1 First Steps (and Stumbles) of Bose-Einstein Condensation

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Introduction

In 1924, Einstein predicted the occurrence of condensation in an ideal gas. He published the prediction at the beginning of 1925, in the second of his papers on the application of Bose's statistical method to a gas of particles. The theoretical physicist Chen Ning Yang called this prediction "a most daring and insightful extrapolation which has only now been brilliantly experimentally confirmed."[1] Yang was referring to the experimental observation of the phenomenon known as Bose-Einstein condensation in dilute gases, which was achieved in 1995 and was awarded the Nobel Prize in physics in 2001. The Bose-Einstein condensation produced and observed in 1995 in real gases, in fact, is universally identified with the process predicted by Einstein seventy years earlier.

There are two kinds of historical narratives in which Einstein's prediction appears. When the history of Bose-Einstein condensation is outlined, it is often said that Einstein predicted a new kind of phase transition. For example, a text of the Royal Swedish Academy of Sciences reads,

> Einstein noted that if the number of particles is conserved even totally non-interacting particles will undergo a phase transition at low enough temperatures. This transition is termed Bose-Einstein condensation (BEC).[2]

Einstein's prediction is cast against the backdrop of a supposedly familiar notion of phase transitions, while its novelty of being caused solely by quantum statistics and not by intermolecular interactions is highlighted. It is implicitly suggested that Einstein relied on a pre-existing theory of phase transitions to make the prediction.

Yet, when the history of phase transitions is recalled, Bose-Einstein condensation is listed as one of a group of phenomena, along with ordinary gas-liquid transitions, ferromagnetism, the He-I to He-II transition, and superconductivity, from which a general idea of phase transition gradually emerged, making it possible to attempt formulating an encompassing classification, common theoretical concepts, and a unified theoretical picture.

My main point will be that the history of Bose-Einstein condensation is more complex than the script about the final verification of an "insightful" theoretical prediction implies. In particular, the history of Bose-Einstein condensation cannot be decoupled from

[1] Chen Ning Yang, "Remarks About Some Developments in Statistical Mechanics", HFPN, Number 06, March 15, 1996, available at http://chris.kias.re.kr/yang.htm.

[2] Royal Swedish Academy of Sciences, "Advanced information on the Nobel Prize in Physics 2001", http://nobelprize.org/nobel_prizes/physics/laureates/2001/phyadv.pdf .

the history of phase transitions. I shall concentrate on an episode to which neither of the two narratives I sketched above pays much attention. We find this episode recounted, instead, when the focus is on the anecdotic or the biographical; it is typically characterized as a detour that "delayed the general acceptance of the Bose-Einstein condensation for 10 years".[3] For over a decade Einstein's prediction was "not taken terribly seriously even by Einstein himself", and "rather got the reputation of having only a purely imaginary existence," until it was "resurrected" by Fritz London in 1938 in connection with a possible clarification of the "lambda transition" in liquid He.[4] Yet, this very detour might offer an insight on how the history of Bose-Einstein condensation and the history of phase transitions are interrelated.

There appear to be two reasons for the long neglect of Einstein's prediction. The first is that in 1927 George E. Uhlenbeck severely questioned Einstein's argument. Uhlenbeck's criticism persuaded even Einstein that the prediction was mistaken. The second reason is that the predicted phenomenon "appeared to be devoid of any practical significance[.]"[5] Einstein himself had admitted that, although the densities of real gases such as helium and hydrogen could reach values not too far from the saturation values that would mark the onset of condensation in the corresponding ideal gases, the effects of quantum degeneracy would be obscured by molecular interactions.[6] In the following decades, although the onset of Bose-Einstein condensation was not in itself considered to be beyond the reach of experiment, the densities required were so high and the temperatures so low that, as Schrödinger wrote in 1946,

> 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.[7]

The conviction that Bose-Einstein condensation could never be observed in real gases was abandoned only in the late 1970s, when the suggestion that spin-polarized hydrogen would remain gaseous down to zero temperature, together with tremendous advances in the technology of ultracold temperatures, triggered the first efforts toward an experimental realization of the phenomenon.

Uhlenbeck, however, withdrew his objection in 1937, thus clearing the way for London's resurrection of Bose-Einstein condensation as a possible theoretical model for the underlying mechanism of the lambda transition in liquid helium. As I shall try to show, this alleged resurrection was in fact a new formulation of the condensation prediction based on a new understanding of phase transitions.

