless factor), Einstein arrives at:

$$h = \frac{e^2}{c} \quad \text{and} \quad \kappa = \frac{R}{N}. \quad (3)$$

Einstein's 1911 dimensional argument

Einstein tried to find an expression for the thermal conductivity K . Using the dimensional method, he arrived at the functional dependence:

$$K = C \frac{\nu}{d} \varphi \left(\frac{md^2\nu^2}{\kappa T} \right) \quad (4)$$

(m is the mass of an atom, d the interatomic distance, ν the oscillation frequency and C a constant). In order to determine the function φ Einstein appealed to recently published measurements by Arnold Eucken, which indicated a dependency of K with the inverse of temperature. Accordingly, the final expression should be:

$$K = C \frac{md\nu^3}{\kappa T}. \quad (5)$$

Fruitful procedure by combination of dimensional analysis with an empirical law.

Back to 1925: Two “undoubtful hypotheses”

- 1 The entropy of an ideal gas does not change in an “infinitely slow adiabatic” compression.

$$\frac{\Delta l_1}{l_1} = \frac{\Delta l_2}{l_2} = \frac{\Delta l_3}{l_3} = \frac{1}{3} \frac{\Delta V}{V} \Rightarrow \Delta \rho = 0 \Rightarrow \rho = \Psi \left(\frac{L}{\kappa T} + B \right)$$

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- 2 The required velocity distribution is valid for an ideal gas also in an external field of conservative forces.

$$\frac{\partial \rho}{\partial x_i} \dot{x}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0. \Rightarrow \rho = \Psi^*(L + \Pi)$$

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Interactions between molecules and container walls	Classical elastic collisions
Interactions between molecules	Not taken into account
Free motion of the molecules	According to classical mechanics

The adiabatic compression argument (1)

An (infinitesimal) adiabatic compression in an parallelepipedal container

$$\frac{\Delta l_1}{l_1} = \frac{\Delta l_2}{l_2} = \frac{\Delta l_3}{l_3} = \frac{1}{3} \frac{\Delta V}{V}. \quad (6)$$

Kinetic energy variation:

$$\Delta L = \frac{1}{m} (|p_1| \Delta |p_1| + \dots + \dots) = -\frac{2}{3} L \frac{\Delta V}{V}. \quad (7)$$

Since

$$\Delta d\Phi = 2\pi(2m)^{\frac{3}{2}} \left(L^{\frac{1}{2}} \Delta dL + \frac{1}{2} L^{-\frac{1}{2}} \Delta L dL \right), \quad (8)$$

it follows that:

$$\Delta(Vd\Phi) = 0. \quad (9)$$

The adiabatic compression argument (2)

Entropy assumed to be of the form:

$$\frac{dS}{\kappa} = \frac{V}{h^3} s(\rho, L) d\Phi, \quad (10)$$

with s an unknown function. In adiabatic processes one has:

$$\Delta dS = 0, \quad (11)$$

and therefore:

$$0 = \Delta s = \frac{\partial s}{\partial \rho} \Delta \rho + \frac{\partial s}{\partial L} \Delta L. \quad (12)$$

Since an adiabatic transformation does not change the number of molecules, one has:

$$\Delta \rho = 0. \quad (13)$$

and hence

$$s = s(\rho). \quad (14)$$

The adiabatic compression argument (3)

In thermodynamic equilibrium the entropy is a maximum with respect to variations of ρ , keeping fixed the number of particles and the total energy, which yields:

$$\frac{\partial s}{\partial \rho} = AL + B, \quad (15)$$

where A and B do not depend on L . Since s only depends on ρ , its derivative will do so, too, and Einstein could write:

$$\rho = \Psi(AL + B). \quad (16)$$

In order to determine A , Einstein now considered the process of an infinitesimal isopycnic warming, i.e. a warming that does not alter the density of molecules (a transformation of constant volume in this case). He obtained:

$$A = \frac{1}{\kappa T}. \quad (17)$$

and finally:

$$\rho = \Psi\left(\frac{L}{\kappa T} + B\right). \quad (18)$$

Upshot of 1925 paper

Two arguments to reduce the number of arguments in the distribution function:

$$\rho = \Psi \left(\frac{L}{\kappa T} + B \right) \quad \text{and} \quad \rho = \Psi^*(L + \Pi)$$

$$\text{Finally: } \rho = \Psi \left(\frac{L}{\kappa T} + \chi \left(\frac{m \left(\frac{V}{N} \right)^{\frac{2}{3}} \kappa T}{h^2} \right) \right)$$

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- *Maxwell-Boltzmann*
$$\rho = \frac{N}{V} \left(\frac{h^2}{2\pi m \kappa T} \right)^{\frac{3}{2}} e^{-\frac{L}{\kappa T}}$$

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- *Maxwell-Boltzmann*
$$\rho = \frac{N}{V} \left(\frac{h^2}{2\pi m \kappa T} \right)^{\frac{3}{2}} e^{-\frac{L}{\kappa T}}$$
- *Einstein*
$$\rho = \frac{1}{\exp \left[\frac{L}{\kappa T} + \chi \left(\frac{m \left(\frac{V}{N} \right)^{\frac{2}{3}} \kappa T}{h^2} \right) \right] - 1}$$

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- Smekal, Jordan, Schrödinger, Planck,... *knew the third paper it but did not comment on it.*
- Ehrenfest's role: only a footnote (Ehrenfest, 1925)

"The words of the paper by S.N. Bose, Planck's Law and the Light Quantum Hypothesis [ref.], readily create the impression as though Planck's radiation law could be derived from the assumption of *independent* light corpuscles. But this is not the case. Independent light corpuscles would correspond to Wien's radiation law."

("Energieschwankungen im Strahlungsfeld oder Kristallgitter bei Superposition quantisierter Eigenschwingungen" p. 364, footnote 1)

A Rightfully Forgotten Paper?

- By Contemporaries
 - The lack of interest in the “new statistics”
 - The abandonment of “space-time” pictures (Bohr, 1925)
 - The emergence of Quantum Mechanics
 - An ambiguous paper

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 - On the birth of indistinguishability
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Bose's serendipity and Einstein's dissatisfaction

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Einstein to Halpern, September 1924:

“...Bose's derivation therefore cannot be considered as giving a true theoretical basis to Planck's law.”