Weierstrass Institute for
Applied Analysis and Stochastics

Leibniz
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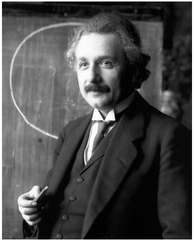
A probabilistic view at the interacting Bose gas

Wolfgang König (WIAS Berlin and TU Berlin)

- In 1924, the unknown young physicist SATYENDRA NATH BOSE asked the famous ALBERT EINSTEIN to help him publishing his latest achievement in *Zeitschrift für Physik*.
- Einstein translated the manuscript into German and had published it there for Bose.
- He stressed that the new method is suitable for explaining the quantum mechanics of the ideal gas. He extended the idea to atoms in a second paper: he predicted the existence of a previously unknown state of matter, now known as the Bose–Einstein condensate.



ALBERT EINSTEIN (1879-1955) in 1921

SATYENDRA NATH BOSE (1894-1974) in 1925

- An experimental realisation had to wait until 1995, where some ten thousands of atoms appeared in that condensate at a temperature of 10^{-9} K. $\Longrightarrow$ Nobel Prize in 2001

Bose’s work from 1924

Plancks Gesetz und Lichtquantenhypothese.

Von **Bose** (Dacca-University, Indien).

(Eingegangen am 2. Juli 1924.)

Der Phasenraum eines Lichtquants in bezug auf ein gegebenes Volumen wird in „Zellen“ von der Größe h^3 aufgeteilt. Die Zahl der möglichen Verteilungen der Lichtquanten einer makroskopisch definierten Strahlung unter diese Zellen liefert die Entropie und damit alle thermodynamischen Eigenschaften der Strahlung.

Plancks Formel für die Verteilung der Energie in der Strahlung des schwarzen Körpers bildet den Ausgangspunkt für die Quantentheorie, welche in den letzten 20 Jahren entwickelt worden ist und in allen Gebieten der Physik reiche Früchte getragen hat. Seit der Publikation im Jahre 1901 sind viele Arten der Ableitung dieses Gesetzes vorgeschlagen worden. Es ist anerkannt, daß die fundamentalen Voraussetzungen der Quantentheorie unvereinbar sind mit den Gesetzen der klassischen Elektrodynamik. Alle bisherigen Ableitungen machen Gebrauch von der Relation

$$\varrho_\nu \, d\nu = \frac{8\pi\nu^2 \, d\nu}{c^3} E,$$

d. h. von der Relation zwischen der Strahlungsdichte und der mittleren Energie eines Oszillators, und sie machen Annahmen über die Zahl der Freiheitsgrade des Äthers, wie sie in obige Gleichung eingeht (erster Faktor der rechten Seite). Dieser Faktor konnte jedoch nur aus der klassischen Theorie hergeleitet werden. Dies ist der unbefriedigende Punkt in allen Ableitungen, und es kann nicht wundernehmen, daß immer wieder Anstrengungen gemacht werden, eine Ableitung zu geben, die von diesem logischen Fehler frei ist.

Eine bemerkenswert elegante Ableitung ist von Einstein angegeben worden. Dieser hat den logischen Mangel aller bisherigen Ableitungen erkannt und versucht, die Formel unabhängig von der klassischen Theorie zu deduzieren. Von sehr einfachen Annahmen über den Energieaustausch zwischen Molekülen und Strahlungsfeld ausgehend, findet er die Relation

$$\varrho_\nu = \frac{\alpha_{mn}}{e^{\frac{\varepsilon_m - \varepsilon_n}{kT}} - 1}.$$

Indessen muß er, um diese Formel mit der Planckschen in Übereinstimmung zu bringen, von Wiens Verschiebungsgesetz und Bohrs Korrespondenzprinzip Gebrauch machen. Wiens Gesetz ist auf die klassische

Daraus folgt zunächst

$$p^s_r = B^s e^{-\frac{r h \nu^s}{\beta}}.$$

Da aber

$$A^s = \sum_r B^s e^{-\frac{r h \nu^s}{\beta}} = B^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right)^{-1},$$

so ist

$$B_s = A^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right).$$

Ferner hat man

$$N^s = \sum_r r p^s_r = \sum_r r A^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right) e^{-\frac{r h\nu^s}{\beta}} = \frac{A^s e^{-\frac{h\nu^s}{\beta}}}{1 - e^{-\frac{h\nu^s}{\beta}}}.$$

