Quantum Theory of the Ideal Monoatomic Gas

Second Treatise

A. Einstein (Published 1925)

A recent paper, published in this journal, derived the theoretical “degeneration” of ideal gases by applying the method developed by Mr. D. Bose for deriving the Planck radiation formula.

The interest in this theory stems from the fact that it hinges on the hypothesis of a far reaching formal similarity between radiation and gas. According to this theory, the “degenerated” gas deviates from mechanical statistics in the same manner as radiation, governed by Planck’s law, deviates from Wien’s law. If Bose’s derivation of the Planck radiation formula is to be taken seriously, then we may not ignore the theory of ideal gases, because if it is justifiable to approach radiation as a quantum gas, then the analogy between quantum gas and molecular gas must hold in its entirety. In this paper, the earlier analysis will be supplemented with additional material, which I believe will highlight the most intriguing aspects of this theory. For better readability and ease on the author I will formally write the following as a continuation of the quoted paper.

§ 6. The Saturated Ideal Gas.

With regards to the theory of ideal gases, it is generally understood that volume and temperature of a given amount of gas can be freely chosen without constraint. The theory then determines the energy or, respectively, the pressure of the gas. Yet a thorough analysis of the state equation captured in (18), (19), (20), and (21) shows that for a given number n of molecules and a given temperature $T$, the volume cannot be made arbitrarily small. This is because equation (18) dictates that for all $s \geq 0$. In turn via equation (20) this implies that $A \geq 0$. As equation (18(b) is applicable in this case this means that $\lambda (= e (a))$ must have a value between 0 and 1. From equation (18(b) then follows that the number of molecules in such a gas at a given volume $V$ cannot be greater than

$$n = \frac{(2\pi m kT)^{\frac{3}{2}}}{h^3} V \sum_{1}^{\infty} \tau^{\frac{3}{2}}$$

So what happens when we increase the density of the substance, $n/V$, at constant temperature (for example by isothermal compression)?

I suggest that in this case, as you increase the overall density, an ever increasing number of molecules drop into the ground state (i.e. the first quantum state, state of no kinetic energy), while the other molecules will distribute according to the parameter $\lambda = 1$.

My prediction is the emergence of something very similar to what occurs when vapor is isothermally compressed beyond the saturation volume. A separation will take place; one part will “condense”, the rest will remain as a “saturated ideal gas” ($A=0 \lambda =1$)

That both parts form in fact a thermodynamic equilibrium can be understood by showing that the “condensed” substance and the saturated ideal gas pro mol have the same Planck function $\phi = \frac{E + pV}{T}$. For the “condensed
substance" disappears, because $S$, $E$ and $V$ each disappear. For the "saturated" gas we find according to (12) and (13) for $A=0$

$$S = k \sum_s \lg (1 - e^{-\alpha s}) + \frac{E}{T} \tag{25}$$

The sum we can write as integral and then recast by partial integration. This way we first get:

$$\sum_s = -\int_0^\infty ds \cdot \frac{e^{-cs^{2/3}/kT}}{cs^{2/3}} \cdot \frac{2}{3} \cdot \frac{cs^{-1/3}}{kT} ds$$

or according to (8) and (11) and (15)

$$\sum_s = \frac{2}{3} \int_0^\infty n(s)E(s)ds = -\frac{2}{3} \frac{E}{kT} = -\frac{pV}{kT} \tag{26}$$

From (25) and (26(a) also follows for the "saturated ideal gas"

$$S = \frac{E + pV}{kT}$$

or – as is required for the coexistence of the saturated ideal gas with the condensed substance -

$$\phi = 0$$

Hence we acquire this theorem: According to the derived state equation of ideal gases, for any given temperature there exists a maximum density of agitated molecules.

When exceeding this density the surplus molecules will drop out as immobile ("condensing" without forces of attraction). What is peculiar is that the "saturated ideal gas" simultaneously represents the situation of maximal possible density of moving gas molecules as well as the specific density at which the gas is in thermodynamic equilibrium with the "condensed substance".

