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a carbon-source, rapidly lead to the accumulation of strong ureum-splitting bacteria forming spores and the *urobacillus jakschii* forming no spores.

5. The irisating of culture-plates and the "irisphenomenon" on the yeast-water-gelatineplate are the consequence of the precipitation of calciumphosphate, whilst calciumcarbonate formed at the same time plays a subordinate part in it.

At the end of this investigation I beg to express my sincere thanks to Professor M. W. BEIJERINCK for advising and supporting me in these experiments wherever and whenever he could.

**Physics.** — "*Statistical Theory of Capillarity.*" By Dr. L. S. ORNSTEIN.  
(Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 24 1908).

In a paper <sup>1)</sup> published in 1893 VAN DER WAALS has developed a theory of capillarity, which leads to results agreeing sufficiently with observation, as has been shown by the experiments of Dr. E. O. DE VRIES.

The methods used in the above mentioned paper have been reproduced with only a slight change in the lectures of VAN DER WAALS recently published by Prof. PH. KOHNSTAMM.

Both in the paper and in the treatise the hypothesis <sup>2)</sup> is introduced, that the entropy of an element of volume is a function only of the number of molecules it contains and of that of their collisions.

By the statistical method of GIBBS we can deduce the condition of equilibrium for the capillary layer without using a hypothesis of this kind and we can easily show that it must be true when certain conditions are fulfilled. This is the object of the present paper in which I shall also determine some quantities that play a part in the theory of capillary action.

§ 1. Let us suppose that  $n$  spherical molecules of diameter  $\sigma$ , perfectly rigid and elastic, are enclosed in a vertical cylinder of height  $Z$ , and of unit of horizontal section, closed at the top and the bottom by horizontal walls. Let the axis of  $z$  be drawn upward and let us further suppose that the molecules exert attractive forces on

<sup>1)</sup> J. D. v. D. WAALS, Thermodynamische theorie der capillariteit in de onderstelling van continue dichtheidsverandering. Verh. d. K. A. v. W. Deel I. 8. 1893.

<sup>2)</sup> Compare l. c, p. 16.

each other up to distances which are large in comparison with the diameter  $\sigma$  and with the distance of neighbouring molecules. I shall denote by  $-\varphi(f)$  the potential energy of this attraction for a pair of molecules whose centres are at a distance  $f$  and I shall suppose that  $\varphi(f) = 0$  for values of  $f$  which are large compared with  $\sigma$  (and the distance between neighbouring molecules) but small compared with finite lengths, the same being also true of the function  $\psi(f)$  determined by the equation

$$f \varphi(f) df = - d\psi(f) \dots \dots \dots (1)$$

Let us now consider a canonical ensemble with modulus  $\theta$  built up of  $N$  systems of the above kind.

We divide the volume of the cylinder by horizontal planes into a great number  $k$  of elements of a height  $dz$ , this height being large compared with  $\sigma$  and small compared with the distance at which the molecules sensibly attract each other. I shall further suppose that the potential energy of attraction changes but little over a distance of the order of magnitude  $(dz, ^1)$ .

We shall determine the number, or, let us say, the "frequency"  $\zeta$  of those systems in the ensemble in which there are  $n_1 \dots n_r \dots n_k$  molecules respectively in the elements  $dz_1 \dots dz_r \dots dz_k$ . I shall suppose that the numbers  $n_r$  are very large; their sum being  $n$  we have the relation

$$\sum_1^k n_r = n \dots \dots \dots (I)$$

The number of molecules per unit of volume in the element  $dz$ , (the molecular density) will be represented by  $n_r$ .

I shall consider the mutual energy of a pair of molecules as belonging for one half to the first and for the other half to the second of the molecules. The energy determined in this way is the same for all the particles of the layer  $dz_r$ . I shall represent this energy per molecule by  $\epsilon_r$ .

The total potential energy can therefore be represented by

$$\sum_1^k n_r \epsilon_r$$

The frequency <sup>2)</sup> in question is given by the formula

<sup>1)</sup> For the sake of simplicity I shall take the elements  $dz_r$  of equal magnitude; our result will be that  $\frac{n_r}{dz_r} = n$ , (the molecular density) is a function of  $z$ , showing that we do not lose in generality by this simplification.

<sup>2)</sup> In explanation of the formula (II) the following may be observed. Let us consider a system constituted of  $n$  molecules of the kind above described enclosed.

$$\zeta = N (2\pi m \Theta)^{\frac{3}{2}n} \frac{\Psi}{e^{\Theta}} \prod_{i=1}^k \frac{1}{n_i!} (\omega_i dz_i)^{n_i} e^{-\frac{n_i \epsilon_i}{\Theta}} \dots \quad (II)$$

§ 2. The properties of an observed system are identical with those

in a vessel of the volume  $V$ . And let us imagine a canonical ensemble built up of  $N$  systems.