[3]E. G. D. Cohen, "George E. Uhlenbeck and statistical mechanics", American Journal of Physics, 58 (1990), 619–625, on 619. See also A. Pais, "Einstein and the quantum theory", *Reviews of Modern Physics*, 51 (1979), 863–914, on 897; G. E. Uhlenbeck, "Some Reminiscences About Einstein's Visit to Leiden", in H. Woolf, ed., Some *Strangeness in the Proportion. A Centennial Symposium to Celebrate the Achievements of Albert Einstein* (Reading, MA: Addison-Wesley Publishing Company, 1980), 524–525.

[4]Eric A. Cornell and Carl E. Wiemann, "Bose-Einstein condensation in a Dilute Gas; The First 70 Years and Some Recent Experiments", *Les Prix Nobel. The Nobel Prizes 2001*, T. Frängsmyr, ed. (Stockholm: Nobel Foundation, 2002), 78–108, on 78; F. London, "The λ-phenomenon of Liquid Helium and the Bose-Einstein Degeneracy", *Nature*, 141, 643–644, on 644.

[5]F. London, "On the Bose-Einstein condensation", *Physical Review*, 54 (1938), 947–954, on 947.

[6]Einstein, "Quantentheorie des einatomigen idealen Gases. Zweite Abhandlung", *Berliner Berichte* (1925), 3–14, on 11–12.

[7]E. Schrödinger, *Statistical Thermodynamics* (Cambridge, 1967), on 54.

Einstein's Argument

Einstein's 1925 prediction was as follows:

> In the theory of the ideal gas, it seems a self-evident requirement that volume and temperature of a quantity of gas can be given arbitrarily. The theory determines then the energy or the pressure of the gas. But the study of the equation of state contained in equations (18), (19), (20), (21) shows that if the number of molecules n and the temperature T are given, the volume cannot be made arbitrarily small. [...] *But then, what happens if* I let the density of the substance, $\frac{n}{V}$, increase further at this temperature (for example, by isothermal compression)?
>
> *I assert that* in this case a number of molecules, a number increasing with the total density, passes into the first quantum state (state without kinetic energy), while the remaining molecules distribute themselves according to the parameter value $\lambda = 1$. Thus, the assertion means that *there occurs something similar to* when isothermally compressing a vapour above the saturation volume. A separation takes place; a part "condenses", the rest remains a "saturated ideal gas" $(A = 0, \lambda = 1)$.[8]

In this text, the expression "I assert [*Ich behaupte*]" makes a contrast with the language of the previous sentences, "The study of the equations shows... It follows from..." Einstein wanted to tell us that his *Behauptung* was no deduction from the preceding theory. In fact, he formulated it as a way out from what would have otherwise been a serious limitation of the theory. And he drew it only on the basis of a physical model, the model of a vapour at the saturation volume, without having a formal analogy to go with it.

Einstein had derived for the total number of particles of his ideal gas the expression,

$$n = \sum_S \frac{1}{\frac{1}{\lambda} e^{\frac{E_S}{kT}} - 1} \tag{1}$$

[8] A. Einstein, "Quantentheorie. Zweite Abhandlung" (note 6), on 3–4, emphasis added. The equations referred to in the quotation are,

$$n = \sum_\sigma \frac{1}{e^{\alpha^S} - 1} \tag{18}$$

$$\bar{E} = \frac{3}{2} pV = c \sum_\sigma \frac{s^{\frac{2}{3}}}{e^{\alpha^S} - 1} \tag{19}$$

$$\alpha^S = A + \frac{cs^{\frac{2}{3}}}{xT} \tag{20}$$

$$c = \frac{E^S}{s^{\frac{2}{3}}} = \frac{h}{2m} \left(\frac{4}{3} \pi V \right)^{-\frac{2}{3}} \tag{21}$$

where A is defined by equation (16), $e^A = \pi^{\frac{3}{2}} h^{-3} \frac{V}{n} (2mxT)^{\frac{3}{2}}$. Einstein defined the parameter λ by the statement, "...the quantity e^{-A}, which we want to indicate by λ..." . Einstein, "Quantentheorie des einatomigen idealen Gases", *Berliner Berichte* (1924), 261–267, on 265–266. Today, the letter λ is commonly used for another quantity, *the thermal de Broglie wavelength* of the gas, $\lambda_{dB} \equiv \frac{h}{\sqrt{2\pi mkT}}$, which is related to Einstein's parameter by $\lambda = \frac{n}{V} \lambda_{dB}^3$.