This analogy with "oversaturated gas" does not exist for ideal gases.

§ 7. Comparison of the derived gas theory with the one that follows from the statistical independence of gas molecules.

Mr. Ehrenfest and other colleagues criticized Bose's theory of radiation and my analog treatment of ideal gasses for not explicitly stating that in these theories the quanta, respectively molecules, are not treated as statistical independent entities.

This is entirely correct. When treating these quanta as statistically completely independent from one another you will obtain Wien's radiation law; if you were to treat the gas molecules in the same manner we would obtain the classical state equation of ideal gases, even if you were to treat the rest identical to what Mr. Bose and I have done.

I will contrast both approaches for gases to make the distinction perfectly clear, and for better comparison of our results with those of independent molecules.
According to both theories, the number \( z \) of the “cells”, which fall into the infinitesimal region \( \Delta E \) of molecule energy (in future reference named: “elemental region”), is given by:

\[
(2a) \quad z_\nu = 2\pi \frac{V}{\hbar^3} (2m)^{3/2} E^{1/2} \Delta E
\]

Let the state of gases be (macroscopically) defined by assigning how many molecules \( n \) are located in each such infinitesimal region. The aim is to calculate the number \( W \) of the realization options (Planck probabilities) for such a state.

a) According to Bose:

A state is microscopically defined by determining how many molecules are located in a cell (“complexion” [ed. microstate]). The number of complexions for the \( \nu \)-th infinitesimal region is then:

\[
(28) \quad \frac{(n_\nu + z_\nu - 1)!}{n_\nu! (z_\nu - 1)!}
\]

Taking the product over all infinitesimal regions we obtain a total number of complexes of a [ed. macro-] state, and by applying Boltzmann’s equation the resulting entropy:

\[
(29a) \quad S = k \sum_\nu \left( (n_\nu + z_\nu) \lg (n_\nu + z_\nu) - n_\nu \ lg n_\nu - z_\nu \ lg z_\nu \right)
\]

It is easy to see that by approaching the calculating in this manner, the distribution of molecules over the cells cannot be treated as statistically independent. This is related to the microstates, here called “complexions”, not being assigned equal probability if the hypothesis of independent distribution of each single molecule over the cells holds. The count of these “complexions” of unequal probability would result in an incorrect entropy if the molecules were in fact statistically independent. So this formula indirectly expresses a certain hypothesis of an, as of yet, unknown mutual interaction of the molecules, an entirely mysterious interaction, which enforces an identical statistical probability for the micro-states (here defined as “complexions”).

b) According to the hypothesis of statistical independent molecules: A state is microscopically defined by recording, for every molecule, which cell (“complexion” [micro-state]) it occupies. How many complexions comprise a macroscopically defined state? I can distribute \( n \), given molecules in

\[
z_\nu^{n_\nu}
\]

different ways over \( z \) cells of the \( \nu \)-th elemental region. If the assignment of the molecules over the elemental regions is already given, then there exist in total

\[
\prod (z_\nu^{n_\nu})
\]

different distributions of molecules over all cells. To recover the correct value in accordance with how we defined complexions this quantity has to be multiplied by the factor

\[
\frac{n!}{\prod n_\nu!}
\]

that represents all possible permutations of how the molecules can be assigned to the elemental regions for a given \( n \).

Then Boltzmann’s principle provides for the entropy the following expression
The first part of this expression is not dependent on the macroscopic distribution, it is just dependent on the total number of molecules.

In the comparison of entropies of various macroscopic states this part functions as a trivial constant. We have to dismiss this – which is the general practice in thermodynamics - when we want to achieve that the entropy of a given inner state of gases is proportional to the number of molecules. So we have to replace it with

\[(29c) \quad S = k \sum \nu (\ln z_\nu - \ln n_\nu)\]

For gases we usually tend to motivate the omission of the factors \(n!\) in \(W\) by not differentiating between complexes that are created by merely swapping molecules, which are regarded as indistinguishable, and therefore are only counted once.