In this ensemble the number of systems — having the coordinates of the centres of the molecules between  $x_1$  and  $x_1 + dx_1 \dots z_n$  and  $z_n + dz_n$  and the components of the velocities of these points between  $\dot{x}_1$  and  $\dot{x}_1 + d\dot{x}_1 \dots \dot{z}_n$  and  $\dot{z}_n + d\dot{z}_n$  — amounts to

$$N m^{3n} e^{\frac{\Psi - \epsilon}{\Theta}} d\dot{x}_1 \dots d\dot{z}_n dx_1 \dots dz_n, \dots \quad (a)$$

Here, the energy of the system is expressed by  $\epsilon$ , and  $\Psi$  is a constant for the ensemble depending on  $\Theta$  and  $V$ . The value of  $\Psi$  can be found by integrating (a) with respect to the coordinates and the velocities. The result of this integration must be  $N$ , which yields a relation for  $\Psi$ . The number of the systems in which the velocities have any values, but whose coordinates are lying between the specified limits is obtained by integrating (a) over the velocity components from  $-\infty$  to  $+\infty$ .

The energy  $\epsilon$  is given by the relation  $\epsilon = \epsilon_q + \sum_{i=1}^n \frac{1}{2} m (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$

in which  $\epsilon_q$  is the total potential energy and  $m$  the mass of a molecule. Therefore the result of the integration is

$$N (2\pi \Theta m)^{\frac{3}{2}n} \frac{\Psi - \epsilon_q}{e^{\Theta}} dx_1 \dots dz_n \dots \quad (b)$$

Let us now divide the volume  $V$  into  $k$  elements  $dV_1 \dots dV_r \dots dV_k$ . If  $n_r$  molecules are situated in an element of volume  $dV_r$  the  $3n_r$  coordinates of their centres may still vary between certain limits; in other terms, a certain extension is left open to the point representing these coordinates in a  $3n_r$ -dimensional space. I shall represent the magnitude of this extension by

$$\chi(n_r, dV_r).$$

The repulsive forces between the molecules are accounted for by excluding from the  $3n_r$ -dimensional space  $(dV_r)^{3n_r}$  all those parts in which there exists a relation of the form

$$(x_\nu - x_\mu)^2 + (y_\nu - y_\mu)^2 + (z_\nu - z_\mu)^2 < \sigma^2 \dots \quad (c)$$

between the ordinary coordinates of the centres of two molecules. We can represent  $\chi(n_r, dV_r)$  by

$$\int dx_1 \dots dz_{n_r}, \dots \quad (d)$$

where the integration has to be extended over the whole space  $(dV_r)^{3n_r}$  with the exception of the parts determined by (c). By a simple reasoning we can show

of the system of maximum frequency in an ensemble (whose modulus

that with a fair approximation  $\chi(n_r, dV_r)$  can be represented by

$$(\omega_r dV_r)^{n_r} \dots \dots \dots (e)$$

where  $\omega_r$  is a function of  $n_r$ . I have calculated for  $\omega$  the approximate value.

$$\log \omega = -n \left( \frac{2}{3} \pi \sigma^3 \right) - \frac{5}{16} n^2 \left( \frac{2}{3} \pi \sigma^3 \right)^2$$

(Cf my dissertation and also these Proceedings 1908 p. 116).

The extension of the  $3n$  dimensional space covered by the systems containing  $n_1 \dots n_r \dots n_k$  definite molecules in the elements  $dV_1 \dots dV_r \dots dV_k$  can now be represented by

$$\prod_1^k \chi(n_r, dV_r)$$

The extension covered by all possible systems of this kind amounts to

$$n! \prod_1^k \frac{\chi(n_r, dV_r)}{n_r!}$$

In the potential energy we may neglect the repulsive forces, these forces having been already taken into account by the exclusions (c). Supposing that the energy is the same for all the molecules of an element  $dV_r$ , we can represent the total potential energy by the formula

$$\sum_1^k n_r \epsilon_r$$

For the frequency we find

$$\zeta = N (2\pi \Theta m)^{\frac{3}{2}n} \frac{\Psi}{e} \prod_1^k \frac{\chi(n_r, dV_r)}{n_r!} e^{-\frac{n_r \epsilon_r}{\Theta}}$$

or, introducing the function  $\omega$  by means of (e)

$$\zeta = N (2\pi \Theta m)^{\frac{3}{2}n} \frac{\Psi}{e} \prod_1^k \frac{(\omega_r dV_r)^{n_r}}{n_r!} e^{-\frac{n_r \epsilon_r}{\Theta}}$$