Mit Rücksicht auf den oben gefundenen Wert von A^s ist also

$$E = \sum_s \frac{8\pi h \nu^{s3} \, d\nu^s}{c^3} V \frac{e^{-\frac{h\nu^s}{\beta}}}{1 - e^{-\frac{h\nu^s}{\beta}}}.$$

Mit Benutzung der bisherigen Resultate findet man ferner

$$S = k\left[\frac{E}{\beta} - \sum_s A^s \lg\left(1 - e^{-\frac{h\nu^s}{\beta}}\right)\right],$$

woraus mit Rücksicht darauf, daß $\frac{\partial S}{\partial E} = \frac{1}{T}$, folgt, daß $\beta = kT$. Setzt man dies in obige Gleichung für E ein, so erhält man

$$E = \sum_s \frac{8\pi h \nu^{s3}}{c^3} V \frac{1}{e^{\frac{h\nu^s}{kT}} - 1} \, d\nu^s,$$

welche Gleichung Plancks Formel äquivalent ist.

(Übersetzt von A. Einstein.)

Anmerkung des Übersetzers. Boses Ableitung der Planckschen Formel bedeutet nach meiner Meinung einen wichtigen Fortschritt. Die hier benutzte Methode liefert auch die Quantentheorie des idealen Gases, wie ich an anderer Stelle ausführen will.

https://www.lorentz.leidenuniv.nl/history/Einstein_archive/Einstein_1925_publication/

Quantentheorie des einatomigen idealen Gases.

Zweite Abhandlung.

Von A. EINSTEIN.

In einer neulich in diesen Berichten (XXII 1924, S. 261) erschienenen Abhandlung wurde unter Anwendung einer von Hrn. D. BOSE zur Ableitung der PLANCKschen Strahlungsformel erdachten Methode eine Theorie der »Entartung« idealer Gase angegeben. Das Interesse dieser Theorie liegt darin, daß sie auf die Hypothese einer weitgehenden formalen Verwandtschaft zwischen Strahlung und Gas gegründet ist. Nach dieser Theorie weicht das entartete Gas von dem Gas der mechanischen Statistik in analoger Weise ab wie die Strahlung gemäß dem PLANCKschen Gesetze von der Strahlung gemäß dem WIENschen Gesetze. Wenn die BOSEsche Ableitung der PLANCKschen Strahlungsformel ernst genommen wird, so wird man auch an dieser Theorie des idealen Gases nicht vorbeigehen dürfen; denn wenn es gerechtfertigt ist, die Strahlung als Quantengas aufzufassen, so muß die Analogie zwischen Quantengas und Molekülgas eine vollständige sein. Im folgenden sollen die früheren Überlegungen durch einige neue ergänzt werden, die mir das Interesse an dem Gegenstande zu steigern scheinen. Der Bequemlichkeit halber schreibe ich das Folgende formal als Fortsetzung der zitierten Abhandlung.

§ 6. Das gesättigte ideale Gas.

Bei der Theorie des idealen Gases scheint es eine selbstverständliche Forderung, daß Volumen und Temperatur einer Gasmenge willkürlich gegeben werden können. Die Theorie bestimmt dann die Energie bzw. den Druck des Gases. Das Studium der in den Gleichungen (18), (19), (20), (21) enthaltenen Zustandsgleichung zeigt aber, daß bei gegebener Molekülzahl n und gegebener Temperatur T das Volumen nicht beliebig klein gemacht werden kann. Gleichung (18) verlangt nämlich, daß für alle s $\alpha^s \geqq 0$ sei, was gemäß (20) bedeutet, daß $A \geqq 0$ sein muß. Dies bedeutet, daß in der in diesem Falle gültigen Gleichung (18b) $\lambda\ (= e^{-A})$ zwischen 0 und 1 liegen muß. Aus (18b) folgt demnach, daß die Zahl der Moleküle in einem solchen Gas bei gegebenem Volumen V nicht größer sein kann als

$$n = \frac{(2\pi m \varkappa T)^{\frac{3}{2}} V}{h^3} \sum_s^\infty \tau^{-\frac{3}{2}}. \qquad (24)$$

Was geschieht nun aber, wenn ich bei dieser Temperatur $\frac{n}{V}$ (z. B. durch isothermische Kompression) die Dichte der Substanz noch mehr wachsen lasse?