Now we have to find, for both cases, the maximum of \(S\) under the restrictions

\[
\bar{E} = \sum E_\nu n_\nu = \text{const.}
\]

\[n = \sum n_\nu = \text{const.}\]

In case (a) we get:

\[(30a) \quad n_\nu = \frac{z_\nu}{e^{\alpha + \beta \bar{E}} - 1}\]

which, if we ignore the difference in notation, is the same as (13).

In case (b) we get

\[(30b) \quad n_\nu = z_\nu e^{-\alpha - \beta \bar{E}}\]

In both cases \(\beta k T = 1\).

Furthermore, we see that in case (b) the Maxwell distribution emerges. Here, the quantum structure can no longer be discerned (at least not when the total volume of the gas is assumed to be infinitely large).

We can easily see that case (b) is not reconcilable with the Nernst theorem. This immediately follows from (29c), since if we want to calculate the entropy at absolute zero temperature, we have to evaluate this equation for the absolute zero point. In this situation all molecules will be in the first quantum state (ground state). So we have to conclude:

\[
\begin{array}{l}
n = 0 \text{ for } \nu \neq 1 \\
n = 1 \text{ for } \nu \neq 1 \\
z = 1 \text{ for } \nu \neq 1
\end{array}
\]

Hence for \(T = 0\) (29c) gives us:

\[(31) \quad S = -n \ln n\]

Therefore, the calculation of type (b) is inconsistent with Nernst theorem.
On the other hand, the calculation of type (a) is in agreement with the Nernst theorem, which we can see immediately when taking into account that at absolute zero the interpretation underlying method (a) allows for only one complexion \((W=1)\). Based on this line of reasoning approach (b) leads either to a violation of the Nernst theorem or a violation of the requirement that the entropy should be proportional to the number of molecules for a given inner state. Therefore, I believe that calculation (a) (which is Boses statistical approach) should be given preference, even if this preference relative to others is not a priori provable.

This result, in turn, provides strong support for the notion of a deep fundamental similarity between radiation and gases, as the identical statistical approach that leads to the Planck formula applied to ideal gases brings the gas theory into agreement with the Nernst theorem.

§ 8. The fluctuation properties of the ideal gas.

A gas of volume \(V\) communicates with one of similar nature and infinite volume. Both volumes are assumed to be separated by a wall that is only permeable for molecules that belong to a particular energy region \(\Delta E\), while molecules of different kinetic energy are reflected. The fiction of such a wall is an analog to the quasi monochromatic transparent wall in the field of radiation theory. We ask for the fluctuation \(\Delta\) of the molecule number \(n\) which corresponds to the energy domain \(\Delta E\), under the assumption that there is no energy exchange between molecules of different energy domains in \(V\). I.e. the fluctuations of molecule numbers belonging to energies outside \(\Delta E\) are disallowed.

Let \(n\) denote the averaged number of molecules that belong to \(\Delta E\) and \(n+\Delta\) the instantaneous value. Then (29a) will deliver the value of the entropy as a function of \(\Delta\), by substituting \(n\) with \(n+\Delta\). When we expand up to quadratic terms [ed. as a Taylor series expansion], we obtain:

\[
S = \bar{S} + \frac{\partial S}{\partial \Delta\nu} \Delta\nu + \frac{1}{2} \frac{\partial^2 S}{\partial \Delta\nu^2} \Delta\nu^2
\]

A similar relation holds for the infinitely large rest system, namely:

\[
S^{(x)} = \bar{S}^{(x)} - \frac{\partial S^{(x)}}{\partial \Delta\nu} \Delta\nu
\]

In this case the quadratic term is relatively infinitely small because of the relatively infinite size of the rest system. When we represent the total entropy by \(\Sigma (= S + S^{(x)})\), then \(\frac{\partial \Sigma}{\partial \Delta\nu} = 0\), because on average there is equilibrium. So we find for the total entropy, by adding these two equations, the following relation:

\[
(32) \quad \Sigma = \bar{\Sigma} + \frac{1}{2} \frac{\partial^2 S}{\partial \Delta\nu^2} \Delta\nu^2
\]