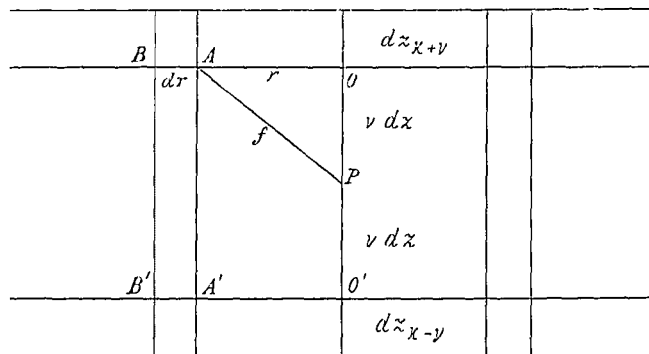
The formula (II) is a direct consequence of the last equation.

As we are treating a case in which there are differences in density in the system of maximum frequency, the question arises as to whether these differences have any influence on the value of the function  $\omega$ . If it were so, this function would depend not only on  $n$ , but also on the derivatives of this quantity with respect to  $z$ .

The difference in question really has an influence on the *energy*, but in consequence of the hypothesis of p.p. 526 and 527 the density changes so little along the length  $dz_r$  and the value of the exclusions at the limits of  $dz_r$  is so small in comparison with the value of those originating from the molecules of  $dz_r$  itself, that we may consider  $\omega_r$  as depending only on  $n_r$ . This, however, will be true no longer if the sphere of action of the attractive forces is not large in comparison with  $\sigma$ ; for this case the following theory would have to be modified considerably.

is proportional to the absolute temperature of the system).<sup>1)</sup>

In order to find the condition of equilibrium we have only to determine the values of the numbers  $n_r$  that make the quantity  $\xi$  or  $\log \xi$  a maximum. Before we proceed to this investigation we have to express the quantity  $\varepsilon_r$  in the numbers  $n_r$ .



Let us suppose that  $P$  is a point of the layer  $dz_r$ . We shall try to determine the potential energy for a molecule situated at that point. Consider first the contributions from the molecules situated in two plane layers at a distance  $\nu dz$  from  $P$ . We shall indicate these layers by  $dz_{,-}$  and  $dz_{,+}$ . We cut from these layers cylindrical rings by circular cylinders having  $OPO'$  as axis and as basis circles with

$$OA = O'A' = r \text{ and } OB = O'B' = r + dr$$

as radii.

The number of the molecules in these elements amounts to

$$2 \pi r dr dz (n_{,-} + n_{,+}).$$

Considering as equal the distance of all these molecules from  $P$  and representing it by  $f$ , we find for their contribution to the potential energy of  $P$

$$- \pi r dr dz (n_{,-} + n_{,+}) \varphi(f) \dots \dots \dots (2)$$

Now we have

$$r^2 + (\nu dz)^2 = f^2$$

and therefore

$$r dr = f df \dots \dots \dots (3)$$

Taking into account (1) and (3) we can replace (2) by

$$\pi dz (n_{,-} + n_{,+}) d\psi(f) \dots \dots \dots (4)$$

<sup>1)</sup> Cf my dissertation § 4 p. 15.

The total contribution to  $\epsilon_x$  from all the molecules of the layers  $dz_{x-v}$  and  $dz_{x+v}$  is found by integrating (4) with respect to  $f$  from  $v dz$  to  $\infty$ . Proceeding in this way we find

$$- \pi dz (n_{x-v} + n_{x+v}) \psi (v dz) \dots \dots \dots (5),$$

from which formula the energy per molecule in the layer  $dz_x$  can be calculated by adding up all the values of this expression which are such that  $\psi (v dz)$  differs from 0.

In this way we find

$$\epsilon_x = - \pi dz \sum (n_{x-v} + n_{x+v}) \psi (v dz) \dots \dots \dots (5')$$

For the potential energy of the system we have the formula

$$\sum_1^k n_x \epsilon_x = - \pi dz \sum_1^k n_x \sum_v (n_{x-v} + n_{x+v}) \psi (v dz), \dots (III)$$

§ 3. We may now proceed to the determination of the condition for the maximum. Consider therefore the change of  $\log \zeta$  when we give the variation  $\delta n_x$  to the numbers  $n_x$ . These variations are subjected to the equation

$$\sum_1^k \delta n_x = 0 \dots \dots \dots (IV)$$

In the following investigation we may replace  $n_x!$  by  $n_x^{n_x} e^{-n_x}$ . We find for  $\delta \log \zeta$

$$\begin{aligned} \delta \log \zeta = & \sum_1^k \left[ - \log n_x - 1 + \log \omega + n_x \frac{d \log \omega_x}{d n_x} \right] \delta n_x + \\ & + \frac{\pi dz}{\Theta} \left\{ \sum_1^k \delta n_x \sum_v \psi (v dz) (n_{x-v} + n_{x+v}) + \right. \\ & \left. + \sum_1^k n_x \sum_v \psi (v dz) (\delta n_{x-v} + \delta n_{x+v}) \right\} \dots (V) \end{aligned}$$

