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ON THE THEORY OF CONDENSATION
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Abstract

A discussion is given of Mayer's theory of the condensation phenomenon. It is shown that the theory is not restricted to classical statistical mechanics, nor that it is necessary to assume the additivity property of the intermolecular forces. The theory is based on Ursell's development of the partition function in powers of the volume (§ 2). Then the reasoning of M a y e r is given (§ 3), which leads to the fundamental equations (I) and (II), which represent the equation of state of a non-ideal gas. In § 4 the analogy is shown between these equations and the equations of E i n s t e i n for the ideal Bose gas. For this latter case E i n s t e i n had predicted already a condensation phenomenon. Attention is drawn to the analogy between his argument and the reasoning, by which M a y e r explains the condensation of a vapour (§ 5). Assuming certain properties $(a — e$, p. 19) of an analytic function $\chi(z)$, which is characteristic for the behaviour of a real gas, a rigorous derivation of the condensation phenomenon is given (§ 6).

§ 1. *Introduction.* In a series of papers M a y e r and collaborators [1] have recently tried to explain the phenomenon of condensation on the basis of classical statistical mechanics. The contribution which M a y e r has made to this fundamental problem, although quite important, was far from convincing, especially from the mathematical standpoint. B o r n *) has succeeded in simplifying and improving the arguments of M a y e r. We have been working on the same lines and have partially reached the same results. Our considerations however are somewhat more general than those of M a y e r and B o r n, in so far that they are not restricted to classical statistical mechanics. Furthermore we shall show [3] the

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*) The first paper of B o r n [2] was presented at the V a n d e r W a a l s Centenary Congress in Amsterdam. The discussions there with him and other members of the congress have been very clarifying for us. A second paper of B o r n and F u c h s will appear in the Proc. roy. Soc. We are greatly indebted to Prof. B o r n for showing us the manuscript of this paper.

analogy which exists between the theory of M a y e r and the well known argument of E i n s t e i n [4]), by which he predicted a condensation phenomenon for an ideal Bose gas. These are the main reasons why we think it useful to publish our account of M a y e r's theory also. Moreover we believe that we are more sceptical than B o r n. Because of the importance of the problem we think it worth while to point out as precisely as possible the assumptions implied in M a y e r's work and the difficulties which still remain.

The problem can be stated as follows. Suppose one has N monoatomic molecules of mass m in a vessel of volume V, then the free energy $\Psi(V, T)$ is determined by:

$$e^{-\Psi/kT} = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-U/kT} \qquad (1)$$

where U is the potential energy of the intermolecular forces, and where the integral over each $\mathbf{r}_i$ has to be taken over the volume V. The pressure follows from Ψ according to:

$$p = -\frac{\partial \Psi}{\partial V} \qquad (2)$$

The question now is whether one can prove from (1) that at sufficiently low temperatures p as a function of V consists of at least *three analytically different parts*, namely one representing the vapour, a second horizontal part representing the saturated vapour in equilibrium with the liquid, and a third one representing the liquid.

The following remarks may help to elucidate the problem.

a. First one should perhaps point out that the wellknown V a n d e r W a a l s theory does *not* give a solution of the problem. One may say that V a n d e r W a a l s calculates the integral (1) approximately. He then extrapolates in a certain way the result, which is valid only for small densities, to higher densities. The famous equation of state, which he obtains in this fashion, gives at constant T the pressure as a *smooth* function of the volume. Below the critical temperature one needs then a thermodynamical argument (the rule of M a x w e l l) to fix the pressure of the saturated vapour. The real, stable isotherm is therefore *not* derived from the integral (1).

b. One might think perhaps that this stable isotherm *cannot* be derived from the integral (1) without further assumptions. One argues

then that (1) gives the free energy for *one* homogeneous phase. One should make a separate calculation for the case when the system consists of *two* phases. For each volume one would obtain therefore two values for the free energy, corresponding to one or to two phases, and the real isotherm would be determined by the lowest value of the free energy. In our opinion this argument is *not* correct. The integral (1) contains all possible states of the system *) and the Ψ, which one calculates from (1), will describe the most probable state, which is the state of equilibrium. The real stable isotherm should therefore follow automatically from (1) without further assumptions.