and had identified the parameter λ as "*ein Maß für die 'Entartung' des Gases.*"[9] In order to examine the dependence of the number of particles on the volume and on the temperature, Einstein had carried out the following manipulations. Observing that the *Entartung* parameter has to be in principle smaller or equal to one, he had expanded each term of the sum into a power series,

$$n = \sum_S \sum_\sigma \lambda^\tau \exp\left(-\frac{E_S \tau}{kT}\right)$$

and then had replaced the sum over s by an integration, thus obtaining,

$$n = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V \sum_\tau \tau^{-\frac{3}{2}} \lambda^\tau$$

He had then noted that this equation expressed an upper limit on the number of particles for a given volume and a given temperature the gas. The maximum number of particle in the gas was given by

$$n_{max} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V \sum_\tau \tau^{-\frac{3}{2}}$$

where the sum in τ is just a finite constant. It was at this point that he had asked, "But then what happens if I let the density of the substance increase further at this temperature (for example by isothermal compression)?", and had asserted that, according to the model of the isothermal compression of a saturated vapour, a separation would take place, and the molecules in excess of the maximum number would "condense" into the quantum state of lowest energy.

Uhlenbeck's Criticism

In 1927, Uhlenbeck, then a student of Paul Ehrenfest in Leiden, studied the Fermi-Dirac and the Bose-Einstein statistics, and their relation to the classical Maxwell-Boltzmann statistics for his doctoral thesis. He came to object to Einstein's prediction of condensation on the following ground. He observed that Einstein's conclusion was in mathematical contradiction with the fact that the first term of the sum (1), which represented the average number of molecules in the state of zero kinetic energy, became infinite for $\lambda = 1$. The appearance of a maximum for the number of gas molecules was caused only by the approximation of the sum by an integral. The exact expression for the number of molecules had no upper limit; on the contrary, it became infinite for $\lambda \to 1$. The value of the *Entartung* parameter was indeed determined by the given number of molecules and temperature, and it was certainly smaller than one for high temperatures and low densities. As the temperature lowered, the lowest quantum states would "be more and more filled, and in much stronger degree than would be the case in Boltzmann statistics." The *Entartung* parameter could reach the value one only asymptotically, and no "splitting into two phases" would occur.[10]

[9] Einstein, "Quantentheorie" (note 7), on 266. I re-wrote Einstein's equation in a compact form. See note 7 for Einstein's original formulae.

[10] G. E. Uhlenbeck, *Over Statistische Methoden in de Theorie der Quanta* ('s Gravenhage: Martinus Nijhoff, 1927), 69–71. I thank Jos Uffink for his help with the original Dutch text.

The criticism came from Leiden, the location of Kamerlingh-Onnes's cryogenic laboratory, powerhouse for the production of new knowledge on condensation phenomena, and the academic home of Paul Ehrenfest. Ehrenfest was the first to whom Einstein had communicated his idea of a "condensation without attractive forces" in a gas governed by Bose's "almost unintelligible" statistics. We know that Ehrenfest was rather sceptical of this new statistical method, which, as Einstein himself admitted, could be justified only *a posteriori* through its success for the radiation law. Possibly, Einstein's had been encouraged in envisioning condensation in such a gas by the fact that, in response to Ehrenfest's criticisms, he had had to recognize that his and Bose's method did not treat the gas molecules as independent. Hence, although there were no attractive forces among molecules, one had to admit a "mutual influence" which was, for the time being, of a "mysterious nature".[11] Ehrenfest was unmoved, and apparently the condensation by mysterious influence did nothing to mitigate his reserves. Not only did Ehrenfest support Uhlenbeck's criticism, but he positively cheered for it, for he wrote his friend Einstein a playful letter in the form of a physics journal article, which began, "Title: Does the Bose-Einstein Statistics Lead for Ideal Gases to a Condensation in the Degenerate State? Summary: No!" In 1933, Ehrenfest published the first attempt at a comprehensive classification of phase transitions. This was his last work before his death. Bose-Einstein condensation was not mentioned in it. But the wind had begun to turn, and Ehrenfest's classification would unintentionally play a major role in reversing the fortune of Einstein's prediction.