Following the Boltzmann Principle we get for the probability of the \(\Delta\), the law:

\[
dW = \text{const} \cdot \frac{e^{\Sigma/k}}{\Delta\nu} d\Delta\nu = \text{const} \cdot e^{\left(\frac{1}{2k} \frac{\partial^2 S}{\partial \Delta\nu^2} \Delta\nu^2\right)} d\Delta\nu
\]

From this follows the average fluctuation level

\[
(33) \quad \bar{\Delta\nu^2} = \frac{k}{\left(\frac{\partial^2 S}{\partial \Delta\nu^2}\right)}
\]
This yields in consideration of (29a)

\[ \Delta_\nu^2 = n_\nu + \frac{n_\nu^2}{z_\nu} \]  

This fluctuation rule is totally analogous to the quasi-monochromatic Planck radiation. We formulate it in the form

\[ \left( \frac{\Delta_\nu}{n_\nu} \right)^2 = \frac{1}{n_\nu} + \frac{1}{z_\nu} \]  

The square of the average relative fluctuation of the molecules in question is comprised of two summands. The first one would be the only remaining one if the molecules were independent of each other. In addition there is a part of the average fluctuation square that is totally independent of the average molecule density, and solely determined by the elemental energy domain \( \Delta E \) and the volume of the gas. For radiation, it corresponds to interference fluctuation. We can also interpret this for gases in a corresponding way, by assigning an appropriate radiation process to the gas and then calculating its interference fluctuation. I want to expand on this interpretation, because I believe this is more than a simple analogy.

How a material particle, for instance a system of particles, could be assigned a (scalar) wave field has been shown by Mr. H.E. De Broglie in his remarkable page. A material particle of mass \( m \) is assigned a frequency \( \nu \) according to the equation

\[ mc = h\nu \]  

The particle rests in respect to the Galilean system \( K' \), in which we imagine an everywhere synchronous oscillation of frequency \( \nu \). Relative to system \( K \), in respect to which \( K' \) moves along the (positive) X-axis with velocity \( v \) and mass \( m \), there exists a wave-like process of the kind

\[ \sin \left( 2\pi\nu_0 \frac{t - \frac{v}{c}x}{\sqrt{1 - \frac{v^2}{c^2}}} \right) \]  

Frequency \( \nu \) and phase velocity \( V \) of this process are there given as

\[ \nu = \frac{n \nu_0}{\sqrt{1 - \frac{v^2}{c^2}}} \]  

\[ V = \frac{c^2}{v} \]  

then \( \nu \) is also - as Mr. de Broglie demonstrated - the group velocity of this wave.

Also interesting is that the energy \( \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} \) of the particles is, according to (35) and (36), precisely equal to \( h\nu \), in agreement with the foundational relation of quantum theory.

We see now that for such a gas, a scalar wave field can be assigned, and by calculation I convinced myself that \( \frac{1}{z_\nu} \) is the squared average fluctuation of this wavefield, insofar as it corresponds to the above studied energy domain \( \Delta E \).

These considerations shed light on the paradox that was referenced in my first paper. For two wave trains to interfere noticeably \( V \) and \( \nu \) must almost be identical. For that to happen, according to (35), (36), (37), it will be
necessary that $v$ as well as $m$ for both gases match so closely as to be almost identical. Two gases with a noticeably different molecule mass can, therefore, not interfere with one another. From this we can conclude that the entropy of a mixture of gases, according to the present theory, is equally additive as any other entropy of any mixture of substances according to classical theory, at least insofar as the components’ molecular weights differ slightly.


According to the previous paragraph, it seems that there is always an undulating field associated to any kinetic process, just as with the movement of light quanta there is always the associated optical undulating field. This wave field - for the time being, of unknown physical nature - has to be, in principle, detectable by its corresponding kinetic phenomena.