c. On the other hand, from the mathematical standpoint, it is hard to imagine how it can follow from (1) that Ψ (and therefore p) as a function of V consists of three analytically different parts. It seems to us that this is possible, because we are really only interested in a *limit property* of Ψ. The problem has only a physical sense when N is very large. One may expect then that for a fixed specific volume

$$v = \frac{V}{N}$$

the free energy Ψ will become proportional to N. Or in other words, the limit

$$\psi(v, T) = \text{Lim} \frac{1}{N} \Psi(V, N, T) \qquad (3)$$

for $V \to \infty, N \to \infty, V/N = v$ fixed, will exist. Strictly speaking the property mentioned above has to be proved for ψ as a function of v. It is not surprising that this function can consist of analytically different parts.

d. One may remark that the stable isotherm does not represent all states of the system which are realizable. There is for instance the well known phenomenon of supersaturation, which is represented by the continuation of the vapour part of the isotherm beyond the point of condensation. These states however are *not* states of stable equilibrium, except in vessels which are everywhere so narrow that capillary phenomena become of importance. Since we shall discuss the integral (1) only for the case that the vessel will become large in all directions, it is clear that we shall *not* obtain the states corresponding to the supersaturated vapour.

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*) This point was especially emphasized by V a n d e r W a a l s Jr. in the discussion of M a y e r's theory at the V a n d e r W a a l s Congress.

§ 2. *The development of Ursell.* To include the quantum theory we will start not from (1) but from the more general expression:

$$e^{-\Psi/kT} = \frac{1}{N!} \cdot \frac{1}{\lambda^{3N}} Q_N$$

where

$$\lambda^2 = \frac{h^2}{2\pi mkT}$$

$$\quad (4)$$

$$Q_N = \int_V \ldots \int_V d\mathbf{r}_1 \ldots d\mathbf{r}_N \, W(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N)$$

$W(\mathbf{r}_1 \ldots \mathbf{r}_N) = W_N$ represents the probability of position in configuration space for a canonical ensemble; it is defined by:

$$W_N = \sum_n e^{-E_n/kT} \varphi_n^* \varphi_n \qquad (5)$$

where E_n and φ_n are the energy states and the eigenfunctions of the whole system, and where one has to sum over all possible eigenfunctions. The φ_n must be normalized in such a fashion that $W_N \rightarrow 1$ when all the particles are far away from each other. W_N has the following properties:

a. W_N is a symmetric function of $\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N$

b. For high temperatures W_N becomes asymptotically the B o l t z m a n n factor $\exp(-U/kT)$.

c. When we divide the N particles into different groups containing $\alpha_1, \alpha_2 \ldots$ particles, then for configurations where particles of different groups are so far away from each other that their interaction vanishes, we have:

$$W_N = W_{\alpha_1} W_{\alpha_2} \ldots \qquad (6)$$

This property is a consequence of the fact that for these configurations the Hamiltonian is separable into the sum of the Hamiltonians of the different groups. In the classical theory (6) follows immediately from this fact. In quantum theory also the proof is quite straightforward. It should be stressed that it is *not* necessary to assume the additivity property of the intermolecular forces *). The W_N has *not* the property that it can be split into factors, each containing only a pair of molecules, as is the case in the classical theory when the forces are additive.

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*) The range of the forces must of course be sufficiently short, so that a division into noninteracting groups is possible.

U r s e l l [5]) has shown that it is possible to write the integral (1) as a polynomial of the Nth degree in the volume. His procedure can easily be extended to (4). One introduces a set of functions $S(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_l) = S_l$, which depend symmetrically on the coordinates of l molecules in the volume V. They are expressed in terms of the probabilities $W_1, W_2 \ldots W_l$ by means of the relations:

$$W(\mathbf{r}_1) = S(\mathbf{r}_1) = 1$$

$$W(\mathbf{r}_1, \mathbf{r}_2) = S(\mathbf{r}_1, \mathbf{r}_2) + S(\mathbf{r}_1) S(\mathbf{r}_2)$$

$$W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = S(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + S(\mathbf{r}_1, \mathbf{r}_2) S(\mathbf{r}_3) + S(\mathbf{r}_2, \mathbf{r}_3) S(\mathbf{r}_1) +$$
$$+ S(\mathbf{r}_3, \mathbf{r}_1) S(\mathbf{r}_2) + S(\mathbf{r}_1) S(\mathbf{r}_2) S(\mathbf{r}_3)$$

(7)

and so on. The general rule is the following. We divide the l particles which occur in W_l into a number of groups, and form the product of the functions S, which depend on the particles of these groups. Then W_l will be the sum of these products for all possible ways of division of the particles. The S_l in terms of $W_1, W_2 \ldots W_l$ are uniquely defined by these relations.