The Reappraisal

In the first place, the advancement of quantum mechanics had dispelled the mystery around the Bose-Einstein gas. In 1926, Paul Dirac had showed that the new quantum statistics, the Bose-Einstein statistics and the one that became known as the Fermi-Dirac statistics, were related to the symmetry of the wave function, and hence to the invariance of observable quantities, under exchanges of particles. This property, which became known as the quantum *indistinguishability* of particles, was adopted as the justification of the appearance of mutual influence among particles subjected to the Bose-Einstein statistics.

Another pivotal development had taken place right in Leiden. It was the immediate motivation of Eherfest's re-thinking of phase transitions. Willem Hendrik Keesom, Kamerlingh-Onnes's successor, and his collaborator Mieczislav Wolfke observed an abrupt variation in dielectric constant of liquid helium. Added to earlier data about other sharp changes in thermodynamic parameters, the change in dielectric constant suggested a phase transition near the critical temperature $T_c = 2.2$ K. Keesom and Wolfke hypothesized two phases in liquid helium and called them He-I and He-II. The helium transition was similar to ordinary phase transitions in the sudden jumps that several thermodynamic parameters underwent around the critical temperature, but it differed in that it involved no latent heat and no change in the appearance of the substance. In 1932–33, Keesom and collaborators measured the variation of specific heat with temperature around the critical temperature, and published a curve which showed a characteristic, very marked jump. Keesom took up a suggestion from Ehrenfest and

[11] Einstein, "Quantentheorie. Zweite Abhandlung" (note 6), on 6.

called the critical temperature "the lambda point" because of the shape of the curve. The transition became known as "the lambda transition".

The existing theoretical treatment of phase transitions was a combination of the van der Waals equation and Gibbs's conditions of thermodynamic equilibrium of coexisting phases. A process like the lambda transition was not contemplated in it. Ehrenfest formulated a characterization of phase transitions capable of including ordinary phase transitions and the lambda transition, as well as other critical phenomena such as the magnetization of ferromagnetic materials and superconductivity. He defined a phase transition as an analytic discontinuity in the derivatives of the Gibbs free energy, $G = U - TS + pV$. He then classified processes as being of the first order if they corresponded to a discontinuity of the first derivative, of the second order if they corresponded to a discontinuity of the second derivative, and so on. Accordingly, ordinary changes of state such as gas to liquid were first order transitions because in them the entropy and the volume, first derivatives of the Gibbs free energy, were discontinuous. In the lambda transition, entropy and volume did not change, but the specific heat, a second derivative of the Gibbs free energy, had a jump, so the lambda transition was a second order transition. The scheme made room naturally for hypothetical transitions of higher orders.

The Ehrenfest classification was a very influential attempt at ordering the growing variety of critical processes under a general definition based on the mathematical properties of thermodynamic functions. It has been described as a major step toward the creation of a new area of study concerned with "cooperative phenomena".[12] These are a subclass of the phenomena pertaining to large assemblies of particles. They are defined as those phenomena in which the states of the assembly are not related in a simple manner to the states of the individual particles because the particles are strongly correlated. Understood as cooperative phenomena in this sense, phase transitions are regarded as paradigmatic of the emergent properties of complex systems.[13] But a subfield centred on this negative definition could only form by differentiating itself from a field founded upon the assumption that large assemblies of particles do have states that can be understood in terms of the states of the individual components. To be more specific, a theoretical understanding of phase transitions as cooperative phenomena required a general statistical mechanical derivation of thermodynamics as a precondition.[14]

Uhlenbeck's reconsideration of his objection to Bose-Einstein condensation was inspired by the first statistical-mechanical theory of condensation, which was formulated in 1937 by the American physical chemist Joseph E. Mayer. Mayer had begun his career at the school of physical chemistry headed by Gilbert N. Lewis in Berkeley. Physical chemistry in those days was, according to Mayer, "almost exclusively the application of

[12] L. Hoddeson et al., "Collective Phenomena", in L. Hoddeson et al., eds., *Out of the Crystal Maze. Chapters from the History of Solid-State Physics* (New York: Oxford University Press, 1992), 489–598. Hoddeson et al. attribute the explicit definition of the statistical mechanical study of cooperative phenomena as a separate subfield to R. H. Fowler, in the 1936 edition of his *Statistical Mechanics*.