Ich behaupte, daß in diesem Falle eine mit der Gesamtdichte stets wachsende Zahl von Molekülen in den 1. Quantenzustand (Zustand ohne kinetische Energie) übergeht, während die übrigen Moleküle sich gemäß dem Parameterwert $\lambda = 1$ verteilen. Die Behauptung geht also dahin, daß etwas Ähnliches eintritt wie beim isothermen Komprimieren eines Dampfes über das Sättigungsvolumen. Es tritt eine Scheidung ein; ein Teil »kondensiert«, der Rest bleibt ein »gesättigtes ideales Gas« ($A = 0$ $\lambda = 1$).

Daß die beiden Teile in der Tat ein thermodynamisches Gleichgewicht bilden, sieht man ein, indem man zeigt, daß die »kondensierte« Substanz und das gesättigte ideale Gas pro Mol dieselbe PLANCKsche Funktion $\Phi = S - \frac{\bar{E} + pV}{T}$ haben. Für die »kondensierte« Substanz verschwindet Φ, weil S, E und V einzeln verschwinden[1]. Für das »gesättigte Gas« hat man nach (12) und (13) für $A = 0$ zunächst

$$S = -\varkappa \sum_s \lg\left(1 - e^{-\alpha^s}\right) + \frac{\bar{E}}{T}. \qquad (25)$$

Die Summe kann man als Integral schreiben und durch partielle Integration umformen. Man erhält so zunächst

$$\sum_s = -\int_0^\infty s \cdot \frac{e^{-\frac{cs^{\frac{2}{3}}}{\varkappa T}}}{1 - e^{-\frac{cs^{\frac{2}{3}}}{\varkappa T}}} \cdot \frac{2}{3} \frac{cs^{-\frac{1}{3}}}{\varkappa T} ds,$$

oder gemäß (8) und (11) und (15)

$$\sum_s = -\frac{2}{3} \int_0^\infty n_s E^s ds = -\frac{2}{3} \frac{\bar{E}}{\varkappa T} = -\frac{pV}{\varkappa T}. \qquad (26)$$

Aus (25) und (26) folgt also für das »gesättigte ideale Gas«

$$S = \frac{\bar{E} + pV}{T}$$

oder — wie es für die Koexistenz des gesättigten idealen Gases mit der kondensierten Substanz erforderlich ist —

$$\Phi = 0. \qquad (27)$$

Wir gewinnen also den Satz:

Nach der entwickelten Zustandsgleichung des idealen Gases gibt es bei jeder Temperatur eine maximale Dichte in Agitation befindlicher Moleküle.

[1] Der »kondensierte« Teil der Substanz beansprucht kein besonderes Volumen, da er zum Druck nichts beiträgt.

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Translator's note: *Bose's derivation of Planck's formula represents an important progress in my opinion. The method used here also provides the quantum theory of the ideal gas, as I will explain elsewhere.*

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Page 3 in the own work:

From (18b) it follows that the number of molecules in such a gas cannot be greater than V *for a given volume*

$$n = \frac{(2\pi m \varkappa T)^{3/2} V}{h^3} \sum_s^\infty \tau^{-3/2}.$$

Page 4:

I claim that [with increasing density] a number of molecules, increasing with the total density, pass into the I. quantum state (state without kinetic energy), while the remaining molecules are distributed according to the parameter value $\lambda = 1$*.*

...

Hence we obtain the theorem:

According to the developed equation of state of the ideal gas, there is a maximum density of molecules in agitation at any temperature.

The degeneracy of the Bose–Einstein gas has rather got the reputation of having only a purely imaginary existence.

(London 1938)

The densities are so high and the temperatures so low that the van der Waals corrections are bound to coalesce with the possible effects of degeneration, and there is little prospect of ever being able to separate the two kinds of effect.