One finds for instance: *)

$$S(\mathbf{r}_1, \mathbf{r}_2) = W(\mathbf{r}_1, \mathbf{r}_2) - W(\mathbf{r}_1) W(\mathbf{r}_2)$$

$$S(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - W(\mathbf{r}_1, \mathbf{r}_2) W(\mathbf{r}_3) - \qquad (8)$$
$$- W(\mathbf{r}_2, \mathbf{r}_3) W(\mathbf{r}_1) - W(\mathbf{r}_2, \mathbf{r}_3) W(\mathbf{r}_1) + 2W(\mathbf{r}_1) W(\mathbf{r}_2) W(\mathbf{r}_3)$$

The importance of the development (7) lies in the following fundamental property of the functions S_l. When we divide the l particles into different groups, containing $\beta_1, \beta_2, \ldots$ particles, then, for configurations where particles of different groups are so far way from each other that their interaction vanishes, we have $S_l = 0$. Less exactly one may say that S_l is different from zero only when all the particles are near together **).

The proof of this theorem follows from the product property (6) of the W_N. For S_3 for instance it can be verified immediately from the explicit expression (8). In this way one could give a general proof. It is simpler however to consider the configuration mentioned in the

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*) The rule which expresses the S in the W is the same as the rule which expresses the W in the S, except for a coefficient $(-1)^{k-1} (k-1)!$ when k is the number of the groups into which the l particles are divided.

**) This does not mean however, that each particle is interacting with all others, but only that all particles are linked together.

product property·of W_N. Develop both sides of (6) according to (7). The right hand side will then contain no S_l referring to particles of different groups. The sum of those terms on the left hand side, which contain S_l of this kind, must therefore be zero for this configuration. By applying this argument successively to W_2, W_3 etc., one shows by induction that each S_l of this kind must be zero, as the theorem requires.

A consequence of this theorem is that the integral of S_l over the coordinates of the l particles will become proportional to the volume V, when V is very large. To see this first perform the integration over the coordinates of $l - 1$ particles, keeping the coordinates of the lth particle fixed. Because of the fundamental property of S_l, the result will be independent of the volume and independent of the position of the l particle, provided that V is sufficiently large and S_l goes sufficiently fast to zero when the $l - 1$ particles are separated from the lth particle. The integration over the coordinates of the lth particle will then contribute a factor V to the integral. We shall write:

$$\int_V \ldots \int_V d\mathbf{r}_1 \ldots d\mathbf{r}_l \, S_l = V \, l! \, b_l \tag{9}$$

It will be clear now that by integrating the development (7) for W_N, one will obtain for Q_N a polynomial of degree N in V. The result can be written in the following form:

$$Q_N = N! \, \underset{}{\sum}{}' \prod_{l=1}^{N} \frac{(V b_l)^{m_l}}{m_l!} \tag{10}$$

The m_l are positive integers or zero. The summation sign means that one has to sum over all sets of values of the m_l, which fulfill the condition:

$$\sum_{l=1}^{N} l m_l = N \tag{11}$$

To prove this, consider a definite partition of N in m_1 groups of one particle, m_2 groups of two particles, and so on. The m_l will then clearly fulfill (11). To a definite set of values of m_l correspond many terms in the development (7), due to the different ways of distributing the N particles over the groups. All these terms will give the same result after integration, namely:

$$\prod_{l=1}^{N} (V \, l! \, b_l)^{m_l} \tag{12}$$

The number of these terms will be:

$$N! \prod_{l=1}^{N} \frac{1}{(l!)^{m_l} \, m_l!} \tag{13}$$

since the permutation of particles in one group and the permutation of groups of equal size will not give rise to new terms. By multiplying (12) and (13) and by summing over the m_l one obtains (10).

§ 3. *The equation of state for the vapour phase.* M a y e r has shown how to derive from the development (10) of U r s e l l a general expression for the equation of state of the vapour phase. We shall give here essentially his first derivation, which, although not rigorous, is very simple and gives the correct result. In § 6 an exact proof will be given.