It is easily seen that the two sums, with which  $\frac{\pi dz}{\Theta}$  is multiplied are equal, both consisting of the same terms, and further that each of them is equal to

$$- \frac{1}{\pi dz} \sum_1^k \epsilon_x \delta n_x.$$

-Attending to the condition (IV) in the usual way, we find that the numbers  $n_r$  in the system of maximal frequency must fulfil the condition

$$\log \frac{\omega_r}{n} + n_r \frac{d \log \omega_r}{d n_r} - \frac{2\varepsilon}{\Theta} = \mu, \dots \dots \dots (VI)$$

whereas the second variation of  $\log \xi$ ,  $\delta^2 \log \xi$  given by the formula

$$\delta^2 \log \xi = \sum_1^k \frac{\delta n_r^2}{2n_r} \left( -1 + \frac{d}{d n_r} \left( n_r^2 \frac{d \log \omega_r}{d n_r} \right) \right) + \frac{\pi d z}{\Theta} \sum_1^k \delta n_r \sum_r \psi(v dz) (\delta n_{r-} + \delta n_{r+}) \dots \dots (VII)$$

must be essentially negative.

The first conditions are equivalent to those given by VAN DER WAALS. It is easy to give the equation (VI) the form which is assigned to it by VAN DER WAALS. We have only to introduce the hypothesis that  $n$  changes continually with the height and then to calculate the energy  $\varepsilon_r$ .

We obtain in this way<sup>1)</sup>

$$\log \frac{\omega_r}{n_r} + n_r \frac{d \log \omega_r}{d n_r} + \frac{2a n_r}{\Theta} + \frac{1}{\Theta} \sum_1^{\infty} C_{2s} \frac{d^{2s} n_r}{d z_r^{2s}} = (\mu_r)^2 \dots \dots (VI')$$

1) To calculate  $\varepsilon_r$  we proceed as follows. On account of our hypothesis we can write

$$n_{r-} + n_{r+} = 2n_r + 2 \frac{(v dz)^2}{2!} \frac{d^2 n_r}{d z_r^2} + \dots + 2 \frac{(v dz)^{2s}}{(2s)!} \frac{d^{2s} n_r}{d z_r^{2s}} \dots$$

Introducing this into the formula for  $\varepsilon_r$  and putting

$$2\pi \int_0^{\infty} \psi(z) dz = a,$$

$$\frac{2\pi}{(2s)!} \int_0^{\infty} z^{2s} \psi(z) dz = \frac{1}{2} C_{2s},$$

we find for  $\varepsilon_r$

$$\varepsilon_r = - a n_r - \frac{1}{2} \sum_1^{\infty} C_{2s} \frac{d^{2s} n_r}{d z_r^{2s}}, \dots \dots \dots (6)$$

I shall write for  $\varepsilon_r$  also

$$\varepsilon_r = - a n_r + \varepsilon_{ex} \dots \dots \dots (6')$$

It is only in the capillary layer that the quantity  $\varepsilon_{ex}$  differs from zero.

2) We may mention as another advantage in the above deduction of (VI') that



§ 4. Before I proceed to the discussion of the stability I shall consider the equation (VI). Using (6') we can put for it

$$\log \frac{\omega_r}{n_r} + n_r \frac{d \log \omega_r}{d n_r} + \frac{2 a n_r}{\Theta} - \frac{2 \varepsilon_{c,r}}{\Theta} = \mu. . . . (VI'')$$

Subtracting the equation (VI'') taken for the height  $z_r + dz_r$  from the corresponding one relating to the height  $z_r$ , we obtain

$$\left( -\frac{1}{n_r} + 2 \frac{d \log \omega_r}{d n_r} + n_r \frac{d^2 \log \omega_r}{d n_r^2} + \frac{2 a}{\Theta} \right) \frac{d n_r}{d z_r} = \frac{2}{\Theta} \frac{d \varepsilon_{c,r}}{d z_r}. . (7)$$

If we introduce the function  $p$ , determined by the equation

$$\frac{p}{\Theta} = n - n^2 \frac{d \log \omega}{d n} - \frac{a n^2}{\Theta}, . . . . . (8)$$

— which quantity represents the pressure in every element of a homogeneous system with the molecular density  $n$  — we easily see that we can replace (7) by

$$-\frac{1}{\Theta n} \frac{d p, d n_r}{d n_r, d z_r} = \frac{2}{\Theta} \frac{d \varepsilon_{c,r}}{d z_r}.$$

This equation leads to

$$-\frac{d p_r}{d z_r} = 2 n_r \frac{d \varepsilon_{c,r}}{d z_r}, . . . . . (9)$$

The form of this relation recalls the statistical condition of equilibrium namely that the difference of pressure between two planes be equal to the force acting on the mass between these planes.