[13] See, for example, Philip W. Anderson, "More is Different", *Science* 177, 4047 (1972), 393–396.

[14] My observation is limited to the statistical definition of cooperative phenomena, which consists of the denial of an otherwise underlying assumption in statistical mechanics. For an history and analysis of early notions of "collectivized entities", that is, individual electrons that are neither "free" nor "bound" to single atoms in solids, or quantized collective excitations, see A. Kojevnikov, "Freedom, collectivism, and quasiparticles: Social metaphors in quantum physics", *Historical Studies in the Physical and Biological Sciences*, 29 (1999), 295–331.

thermodynamics." Mayer and Lewis undertook a systematic study of statistical mechanics in 1928. Here is Mayer's account of his encounter with this discipline:

> I had no knowledge of statistical mechanics and Lewis had never worked in the field either. He had become interested in the discovery that had just been made of the difference between quantum mechanical statistical mechanics and the classical, and the Bose-Einstein versus the Fermi-Dirac systems. During the day I tried to learn statistical mechanics... Gilbert and I spent the evening together ...I still like the methods that we evolved for deriving thermodynamics from statistical mechanics, that is, from the mechanical laws for the motion of molecules.[15]

The result of this effort was a series of papers on the derivation of thermodynamics from statistical mechanics by Lewis and Mayer (Lewis and Mayer, 1928, 1929). The last of the Lewis and Mayer papers dealt with quantum statistics; notably, however, it makes no mention of Bose-Einstein condensation.

In 1937, Mayer wrote, in collaboration with two of his students, "an epochmaking series of papers" which were titled "The Statistical Mechanics of Condensing Systems".[16] In these, he developed a method for deriving the thermodynamic quantities of systems of interacting particles, that is, real systems, starting from simple assumptions about the inter-particle potential. The method used a series expansion of the partition function, in which the first term corresponded to the non-interacting (ideal) gas, and the subsequent terms represented the corrections arising from the interactions. Mayer's method is known as the "method of cluster expansions" because it decomposes the effects of particle-particle interactions in terms of a two-particle function and its two-fold, three-fold, etc. products, each of which can be interpreted as representing a cluster of two, three, etc. particles. The cluster terms will depend on the volume V of the system in a way that can be interpreted as a "surface effect". In the limit of infinite volume, they have a finite value that depends on the temperature. Therefore, the equation of state of the interacting system can be written, in the limit $V \to \infty$, as

$$\frac{P\nu}{kT} = \sum_{l=1}^{\infty} a_l(T) \left(\frac{\lambda_{dB}^3}{\nu} \right)^{l-1}$$

where $\nu = \frac{V}{n}$ is the volume per particle in the system, and λ_{dB} is the parameter called *mean thermal wavelength* , or *thermal de Broglie wavelength* of the particles in the system, and is defined as $\lambda_{dB} \equiv \left(\frac{h}{2\pi mkT}\right)^{\frac{1}{2}}$. This form of the state equation is known as the *virial expansion* of the system, and the $a_l(T)$ are called *virial coefficients.*

Max Born regarded Mayer's theory of condensation "as a most important contribution to statistical mechanics," and presented it at an international conference that was

[15] Joseph E. Mayer, "The Way It Was", *Annual Review of Physical Chemistry*, 33 (1982), 1–23, on 9 and 13–14.

[16] Bruno H. Zimm, "Joseph Edward Mayer", *Biographical Memoirs of the National Academy of Sciences*, 65 (1994), 211–220, on 213. J. E. Mayer, "The Statistical Mechanics of Condensing Systems. I", *Journal of Chemical Physics*, 5 (1937), 67–73; J. E. Mayer and P. G. Ackermann, "The Statistical Mechanics of Condensing Systems. II", *Journal of Chemical Physics*, 5 (1937), 74–83; J. E. Mayer and S. F. Harrison, "The Statistical Mechanics of Condensing Systems. III", *Journal of Chemical Physics*, 6 (1938), 87–100; S. F. Harrison and J. E. Mayer, "The Statistical Mechanics of Condensing Systems. IV", *Journal of Chemical Physics*, 6 (1938), 101–104.

held in Amsterdam in late 1937 for the van der Waals's centenary.[17] Since, however, he found Mayer's treatment obscure and somewhat unconvincing, he undertook a systematization and clarification of it in collaboration with Klaus Fuchs. Meanwhile, he was corresponding with Uhlenbeck, who had also become interested in Mayer's work.