Suppose that all b_l are positive (which they probably are at sufficiently low temperatures), then for large N one may approximate the sum (10) by its largest term. To find the set of m_l which gives this maximum term, one proceeds in a way which is quite analogous to the usual derivation of the M a x w e l l-B o l t z m a n n distribution law in statistical mechanics. One then finds, using S t i r-l i n g's approximation for $m_l!$, that this maximizing set of m_l is given by:

$$\overline{m}_l = V b_l \, z^l \tag{14}$$

where the parameter z has to be determined by the condition (11), so that:

$$\frac{N}{V} = \frac{1}{v} = \sum_{l=1}^{\infty} l b_l \, z_l \tag{I}$$

By introducing this set of m_l one finds that $\log Q_N$ is approximated by:

$$\log \overline{Q}_N = \log N! - N \log z + V \sum_{l=1}^{\infty} b_l \, z^l$$

From (4) and (2) one obtains then for the pressure:

$$p = kT \sum_{l=1}^{\infty} b_l \, z^l \tag{II}$$

In order to find an explicit expression for the equation of state, one has to eliminate z between the equations (I) and (II). One can

do this for instance by successive approximation. In this way one gets:

$$pV = NkT\left[1 - \frac{Nb_2}{V} + \frac{N^2}{V^2}(-2b_3 + 4b_2^2) + \dots\right] \quad (15)$$

This is the well known expansion in virial coefficients. All the other thermodynamical quantities can easily be expressed in terms of z and b_l. One finds for instance for the energy:

$$\varepsilon = \frac{3}{2}NkT + kT^2V\sum_{l=1}^{\infty}\frac{db_l}{dT}z^l$$

and for the thermodynamic potential:

$$\zeta = NkT\log(\lambda^3 z)$$

This equation shows the thermodynamic meaning of the parameter z.

§ 4. *The ideal Bose gas*. The equations (I) and (II) show a remarkable analogy to the equation of state of an ideal Bose gas as given by E i n s t e i n [4]). He obtained:

$$\frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty}\frac{A^l}{l^{3/2}} \quad (Ia)$$

$$p = \frac{kT}{\lambda^3}\sum_{l=1}^{\infty}\frac{A^l}{l^{5/2}} \quad (IIa)$$

from which again the equation of state results by elimination of A. Eqs. (I) and (II) become identical with (Ia) and (IIa) by putting:

$$z = \frac{A}{\lambda^3}, \qquad b_l = \frac{\lambda^{3(l-1)}}{l^{5/2}} \quad (16)$$

This analogy is especially of interest, since E i n s t e i n has shown that the equations (Ia) and (IIa) give rise to a condensation phenomenon. Furthermore the case of the ideal Bose gas furnishes an example where the b_l, which are characteristic for the behaviour of a real gas, can be determined explicitly.

An alternative derivation of Eqs. (Ia) and (IIa) will show more clearly the origin of their analogy with (I) and (II). We shall start again from (4) and (5). When one neglects the influence of the walls of the vessel, one may write for the properly normalized eigenfunctions φ_n:

$$\varphi_n = \lambda^{3N/2}\sum_{P} e^{i/\hbar\sum_{k}(\mathbf{p}_k \cdot \mathbf{r}_{Pk})}$$

where one has to sum over all permutations P of the N indices k. The eigenvalues are:

$$E_n = \frac{1}{2m} \sum_k p_k^2$$

To find W_N one has to sum over all possible eigenfunctions, which means that one must integrate over all values of the momenta p_k and divide the result by $N!$. One gets:

$$W_N = \sum_P e^{-\pi/\lambda^2 \sum_k |r_k - r_{Pk}|^2} \tag{17}$$

It is clear that $W_N \to 1$ when all the particles are far away from each other [*]).

The integral Q_N can now be written in the same form as U r-s e l l's development (10). Observe namely that by integrating one term of (17), corresponding to a definite permutation P, over r_1, $r_2 \ldots r_N$, one obtains a power of V, which is equal to the number of cycles into which this permutation can be decomposed. The sum (17) is therefore analogous to the development (7) of W_N in the S_l. Suppose that the permutation P can be decomposed into m_1 cycles of one particle, m_2 cycles of two particles and so on. The m_l will then again fulfill the condition (11). To a definite set of values of m_l there will correspond many terms in (17), each of which gives the same contribution to the integral Q_N. The number of these terms will be:

$$N! \prod_{l=1}^{N} \frac{1}{l^{m_l} \, m_l!} \tag{18}$$

This is different from (13) because only the l cyclic permutations of the particles in one cycle will not give rise to new terms. To obtain Q_N in exactly the same form as in (10) we must write Vlb_l for the integral over the coordinates of the particles of a cycle of length l. Therefore:

$$Vlb_l = \int_V \ldots \int_V dr_1 \, dr_2 \ldots dr_l \, e^{-\pi/\lambda^2 (r^2_{12} + r^2_{23} + \cdots + r^2_{l1})} \tag{19}$$

where $r_{ij} = |r_i - r_j|$. The contribution of a term of (17) corresponding to a definite set of values of m_l will then be:

$$\prod_{l=1}^{N} (Vlb_l)^{m_l} \tag{20}$$

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[*]) W_N becomes larger than one in all regions of configuration space where some particles are near together. One may say therefore that there is an apparent attraction between the particles of an ideal Bose gas. For a pair of particles this was already previously noted [6]). One should point out however, that this attraction can *not* be represented by a potential which has the property of additivity.

By multiplying (18) and (20) and by summing over the m_l one gets again (10) .

The integral (19) *) can be performed straightfordwardly by integrating successively over the coordinates of the l particles. One finds then for b_l the result (16), and we saw already that with this value of b_l the equations (I) and (II) of M a y e r become the equations (Ia) and (IIa) of E i n s t e i n.

§ 5. *The condensation phenomenon.* The reasoning by which E i n-s t e i n derived the condensation phenomenon for and ideal Bose gas from Eqs. (Ia) and (IIa) is as follows. For small values of the density the corresponding value of A will be small. By increasing the density A will increase monotonically. This goes on until for a finite value of the density A reaches the value one. Then:

$$\frac{N}{V} = \frac{1}{v_c} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{1}{l^{3/2}} = \frac{2.61}{\lambda^3}$$

$$p = p_s = \frac{kT}{\lambda^3} \sum_{l=1}^{\infty} \frac{1}{l^{5/2}} = 1.34 \frac{kT}{\lambda^3}$$

For $A > 1$ the series (Ia) and (IIa) diverge. According to E i n-s t e i n $1/v_c$ is the maximum density which can be reached. By further compression of the gas the superfluous particles will ,,con-dense'' into the state of zero energy and will not contribute to the pressure nor to the density so that the pressure will remain p_s. We have therefore indeed a kind of condensation phenomenon, which has however some uncommon features, namely:

a. The volume of the condensed phase is zero.

b. There does not exist a critical temperature.

c. There is no discontinuity in $(\partial p/\partial v)_T$ at the condensation point.

In fact one finds from (Ia) and (IIa):

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{kT}{\lambda^3 v} \frac{(\sum\limits_{1}^{\infty} A^l/l^{3/2})^2}{\sum\limits_{1}^{\infty} A^l/l^{1/2}} \tag{21}$$

and this becomes zero for $A = 1$, since $\Sigma 1/l^{1/2}$ diverges. On the other hand it can be easily verified that the thermodynamical requirements (equality of the ζ for the two phases. C l a p e y r o n's equation, etc.) are fulfilled.

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*) The same integral occurs in a paper of K r a m e r s [7]) on ferromagnetism.

The reasoning by which M a y e r first derived the condensation phenomenon for a real gas is quite analogous to the argument of E i n s t e i n. It can be expressed as follows. Suppose that the series (I) and (II) have a certain finite convergence radius $\bar{z}$, and that they are still convergent for $z = \bar{z}$ *). When in addition the b_l are positive, then by increasing the density the corresponding value of z will increase monotonically till the maximum value $z = \bar{z}$ is reached. For higher densities the series (I) and (II) cease to have significance. Using a physical interpretation of the equations, M a y e r tries to show that by further compression of the vapour condensation will occur, while the pressure remains constant and equal to the value:

$$p_s = kT \sum_{l=1}^{\infty} b_l \bar{z}^l \qquad (22)$$

These explanations of the condensation phenomenon are certainly not yet complete. An instructive example is furnished by the ideal Fermi-Dirac gas. One shows easily that for this case the equation of state is determined by:

$$\frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{A_l}{l^{5/2}} \qquad (Ib)$$

$$p = \frac{kT}{\lambda^3} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{A^l}{l^{5/2}} \qquad (IIb)$$

when $A \leq 1$. At first sight one might think that these equations will also predict a condensation phenomenon. This however is *not* correct. Although the series (Ib) and (IIb) are convergent only for $A \leq 1$, they represent analytic functions of A, which can be continued along the positive real axis for all values of $A > 1$, so that the pressure will be given by *one* analytic function of v for all values of the volume. This can also be seen directly from the usual derivation of the equation of state by means of the Fermi-Dirac distribution law. This is in contrast to the case of the ideal Bose gas, where the point $A = 1$ is a *singular* point of the functions (Ia) and (IIa). It can be shown (see § 6) that also for the real gas an essential condition for condensation is that the functions (I) and (II) have a singularity on the positive real axis of z.