By integrating (9) from a point of the homogeneous phase (indicated by the index  $h$ ) to a point of the capillary layer (index  $c$ ) we find

$$p_h - p_c = 2 \int_{z_h}^{z_c} n \frac{d \varepsilon_c}{d z} dz = 2 n_c \varepsilon_{c,c} - 2 \int_{z_h}^{z_c} \frac{d n}{d z} \varepsilon_c dz,$$

we have avoided to prove for each of the integrals  $\int n \delta \frac{d^2 s n}{d z^2 s} dz$  separately that

we can put for it  $\int \delta n \left( \frac{d^2 s n}{d z^2 s} \right) dz$ , as is done in the treatise of VAN DER WAALS—KOHNSTAMM p. 238.

In the paper of VAN DER WAALS this gives something accidental to the appearing of  $\varepsilon_r$  in the condition (VI). This advantage is due to the fact that the hypothesis of continuous transition and the expansion  $\varepsilon_r$  in a series have been introduced after the deduction of the condition (VI).

or  $\varepsilon_{c'}$  is zero in the homogeneous layer. Instead of the former formula we may put

$$p_r = p_h - 2\varepsilon_c \varepsilon_{c'} + 2 \int_{z_h}^{z_r} \frac{dn}{dz} \varepsilon_c dz \dots \dots \dots (10)$$

Introducing now for  $\varepsilon_{c'}$  the series that follows from (6) and (6') we find for the pressure

$$p_r = p_h + n_r \sum_1^{\infty} C_{2s} \frac{d^{2s} n_r}{dz_r^{2s}} - \frac{1}{2} C_2 \left( \frac{dn_r}{dz_r} \right)^2 - \sum_2^{\infty} C_{2s} \int_{z_h}^{z_r} \frac{dn}{dz} \frac{d^{2s} n}{dz^{2s}} dz \dots (VIII)^1$$

It follows from the above reductions that we obtain for the pressure  $p_r$

$$p_r = p_h + C_2 \left( n_r \frac{d^2 n_r}{dz_r^2} - \frac{1}{2} \left( \frac{dn_r}{dz_r} \right)^2 \right) + \sum_{s=2}^{\infty} C_{2s} \left[ \sum_{r=0}^{s-1} (-1)^r \frac{d^r n_r}{dz_r^r} \frac{d^{2s-r} n_r}{dz_r^{2s-r}} - \frac{1}{2} (-1)^s \left( \frac{d^s n_r}{dz_r^s} \right)^2 \right] \dots (VIII')$$

An approximation for  $p_r$  may be obtained by breaking off the series at  $s=1$ : we then find a formula, which agrees with one given by VAN DER WAALS namely

$$p_r = p_h + C_2 \left( n_r \frac{d^2 n_r}{dz_r^2} - \frac{1}{2} \left( \frac{dn_r}{dz_r} \right)^2 \right) \dots \dots (VIII'')$$

<sup>1)</sup> In order to reduce the integrals contained in the sum, we have the formula

$$\int_{z_h}^{z_r} \frac{dn}{dz} \frac{d^{2s} n}{dz^{2s}} dz = \frac{dn_r}{dz_r} \frac{d^{2s-1} n_r}{dz_r^{2s-1}} - \int_{z_h}^{z_r} \frac{d^2 n}{dz^2} \frac{d^{2s-1} n}{dz^{2s-1}} dz \dots$$

Where the remaining integral may again be transformed by the same operation. In this way we are finally led to a term in which the integration may be performed namely

$$(-1)^s \int_{z_h}^{z_r} \frac{d^s n}{dz^s} \frac{d^{s+1} n}{dz^{s+1}} dz = \frac{(-1)^s}{2} \left( \frac{d^s n}{dz^s} \right)^2$$

It follows from (VIII) together with the above reductions that by integrating from the one homogeneous phase  $h_1$  to the other  $h_2$  we obtain:

$$p_{h_1} = p_{h_2},$$

which is the well known condition for thermodynamical equilibrium.

The constant  $\mu$  of the equation (VI) can be determined, if we observe that in the homogeneous phases  $\varepsilon_{c'} = 0$ . Representing the molecular density of these phases by  $n_1$  and  $n_2$ , we have

$$\log \frac{\omega_1}{n_1} + n_1 \frac{d \log \omega_1}{d n_1} + \frac{2an_1}{\Theta} = \log \frac{\omega_2}{n_2} + n_2 \frac{d \log \omega_2}{d n_2} + \frac{2an_2}{\Theta} = \mu, \quad (11)$$

which yields one equation between  $n_1$  and  $n_2$ . We can find a second by means of the observation made at the end of the note of p. 534. We have

$$p_{h_1} = p_{h_2} \dots \dots \dots (12)$$

where the  $p$ 's are known functions of  $n_1$  and  $n_2$  (c.f. (8)).