For instance, a beam of gas molecules, passing through an opening, will have to experience a diffraction, analogous to a beam of light.

For this to be observable, the wave length $\lambda$ should be of the same magnitude as the size of the opening. From (35), (36) and (37) follows that for velocities relatively small compared to $c$

$$\lambda = \frac{V}{v} = \frac{h}{mv}$$

This $\lambda$ is for gas molecules, which move at thermal velocities, at all times exceedingly small, even significantly smaller than the diameter of the molecule $\sigma$. Hence any observable diffraction with fabricable apertures or gratings is out of the question.

However, it turns out that for low temperatures, hydrogen and helium $\lambda$ approach the same scale of size compared to $\sigma$, and it seems in fact that their coefficient of friction is influenced in the manner as to be expected according to the theory.

That is, when a bunch of molecules with velocity $v$ hits another molecule, which we, for the sake of convenience, imagine as motionless, then this is similar to the case of a wave train with a certain wavelength $\lambda$ hitting a little leaflet of size $2\sigma$. At this point a (Fraunhofer) diffraction will manifest, identical to one caused by any opening of the same size. Large diffraction angles will occur when $\lambda$ is larger or of the same magnitude as $\sigma$. In addition to the purely mechanical impact deflections, there will then also be deflections of the molecules which can not be understood in mechanical terms. These will occur with comparable frequency and constrain the free path. Therefore, close to this temperature regime, we expect to see a sudden drop in viscosity with decreasing temperature.

An estimate of that temperature according to the relation $\lambda=\sigma$ gives the following results: For H, $56^\circ$ for He $40^\circ$.

Obviously these are very rough estimations; however they can be refined by more accurate calculations. This amounts to a new interpretation of the experimental results about the temperature dependence of the coefficients of viscosity for hydrogen. Data that was obtained by P.Guenther, following Nernst’s suggestion. Nernst also already proposed a different quantum theoretical explanation for the observed phenomenon.


Previously, § 6 showed that for a gas that exists in an equilibrium with “condensed substance”, the degeneration parameter $\lambda$ is equal to 1. Concentration, energy and pressure on the part of the molecules that have mobility, are, according to (18b),(22) and (15), determined by $T$ only.

So the following equations hold:
With the connotation:

- $\eta$ means the concentration in moles,
- $N$ means the number of molecules in a mole,
- $M$ the molar mass (molecular weight).

Via (39) we find that real gases do not reach values of density at which the corresponding ideal gas would be saturated. However, the critical density of Helium is only about five times smaller than the saturation density $\eta$ of the ideal gas of the same temperature and same molar weight. For hydrogen, the corresponding ratio is about 26.

As the real gases exist at densities that come close to the level of the saturation density, and since the degeneration will, according to (41), have a considerable impact on the pressure, this theory, if correct, predicates that a non-negligible quantum effect will show up in the state equation; in particular, this necessitates further investigation as to whether the deviations from Van der Waal’s law of corresponding states can be explained in this manner.

In addition we should also expect that the diffraction phenomenon, introduced in the previous paragraph, will have an impact on the state equation at lower temperatures, as it will give the impression of a seemingly larger molecular volume.

There is one instance where nature may have realized the saturated gas in its essence, namely for conduction electrons in metals\cite{d}. It is well known that the electron theory of metals explains the relationship between electrical and thermal conductivity inside metals with remarkable quantitative accuracy, (Drude-Lorentz law) by assuming that free electrons are present inside metals, which conduct electricity as well as heat.

In spite of this impressive success, the theory is currently still regarded as incorrect, in part because it cannot explain why free electrons do not provide a noticeable contribution to the specific heat of metals. However this difficulty can be made to disappear by applying the here-presented theory of gases. That is because, from (39), it follows that the saturation at normal temperatures is equal to about $5.5 \cdot 10^{-5}$, and therefore only a vanishingly small portion of the free electrons will contribute to the thermal energy.