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*) In fact, M a y e r tries to prove that for large l the b_l become asymptotically equal to $b_0{}^l - 1/l^{5/2}$, which would make the analogy with the ideal Bose gas still closer. This result o M a y e r seems to us incorrect (see § 7); it does not affect however his explanation of the condensation phenomenon.

Another objection against the reasoning of E i n s t e i n has been raised by one of us [8]). The Eqs. (I*a*) and (II*a*) are derived namely by neglecting the quantization of the translational motion of the molecules *). This is justified for small values of A, but it becomes essential in the neighbourhood of $A = 1$. The strict calculation shows that for every finite volume N/V approaches infinity for $A \to 1$, so that then the reasoning above fails. It remains true however that for densities larger than $1/v_c$ the isotherm will be almost horizontal and that this will be the more pronounced the larger the volume is. Only in the limit $V \to \infty$ the isotherm will consist of two different parts. When we understand the condensation phenomenon always in the sense of such a limit property (comp. remark c of § 1) then this objection therefore loses its validity.

§ 6. *The rigourous treatment.* We shall start from U r s e l l's development (10). Instead of making the approximations of § 3, we shall now determine strictly for $N \to \infty$, $V \to \infty$, $V/N = v$ finite

$$\text{Lim.} \left(\frac{Q_N}{N!} \right)^{1/N} \tag{23}$$

which according to (3) and (4) is equal to $\lambda^3 \exp \left(- \psi/kT \right)$ **).

With the help of a generating function one can show in the usual way that U r s e l l's development can be written in the form:

$$\frac{Q_N}{N!} = \frac{1}{2\pi i} \oint \frac{dt}{t^{N+1}} e^{Nv\chi(t)} \tag{24}$$

where:

$$\chi(t) = \sum_{l=1}^{\infty} b_l t^l \tag{25}$$

and the integral has to be taken around the origin of the complex t-plane, excluding the singularities of $\chi(t)$. The function $\chi(t)$ is the fundamental function or the problem.

The first method which presents itself for treating the integral (24) is the method of steepest descents †). We have found another

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*) In the derivation of § 4 this corresponds to the neglect of the influence of the walls of the vessel.

**) The Q_N are of course all *positive*, since they are integrals over the probabilities W_N.

†) In a paper by K r a m e r s [7]) on ferromagnetism occurs an integral, which is identical with (24) for the case of the ideal Bose gas, and which has been treated by him with the method of steepest descents. K r a m e r s was the first to show that for this case at least, the limit (23) as a function of v consists of two analytically different parts. We are greatly indebted to him for pointing out to us the bearing of his results on the problem of condensation.

method, however, more appropriate for the discussion of the limit (23) *).

Consider the power series:

$$F(x) = \sum_{N=1}^{\infty} \frac{Q_N}{N!} x^N \qquad (26)$$

where the different Q_N have to be taken for the *same* value of $V/N =$ $= v$. According to the well known theorem of C a u c h y the limit (23) is now just equal to the inverse of the radius of convergence R of $F(x)$. On the other hand the series (26) defines an *analytic* function of x, and we can therefore find the convergence radius R by determining the singularity of this function which is nearest to the origin.

Another expression of $F(x)$ can be found as follows. Introduce (24) into (26); then the summation and integration can be interchanged when x is so small that on the whole contour:

$$| x\xi(t) | < 1$$

where:

$$\xi(t) = \frac{e^{v\chi(t)}}{t} \qquad (27)$$

It is always possible to find such an x because $| \xi(t) |$ is bounded on the contour. The summation of the geometric series gives then:

$$F(x) = \frac{1}{2\pi i} \oint \frac{dt}{t} \frac{x\xi(t)}{1 - x\xi(t)} \qquad (28)$$