After having determined  $n_1$  and  $n_2$  by means of the foregoing equations we can use the first to determine  $\mu$ .

The thickness of the capillary layer depends on the modulus  $\Theta$ , it can be determined by means of (VI); we can also calculate the number of the molecules in this layer. This number being known, the equation (I) enables us to calculate the height of the liquid and gaseous phases.

§ 5. We have now to examine whether the frequency of the system determined by (II) and (VI) is really maximum, in other terms whether the condition of the system is one of stable equilibrium. The quantity  $\delta^2 \log \zeta$  consists of three parts, the two first of which belong to the elements of the homogeneous phases  $h_1$  and  $h_2$ , whereas the third relates to the capillary layer  $c$ .

We may put the first parts in the form

$$\delta_{h^2}^2 \log \zeta = \sum_h \frac{\delta n_r^2}{2n_r} \left( -1 + \frac{d}{dn_r} \left( n_r^2 \frac{d \log \omega_r}{d n_r} \right) + \frac{2an_r}{\Theta} \right), \quad (13)$$

where  $\sum_h$  has to be extended over the elements of the homogeneous layers  $h_1$  and  $h_2$ . For the part belonging to the capillary layer we have the formula

$$\delta_c^2 \log \zeta = \sum_c \frac{\delta n_r^2}{2n_r} \left( -1 + \frac{d}{dn_r} \left( n_r^2 \frac{d \log \omega_r}{d n_r} \right) \right) + \frac{\pi dz}{\Theta} \sum_c \delta n_r \sum_y \psi(vdz) (\delta n_{r-} + \delta n_{r+}). \quad \dots \quad (VII'')$$

In order that  $\delta^2 \log \zeta$  be negative, it is necessary that  $\delta_{h_1}^2 \log \zeta$ ,  $\delta_{h_2}^2 \log \zeta$  and  $\delta_c^2 \log \zeta$  be negative for all possible values of the numbers  $\delta n_r$ .

The parts relating to the homogeneous layers may be written in the form

$$\sigma^2_{\alpha} \log \zeta = \left( -1 + \frac{d}{dn_{\alpha}} \left( n^2_{\alpha} \frac{d \log \omega_{\alpha}}{dn_{\alpha}} \right) + \frac{2an_{\alpha}}{\Theta} \right) \sum_{h_{\alpha}} \frac{\delta n^2_{\alpha}}{2n_{\alpha}},$$

where  $\alpha$  is 1 or 2. These contributions are negative, if

$$-1 + \frac{d}{dn_{\alpha}} \left( n^2_{\alpha} \frac{d \log \omega_{\alpha}}{dn_{\alpha}} \right) + \frac{2an_{\alpha}}{\Theta} < 0 \quad \dots \quad (IX)$$

Now, we can transform this condition by means of the function  $p$  (c. f. (8)). We then find as a condition for the stability

$$\frac{dp_{\alpha}}{dn_{\alpha}} > 0 \quad \dots \quad (IX')$$

for the homogeneous phases. As for these phases, the function  $p_{\alpha}$  represents the pressure, the condition (IX') is nothing else than the known thermodynamical condition for stability.

Not only must (IX) be fulfilled, it is also necessary that  $\sigma^2_c \log \zeta$  be negative, for there are possible variations in which  $\delta n_{\alpha}$  is zero everywhere in the homogeneous layers.

I shall transform the first sum in  $\sigma^2_c \log \zeta$  by means of (VI). I shall write for it

$$\sum_c \frac{\delta n_{\alpha}}{2} \delta n_{\alpha} \left( -\frac{1}{n_{\alpha}} + \frac{1}{n_{\alpha}} \frac{d}{dn_{\alpha}} \left( n^2_{\alpha} \frac{d \log \omega_{\alpha}}{dn_{\alpha}} \right) \right),$$

which may be replaced by

$$\sum_c \frac{\delta n_{\alpha}}{2} \delta n_{\alpha} \frac{d}{dn_{\alpha}} \left( \log \frac{\omega_{\alpha}}{n_{\alpha}} + n_{\alpha} \frac{d \log \omega_{\alpha}}{dn_{\alpha}} \right).$$

By a transformation of the same kind as that which leads to (7), we can replace the foregoing expression by

$$\frac{1}{\Theta} \sum_c \delta n_{\alpha} \delta n_{\alpha} \frac{\frac{d\varepsilon_{\alpha}}{dz_{\alpha}}}{\frac{dn_{\alpha}}{dz_{\alpha}}}.$$