Mayer's theory and Born's elaboration of it dealt with a classical system. Uhlenbeck and his student Boris Kahn extended it to quantum statistics. Furthermore, they were able to modify the method so that it could be also applied to an ideal gas. In particular, Kahn and Uhlenbeck noticed a strong formal analogy between the virial expansion of Mayer's theory and Einstein's series expansions, and between Mayer's and Einstein's arguments for condensation. A physical interpretation of the analogy was enabled by a result obtained by Uhlenbeck in 1932, according to which the assumption of Bose-Einstein statistics was equivalent to the assumption of "quasiattractional forces" among the molecules.[18] Having simplified Mayer's forbidding formalism, Uhlenbeck and Kahn obtained formulae for the density and pressure of the non-ideal gas that were "identical with Einstein's equations" for the ideal gas. They wrote,

> Einstein has already shown that these equations describe a condensation phenomenon. In fact the series for N converges for the maximum value of A and there exist therefore a maximum density. For smaller volumes a certain number of molecules will condense into the state of zero energy, and the pressure remains constant.[19].

Uhlenbeck and Kahn repeated Uhlenbeck's earlier remark, that Einstein's formulae were valid only if one neglected the quantization of the translational energy of the molecules. They endorsed Mayer's argument for condensation adducing that it coincided with the argument given by Einstein for the ideal gas, even though they still considered Einstein's formulae inapplicable. In turn, as we will see, Mayer's theory and the reflections that it stirred would afford Uhlenbeck and Kahn the means to rehabilitate Einstein's formulae. The argument, as they articulated it, consisted of two points. The first was that for a given volume the number of particles of the gas had a finite maximum. The reaching of the maximum would mark the saturation point, beyond which the molecules in excess would begin to accumulate in the state of zero energy. The second was that the pressure of the gas would remain constant as the volume decreased beyond the saturation point, as was expected in a condensation process. Even thought Kahn and Uhlenbeck attributed the reasoning to Einstein and Mayer, only the first of the two points had been presented by Einstein in the 1925 paper. And only the second had been part of Mayer's discussion of how to read the occurrence of condensation out of his involved mathematical formalism.

Born, and Kahn and Uhlenbeck's treatments of condensing systems caused a "vigorous discussion" at the Amsterdam conference, "on the question as to whether Mayer's

[17] Max Born and Klaus Fuchs, "The Statistical Mechanics of Condensing Systems", *Proceedings of the Royal Society of London*, A166 (1938), 391–414, on 391; Max Born, "The Statistical Mechanics of Condensing Systems", *Physica*, 4 (1937), 1034–1044.

[18] B. Kahn and G. E. Uhlenbeck, ""On the theory of condensation", *Physica*, 4 (1937), 1155–1156, on 1155; G. E. Uhlenbeck and L. Gropper, "The Equation of State of a Non-ideal Einstein-Bose or Fermi-Dirac Gas", *Physical Review*, 41 (1932), 79–90.

[19] B. Kahn and G. E. Uhlenbeck, "On the theory of condensation", *Physica*, 4 (1937), 1155–1156, on 1155. Kahn and Uhlenbeck's parameter A is $A = \frac{\lambda}{\lambda_{dB}^3}$

explanation of the phenomena of condensation is correct."[20] By this time, following the Ehrenfest classification, phase transitions had come to be defined as analytical discontinuities in thermodynamic functions. At the same time, it had become self-evident that the thermodynamic functions of a system were to be derived from its statistical mechanics. A conflict arose, for it was difficult to see how one could obtain analytical discontinuities from the partition function of a system of particles, which was thoroughly analytic. The debate was so undecided that the question was put to vote, and the votes turned out to be evenly divided. Here is how Uhlenbeck later recounted this episode:

> Can one prove with mathematical rigor from the foundations of statistical mechanics, i.e. from the partition function, that a gas with given intermolecular forces will condense at sufficiently low temperature at a sharply defined density, so that the isotherms will exhibit a discontinuity? It may seem strange now that there could be any doubt that this would be possible but at the Conference (so still 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 that the isotherm will exhibit the two known discontinuities.[21]

Kahn and Uhlenbeck embraced Kramers's proposal, which allowed them to reconcile Ehrenfest's definition of phase transitions with their belief that the statisticalmechanical partition function contained "all possible states of a system". They converted to the idea that a mathematical description of phase transitions could only be obtained in the limit of infinite volume and infinite number of particles, with the density remaining finite, and that the physical sense of such operation would be recovered by stating that "the problem has only physical sense when N is very large."[22] This new logic entailed a tacit reversal of position. Ten years earlier Uhlenbeck had maintained that, since the *Entartung* parameter of Einstein's gas would approach the value one without ever reaching it, a splitting of the gas into two phases would not occur. Now, he and Kahn were ready to champion the new understanding of phase transitions as "limit properties", and hence to accept that also in an ideal Bose-Einstein gas condensation would occur in the thermodynamic limit.

Deepening the analogy between Mayer's and Einstein's theories, Kahn and Uhlenbeck were able to adapt the cluster summation to the ideal gas and to derive the condensation formulae with a "strict calculation" that avoided the questionable approximation used by Einstein. They stressed, however, that Einstein's and Mayer's arguments for condensation were incomplete.

Comparing the thermodynamic functions obtained in Mayer's and Einstein's case with those of the Fermi-Dirac statistics, Uhlenbeck and Kahn came to the conclusion that condensation would occur in Mayer's and in Einstein's gases, but not in a Fermi-Dirac

[20] Born and Fuchs, "The statistical mechanics of condensing systems" (note 17), on 391.
[21] Uhlenbeck, quoted in Cohen, "George E. Uhlenbeck and statistical mechanics" (note 3), on 619.
[22] B. Kahn and G. E. Uhlenbeck, "On the Theory of Condensation", *Physica*, 5 (1938), 399–415, on 401.

gas. Along with the recursive application of the formal analogy between the Bose-Einstein ideal gas and Mayer's real gas, the crucial ingredient of this conclusion was an enlarged notion of condensation according to Ehrenfest's definition of phase transitions, complemented by the idea of phase transitions as "limit properties". Uhlenbeck and Khan pointed out that Einstein's condensation would have "some uncommon features"; for instance, the isothermal variation of the pressure with the volume would have no discontinuity at the critical point.[23] Nonetheless, in the Mayer and Einstein cases the value one of the Entartung parameter would represent a singular point for density and pressure, while it would not represent a singular point in the Fermi-Dirac case. In the same vein, shortly later Fritz London would observe that the condensation of the Bose-Einstein gas represented "a discontinuity of the derivative of the specific heat (phase transition of the third order)."[24]

Conclusion

To summarize, the first theory of phase transitions founded on classical statistical mechanics was produced by a physical chemist, who had trained himself in statistical mechanics in the wake of enthusiasm and curiosity that followed the birth of quantum statistics and quantum mechanics. This theory, in turn, led to a systematic re-formulation, on the basis of a quantum statistical method and a new definition of phase transitions, of Einstein's argument for condensation in an ideal gas. From this outline of the story of the early days of Bose-Einstein condensation, it would seem that, contrary to the suggestions implied by the terminology of "classical" statistics and quantum "revolution", quantum statistical mechanics did not come to overthrow and supplant a normal-science regime of classical statistical mechanics. It arrived, rather, at a stage in which statistical mechanics was itself young, and the classical and quantum branches of it developed to a considerable extent in parallel, or better, interacting with each other.

In the way of conclusion I shall formulate two questions for my ongoing research. How much did the advent of quantum mechanics and quantum statistics influence, or even favour, the widespread adoption of statistical mechanics as the effective foundation of thermodynamics? And how much did Bose-Einstein condensation, being the first phase transition fully rooted in the statistical treatment of a thermodynamic system, contribute to the emergence of the new category of "cooperative phenomena"?

[23] Kahn and Uhlenbeck, "On the Theory of Condensation" (note 22), on 408–409.

[24] F. London, "The λ-Phenomenon in Liquid Helium and the Bose-Einstein Degeneracy", *Nature, 141* (1938), 643–644, on 644.