The integral can be calculated by means of the theorem of residues. The only poles of the integrand within the contour are $t = 0$ and the zero's of the function $1 - x\xi(t)$. For sufficiently small x this function has only one simple zeropoint. One sees this from C a u c h y's integral. The excess of the number of zero's over the number of poles of $1 - x\xi(t)$ within the contour is given by:

$$n - p = - \frac{x}{2\pi i} \oint \frac{\xi'(t)}{1 - x\xi(t)} dt$$

The integral has always a certain finite value, so that $n - p$ can be made as small as one pleases by taking x small enough. Therefore $n - p$ must be zero, since it can assume only integral values. Now $1 - x\xi(t)$ has one simple pole within the contour, namely $t = 0$, and

*) The idea of this method is due to the junior author. We wish to thank Prof. J. W o l f f for his help in completing certain parts of the proof.

therefore also one simple zero, say at $t = t_0$. The evaluation of (28) by means of the theorem of residues gives then:

$$F(x) = \frac{vt_0\chi'(t_0)}{1 - vt_0\chi'(t_0)} \qquad (29)$$

where:

$$1 - x\xi(t_0) = 0 \qquad (30)$$

If we start from the origin and move along a definite path in the x-plane, the equation (30) will determine t_0 as an analytic function of x. Along the corresponding path in the t_0-plane *) $\chi'(t_0)$ will be again an analytic function of t_0 and therefore of x. In this way (29) defines an analytic function of x, which for small x coincides with the power series (26), and which therefore represents its analytical continuation.

We have now to determine the singularity of $F(x)$ which is nearest to the origin. One needs to consider only real positive values of x, because of the fact that the series (26) has real and positive coefficients, so that the real positive point on its circle of convergence will be a singularity of $F(x)$ [9]). One sees from (29) and (30) that the *possible* singularities of $F(x)$ are the values of x which correspond to the zero's of the denominator $1 - vt_0\chi'(t_0)$ and which correspond to the singularities of $\chi(t_0)$. Whether these values of x are actually singularities of $F(x)$ and which of them is nearest to the origin depends on the properties of the function $\chi(t_0)$ and on the value of v. We know that for small values of t_0, $\chi(t_0) \cong t_0$. We will assume further:

a. $\chi(t_0)$ has a *finite* radius of convergence equal to r.

b. $\chi(t_0)$ has a singularity $\bar{z}$ on the real positive axis; $\bar{z}$ may be greater than or equal to r. The latter case will occur for instance when all the b_l are positive.

c. $\chi(\bar{z})$ and $\chi'(\bar{z})$ are finite; the point $\bar{z}$ will therefore be a branch point of $\chi(t_0)$.

d. The inverse function of $\chi(t_0)$ is singular at the point corresponding to $t_0 = \bar{z}$.

e. $t_0\chi'(t_0)$ is monotonically increasing on the real axis between $t_0 = 0$ and $t_0 = \bar{z}$ †); this will again be the case when the b_l are positive.

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*) which also starts from the origin, since $t_0 = 0$ for $x = 0$.

†) One must also exclude the possibility that $t_0\chi'(t_0)$ has a horizontal inflexion point in this region.

To find the singularities of $F(x)$ we shall start from the origin and move along the real positive axis in the x-plane. When v is large enough one sees that the first singularity of $F(x)$ which one meets will be determined by the zeropoint of the denominator in (29). Let us call this zero point $t_0 = z$, so that:

$$vz\chi'(z) = 1 \qquad (31)$$

The corresponding value of x, and therefore the radius of convergence R, according to (30) will be:

$$R = ze^{-v\chi(z)}$$

This is therefore the inverse of the limit (23), from which one obtains immediately the expression for the pressure:

$$p = kT\chi(z) \qquad (32)$$

The equations (31) and (32) are identical with the Eqs. (I) and (II) which are now therefore proved rigorously when v is large enough.

It should be pointed out that for this proof *none* of the assumptions *a—e* are necessary. Because of assumption *e* *) the equations (31) and (32) will remain valid until:

$$v = v_c = \frac{1}{\bar{z}\chi'(\bar{z})} \qquad (33)$$

In the case that $\bar{z} > r$, and for values of z between r and $\bar{z}$, the equations (31) and (32) are no longer identical with the series (I) and (II), but represent their analytical continuations. For all these values of v the pressure remains a smooth function of the volume.