Introducing the value of  $\varepsilon_{\alpha}$  by means of (5'), and considering that the differentiation of  $n_{\alpha,-}$  with respect to  $z_{\alpha}$  gives the same result as that with respect to  $z_{\alpha,+}$ , we find for the sum under consideration

$$-\frac{\pi dz}{\Theta} \sum_c \frac{\delta n_{\alpha} \delta n_{\alpha}}{dn_{\alpha}} \sum \psi(v dz) \left( \frac{dn_{\alpha,-}}{dz_{\alpha,-}} + \frac{dn_{\alpha,+}}{dz_{\alpha,+}} \right),$$

therefore (VII'') may be reduced to

$$\frac{\pi dz}{\theta} \left\{ \sum_c \delta n_c \sum, \psi(v dz) (\delta n_{c,-} + \delta n_{c,+}) - \right. \\ \left. - \sum_c \frac{\delta n_c \delta n_c}{\frac{dn_c}{dz_c}} \sum, \psi(v dz) \left( \frac{dn_{c,-}}{dz_{c,-}} + \frac{dn_{c,+}}{dz_{c,+}} \right) \right\}. \quad (VII''')$$

Now we can easily show that this sum is essentially negative. For this purpose we arrange the terms in the following way. From the first sum we take the term  $\delta n_c \psi(v dz) \delta n_{c,-}$ , and also the term  $\delta n_{c,-} \psi(v dz) \delta n_c$ . These are equal, and their sum is

$$\frac{2}{dz} \delta n_c \delta n_{c,-} \psi(v dz).$$

Next from the second sum we take the term

$$- \frac{\delta n_c \delta n_c \frac{dn_{c,-}}{dz_{c,-}}}{\frac{dn_c}{dz_c}} \psi(v dz),$$

and also the term

$$- \frac{\delta n_{c,-} \delta n_{c,-} \frac{dn_c}{dz_c}}{\frac{dn_{c,-}}{dz_{c,-}}} \psi(v dz).$$

Adding those four we find

$$- \frac{1}{dz} \frac{dn_c}{dz_c} \frac{dn_{c,-}}{dz_{c,-}} \left( \frac{\delta n_c}{dn_c} - \frac{\delta n_{c,-}}{dn_{c,-}} \right)^2 \psi(v dz).$$

This result is essentially negative, for  $\frac{dn}{dz}$  has the same sign at all points.<sup>1)</sup>

We can arrange all the terms of (VII''') in the same way. Accordingly, the whole sum may be written as a sum of essentially negative quantities, and therefore  $\sigma_c^2 \log \xi$  is essentially negative. From this it follows that a system consisting of two coexisting phases with a capillary layer between them is stable, if the homogeneous phases taken by themselves are stable.

§ 6. I shall now determine the entropy and the free energy of the system considered.

GIBBS<sup>2)</sup> showed that  $\mathcal{F}$ , the constant in the equation (II) has

<sup>1)</sup> A similar transformation does not hold for the elements of the homogeneous phases for there  $\frac{dn}{dz} = 0$ .

<sup>2)</sup> J. W. GIBBS. Elementary principles in Statistical Mechanics 1902.

the properties of the thermodynamical free energy. I shall therefore determine the quantity  $\Psi$ , which may properly be called the statistical free energy.

Taking the sum of the numbers  $\zeta$ , obtained by giving to the numbers  $n$  all possible values, we get the total number  $N$  of the systems in the ensemble. I shall represent this sum by  $\Sigma_e$ , so that we have the identity

$$N = \sum_e \zeta = (2\pi\Theta m)^{\frac{3}{2}n} N e^{\frac{\Psi}{\Theta}} n! \sum_e \prod_1^k \frac{(\omega_r dz_k)^{n_r}}{n_r!} e^{-\frac{n_r \epsilon_r}{\Theta}}. \quad (X)$$

This equation enables us to determine  $\Psi$ . In order to find the value of  $\Sigma_e \zeta$ , we may by means of (VII) express the frequency  $\zeta$  of an arbitrary system in that  $\zeta_0$  of the system of maximum frequency. From (VII) it follows that

$$\zeta = \zeta_0 \sum_{e=1}^k \left[ \frac{\delta n_r^2}{2n_r} \left( -1 + \frac{d}{dn_r} \left( n^2, \frac{d \log \omega_r}{dn_r} \right) \right) + \right. \\ \left. + \frac{\pi}{\Theta} \sum_1^k \delta n_r \sum \psi(v dz) (\delta n_{r,-} + \delta n_{r,+}) dz. \right]$$