(Schrödinger 1946)

Can one prove with mathematical rigor [...] that a gas with given intermolecular forces will condense at sufficiently low temperature at a sharply defined density [...]? It may seem strange now that there could be any doubt that this would be possible but [...] in 1937 one wasn't so sure and I remember that Debye, for instance, doubted it. In my opinion, the liberating word was spoken by Kramers. He remarked that a phase transition (such as condensation) could mathematically only be understood as a limiting property of the partition function. Only in the limit, where the number of molecules N and the volume V go to infinity such that N/V remains finite (one calls this now the thermodynamic limit) can one expect the two discontinuities [...].

(Uhlenbeck 1974))

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And for me as a mathematician:

- driving force for many mathematical ansatzes, in particular probabilistic ones.

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- Functionalanalytic ansatz: large-N behaviour of the trace of the symmetrisation of an interacting N-particle Hamilton operator ($\Longrightarrow$ later). The wave functions have a probabilistic interpretation as the joint location densities of the N particles.
- Probabilistic ansatz: This trace was translated in the 1950s by JEAN GINIBRE and RICHARD FEYNMAN into a system of interacting Brownian motions, using the Feynman–Kac formula ($\Longrightarrow$ later).

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- Various authors showed that the occurrence of ”long Feynman cycles” in the ideal ($=$ non-interacting) gas and in mean-field approximations is characteristic for BEC.
- The only known proof for BEC in an interacting model exploits ”hard” repulsion and symmetry in a $\mathbb{Z}^d$ system (FREEMAN DYSON et al. 1978).

- Hunt for experimental realization from 1985, when sufficiently low temperatures came within reach. 10^{-6} Kelvin was reached in 1992 $\Longrightarrow$ Nobel Prize 1997.
- Difficulty: At such low temperatures almost every substance is solid (not gaseous). Dilute solution: heavily and cool quickly, holding particles together with a magnetic trap.
- The group of Eric A. Cornell and Carl E. Wieman succeeded in 1995 at the *Joint Institute for Laboratory Astrophysics* in Boulder (USA) in a gas of several thousand rubidium atoms at a temperature of about 10^{-9} Kelvin.
- Four months later, the group around Wolfgang Ketterle at the *Massachusetts Institute of Technology* also succeeded in doing this with sodium.
- All three scientists were awarded the Nobel Prize in Physics in 2001 for this achievement.

We have N particles in a box $\Lambda \subset \mathbb{R}^d$.

Each particle has three attributes:

- kinetic energy (in the form of the Laplace operator Δ),
- a (soft or hard) trap energy,
- interaction energy with every other particle.

The system is described with the help of a Hamiltonian for N particles at the locations $x_1, \dots, x_N$ in a box $\Lambda \subset \mathbb{R}^d$, subject to a pair interaction via a symmetric pair potential $v\colon \mathbb{R}^d \to [0, \infty]$:

$$\mathcal{H}_N^{(\Lambda)} = -\sum_{i=1}^{N} \Delta_i + \sum_{1 \leq i < j \leq N} v\big(x_i - x_j\big), \qquad x_1, \dots, x_N \in \Lambda.$$

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- $\mathcal{H}_N^{(\Lambda)}$ is applied to wave functions $\phi \colon \Lambda^N \to \mathbb{R}$.
- $|\phi(x_1, \dots, x_N)|^2 =$ probability density for N particles at the locations $x_1, \dots, x_N$.
- Clear: $|\phi(x_1, \dots, x_N)|^2$ is symmetric ($=$ invariant under permutations).
- Boson system (Quantum mechanics!): also $\phi(x_1, \dots, x_N)$ is symmetric.

- Main object:

  symmetrised trace $\qquad Z_N(\beta,\Lambda) = \mathrm{Tr}_+\big(\exp\{-\beta\mathcal{H}_N^{(\Lambda)}\}\big).$

- Physics $\Longleftrightarrow$ Mathematics:

temperature	$\Longleftrightarrow$	$1/\beta$
kinetic energy	$\Longleftrightarrow$	$\mathrm{e}^{\beta\Delta} \Longleftrightarrow$ Brownian motion on $[0,\beta]$
interaction	$\Longleftrightarrow$	$\mathrm{e}^{-v(x_i-x_j)}$
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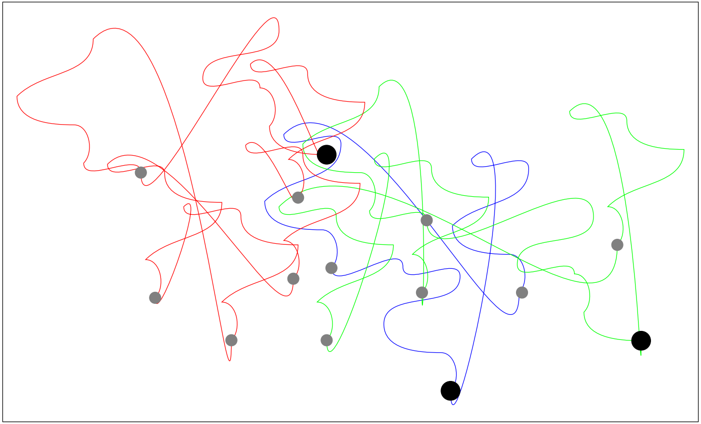
- Feynman–Kac formula:

$$Z_N(\beta,\Lambda) = \underbrace{\int_\Lambda \mathrm{d}x_1 \cdots \int_\Lambda \mathrm{d}x_N}_{N \text{ points in } \Lambda} \overbrace{\frac{1}{N!}\sum_{\sigma\in\mathfrak{S}_N}}^{\text{random permutation}} \underbrace{\bigotimes_{i=1}^N \mu^{(\beta)}_{x_i,x_{\sigma(i)}}}_{N \text{ Brownian bridges}} \Big[\overbrace{\mathrm{e}^{-\sum_{1\le i<j\le N} V_\beta(B^{(i)},B^{(j)})}}^{\text{interaction}}\Big].$$



Bose gas consisting of 14 particles, organised in three Brownian cycles, assigned to three Poisson points. The red cycle contains six particles, the green and the blue each four.

- We consider here the canonical ensemble, where the number N of particles is fixed. If N is random and Poisson-distributed, we look at the grandcanonical system.
- The interacting Bose gas is an ensemble of interacting Brownian cycles with various lengths in a large box. A cycle of length k (i.e., with time interval $[0, \beta k]$) accomodates precisely k particles. Altogether, the system has $N = \sum_{k=1}^{\infty} kN_k$ paticles (if N_k is the number of cycles of length k).

The BEC Question Does a macroscopic part of the N particles lie in ”very long” cycles?

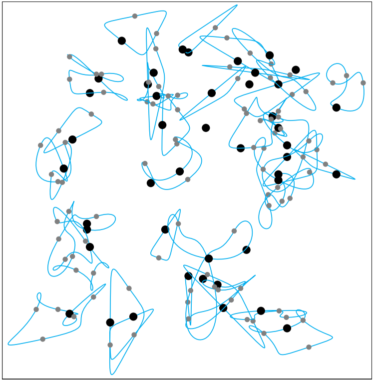
- Philosophical question: What is the right box size?

thermodynamic limit $|\Lambda_N| = N/\rho$ or dilute limit $|\Lambda_N| \gg N$?

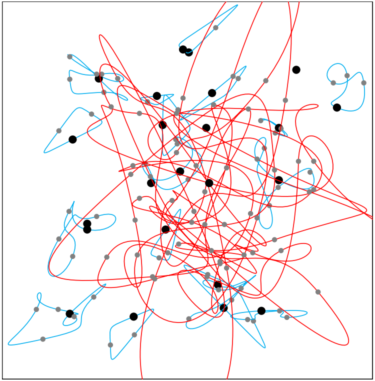
- Answer by Kramers in 1937: the thermodynamic limit!

Free energy in the thermodynamic limit (d.h. $|\Lambda_N| = N/\rho$):

$$f(\beta, \rho) = -\lim_{N\to\infty} \frac{1}{|\Lambda_N|} \log Z_N(\beta, \Lambda_N).$$



Subcritical (low ρ) Bose gas
without condensate



Supercritical (large ρ) Bose gas
with additional condensate (red)

- Proof for phase transition in the thermodynamic limit widely open; considered very deep.
- Many simplified models and regimes have been settled.
- Feynman–Kac formula is by far not the only ansatz.
- Interacting Brownian cycles triggered much probabilistic research and will continue to do so.
- Experimentally, BEC could not obtained at sginificantly higher temperatures than in 1995, but for many more different substances.
- Applications are not in sight, but it is tremendously fascinating!