Because of assumption c, v_c has a finite value. Suppose now that v is smaller than v_c. When we again move along the real positive x-axis, we shall reach the point corresponding to $t_0 = \bar{z}$ before meeting a zero of the denominator of (29). Because of assumption d this value of x will be a singularity of $F(x)$. In this case therefore:

$$R = \bar{z}\, e^{-v\chi(\bar{z})}$$

This corresponds to the *constant* pressure:

$$p = p_s = kT\chi(\bar{z}) \qquad (34)$$

When $\bar{z} = r$ this is identical with equation (22) of M a y e r. The

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*) When this assumption is not fulfilled, so that $t_0\chi'(t_0)$ has at least one maximum (say at $t_0 = t$), then one can show that for a value of v corresponding to $z = t$, $\partial p/\partial v$ becomes infinite. This has been pointed out by B o r n and F u c h s (comp. also Eq. (21)). It gives the *physical* reason for the assumption e.

pressure as a function of v consists therefore of two analytically different parts, namely the curve represented by (31) and (32) for $v > v_c$ and the horizontal line (34) for $v < v_c$.

§ 7. *Further remarks.* 1. B o r n a n d M a y e r have given a formal solution of the problem of eliminating z between the fundamental equations (I) and (II). Their result can be stated as follows. Define a function:

$$\varphi(\xi) = \sum_{\nu=1}^{\infty} \beta_\nu \, \xi^\nu$$

by means of the equations:

$$l^2 b_l = \frac{1}{2\pi i} \oint d\xi \, \frac{e^{l\phi(\xi)}}{\xi^l} \tag{35}$$

This gives the b_l expressed in terms of the β_ν. One can solve these equations successively for β_ν, and thus express the β_ν uniquely in terms of the b_l. Applying the theorem of L a g r a n g e [10]) one can solve Eq. (I) for z. With the help of the function $\varphi(\xi)$ the result can be written in the form:

$$z = \frac{1}{v} e^{-\phi(1/v)}$$

By introducing this into (II), one obtains:

$$pv = kT \left(1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu + 1} \frac{\beta_\nu}{v^\nu}\right) \tag{36}$$

M a y e r and B o r n were led to (35) by the consideration of the integrals defining the b_l in the case of classical statistical mechanics. They showed that these integrals can be split up into the sums of products of certain „irreducible" integrals, which are immediately related to the β_ν. We have *not* been able to generalize this physical interpretation of the β_ν to the quantum theory.

2. M a y e r and B o r n have tried to derive from (35) certain general properties of the characteristic function $\chi(z)$. In particular M a y e r has tried to make plausible that in a certain range of temperatures below the critical temperature b_l behaves asymptotically for large l as:

$$b_l \cong \frac{b_0^{l-1}}{l^{5/2}} \tag{37}$$

One would obtain this from (35) if it were permitted to apply the method of steepest descents to this integral. A consequence of (37) is

that $\partial p/\partial v$ becomes zero at the condensation point $v = v_c$ (comp. Eq. (21)).

These considerations seem to us very doubtful, since they are based *only* on the formal expression (35) for the b_l. The physical interpretation of the β_ν is nowhere used. It is clear that one can hope to make a further advance only by going back to the physical meaning of the b_l or the β_ν. In particular it seems to us impossible to say anything in general about the behaviour of $\partial p/\partial v$ near the condensation point. This will depend on the series:

$$\sum_{l=1}^{\infty} l^2 b_l \bar{z}^l$$

which may be divergent or convergent. In the first case $\partial p/\partial v$ will be zero for $v = v_c$, while in the latter case it will have a finite value.

3. From the further investigation of the integrals representing b_l must follow especially the properties a—e (§ 6) of $\chi(z)$, which are necessary to explain the condensation phenomenon. An *essential difficulty* seems to us to lie in the fact, that even with the assumptions a—e for $\chi(z)$ it is impossible to obtain the *third* part of the isotherm, corresponding to the liquid state. The reason is that for all $v < v_c$ the singularity of $F(x)$ which is nearest to the origin, is determined by the singularity $\bar{z}$ of $\chi(z)$, which is independent of v. Therefore the isotherm will remain horizontal for all $v < v_c$.

It is clear that the origin of this difficulty has to be found in the neglect of the dependance of the b_l on the volume V. It is true of course that for every finite l the quantity b_l has a definite limit for $V \to \infty$. We have assumed however more than this, since the properties of $\chi(z)$ depend on the behaviour of b_l for large l. There is clearly a double limiting process involved and it may be that the solution of the difficulty will be found by a more correct treatment of these limits.

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