The mean thermal energy per electron in thermal motion is only about half as big as according to the classical theory. If there are even only very small forces present that hold the immobile electrons to their rest position, then it is understandable that they will not participate in conduction. Possibly the vanishing of these binding forces at very deep temperatures could even explain superconductivity [Ed. this speculation does not pan out]. The thermal forces would not be understandable at all on the basis of the theory if electron gas would be treated as ideal gas. Obviously such an electron theory could not be based on the Maxwell velocity distribution, but must be based on the saturated ideal gas according to the present theory; with (8),(9),(11) one finds for this specific case:

\begin{equation}
\frac{dE}{E^2} = \frac{dW}{E^2 - 1}
\end{equation}

Thinking through this theoretical possibility we encounter the difficulty to explain the measured conductivity of electricity and heat. The very low density of volume of electrons, that take part in thermal agitation, according to our results, require a very large free path (of the scale of $10^{-3}$ cm).
It may also be possible to understand the properties of metals with regards to infrared radiation (reflection, emission) on the basis of this theory.

§ 11. State Equation of the Unsaturated Gas

Let us take a closer look at the difference of the state equation for the ideal gas in comparison to the classical state equation in the unsaturated domain. We start again building on equations (15), (18(a) and (19(b)).

For abbreviation we define,

\[ \sum_{\tau=1}^{\infty} \tau^{-5} \lambda^\tau = y(\lambda) \]

and set ourselves the task of expressing \( z \) as a function of \( y \) \((z=\Phi(y))\). The solution to this problem, which I owe to Mr. J. Grommer, rests on the following general theorem (Lagrange):

Under the condition, which in our case is satisfied, that \( y \) and \( z \) vanish for \( \lambda=0 \) and that \( y \) and \( z \) are regular functions in a particular interval around zero, then there exists for sufficiently small values of \( y \) the Taylor expansion,

\[ z = \Phi(y) = y - 0.1768 y^2 - 0.0034 y^3 - 0.0005 y^4 \]

which is convergent up to \( \lambda = 1 \) and convenient for numerical evaluation.

We now define

\[ \frac{z}{y} := F(y) \]

For the unsaturated ideal gas, i.e. between \( y=0 \) and \( y=2.615 \), the following relationship holds:

\[ \frac{\bar{E}}{n} = \frac{3}{2} kT F(y) \]

\[ p = RT \eta F(y) \]

where we use
From (19b) we obtain the specific heat in relation to one mole at constant volume $c_v$:

$$c_v = \frac{3}{2} R \left( F(y) - \frac{3}{2} y F'(y) \right) = \frac{3}{2} RG(y)$$

For a better overview we include a plot of $F(y)$ and $G(y)$.

When taking into account the almost constant slope of $F(y)$, we can produce the following good approximation

$$(22c) \quad c_v = \left[ 1 - 0.186 \frac{h^3 N^4 \eta}{(2\pi MRT)^{\frac{3}{2}}} \right]$$

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[1] The “condensed” part of the substance does not claim a particular volume, because it does not contribute to the pressure.


[4] This is not the case, as I have learned later by comparison with empirical data. The sought influence is masked by molecular interactions of other kinds.

**Editor Notes**

[a] Sitzungsberichte der Preussischen Akademie der Wissenschaften (Berlin), Physikalisich-mathematische Klasse, XXII 1924, p. 261

[b] Calling it the 1. quantum state as Einstein does in the original is no longer in common usage.

[c] In the original, the last two equations are numbered (34) and (34a) - this has been edited to adhere to a consistent numbering scheme.

[d] Einstein was wrong about this, but his speculations on the nature of the "electron gas" contributed
significantly to the subsequent insights published by Dirac and Fermi two years later. At this point the enigmatic puzzle about the nature of the quantum statistics became even more poignant as it became clear that all particles fundamentally fall into two categories - either adhering to the here-introduced Bose-Einstein or the Fermi-Dirac statistic. This comes down to the question as to why nature under normal circumstances does not allow a mixing of symmetric and antisymmetric quantum states, a conundrum that coincidentally is of uttermost importance for topological quantum computing.

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