Introducing this into the sum  $\Sigma_e$ , we obtain

$$\sum_e \zeta = \zeta_0 \sum_{e=1}^k \left[ \frac{\delta n_r^2}{2n_r} \left( -1 + \frac{d}{dn_r} \left( n^2, \frac{d \log \omega_r}{dn_r} \right) \right) + \right. \\ \left. + \frac{\pi}{\Theta} \sum_1^k \delta n_r \sum \psi(v dz) (\delta n_{r,-} + \delta n_{r,+}) dz. \right]$$

In my dissertation <sup>1)</sup> I have shown, that this may be replaced in a fair approximation by

$$\sum_e \zeta = \zeta_0 \sum_e \sum_1^k - \frac{\delta n_r^2}{2n_r} \dots \dots \dots (13)$$

The quantity  $\zeta_0$  is given by the equation

$$\zeta_0 = \frac{N e^{\frac{\Psi}{\Theta}} n! (2\pi\Theta m)^{\frac{3}{2}n} \sqrt{2\pi n}}{(2\pi)^{k/2} (n_1 \dots n_k)^{1/2}} \prod_1^k \left( \frac{\omega_r}{n_r} \right)^{n_r} e^{-\frac{n_r \epsilon_r}{\Theta}}, \dots (14)$$

<sup>1)</sup> p.p. 111 and 126.

where the numbers  $n_r$  and  $n_r$  have the values following from (VI).

We now have

$$\sum_e e^{-\sum_1^k \frac{\delta n_r^2}{2n_r}} = (2\pi)^{\frac{k-1}{2}} (n_1 \dots n_k)^{1/2} n^{-1/2}$$

and therefore, using (13) and (14), we find for  $\Psi$

$$e^{-\frac{\Psi}{\Theta}} = (2\pi\Theta m)^{\frac{3}{2}n} n^n \prod_1^k \left(\frac{\omega_r}{n_r}\right)^{n_r} e^{-\frac{n_r \varepsilon_r}{\Theta}} \quad (XI)$$

GIBBS showed that the quantity  $-\bar{\eta}$  defined by the equation

$$-\bar{\eta} = \frac{\bar{\varepsilon} - \Psi}{\Theta} \quad (XII)$$

has the properties of the entropy  $s$ . Here the quantity  $\bar{\varepsilon}$  is the average energy in the canonical ensemble, it is equal to the energy of the system of maximum frequency<sup>1)</sup>.

The kinetic energy of this system amounts to

$$\frac{3}{2} n \Theta .$$

For the potential energy we have written

$$\sum_1^k n_r \varepsilon_r ,$$

and the value of  $\bar{\varepsilon}$  is therefore

$$\bar{\varepsilon} = \frac{3}{2} n \Theta + \sum_1^k n_r \varepsilon_r .$$

For  $s$  we have the equation

$$\begin{aligned} s &= \frac{3}{2} n + \frac{3}{2} n \log (2 \pi \Theta m) + n \log n + \sum_1^k n_r \log \frac{\omega}{n_r} \\ &= Const + \frac{3}{2} n \log \Theta + \sum_1^k n_r \log \frac{\omega_r}{n_r} \\ &= Const + \frac{3}{2} n \log \Theta + \int_0^Z n \log \frac{\omega}{n} dz. \quad (XIII) \end{aligned}$$

<sup>1)</sup> GIBBS showed that the average energy in an ensemble is equal to the most common energy in that ensemble. Now not every system with this energy is equivalent to the system of maximum frequency, but the most common energy is equal to the energy of the latter system therefore the same is true for the average energy. This result may also be obtained by determining  $\bar{\varepsilon}$  directly by means of (VII).

This formula can be used to determine  $s$ , if we know the manner in which  $n$  depends on  $z$ . We easily see from (XIII), that, just as VAN DER WAALS supposed, the entropy in each element of volume depends only on the density  $n$  and on the number of collisions in that element<sup>1)</sup>. We could expect this, having found exactly the same condition of equilibrium to which his theory leads.

It must, however, not been forgotten that the whole above development and therefore the hypothesis of VAN DER WAALS are only valid, if the assumptions about the attractive forces introduced at p. 526 and 527 are true. The changes that will have to be made in the theory, when these assumptions are relinquished, must be a matter of further examination<sup>2)</sup>.

7. Finally I shall determine the force exerted in a horizontal direction by the system. Consider a system identical with the former; only let the section be no longer equal to unit of area, but let it be  $o$ . It is easily seen that this has no influence at all on the former developments. The density  $n$ , and the energy  $\epsilon$ , are determined by analogous equations; the only difference is that  $n$ , (the number of molecules in the layer  $dz$ ,) is now given by  $n \cdot o \cdot dz$ , instead of by  $n \cdot dz$ .

For  $\Psi$  we have therefore the formula

$$-\frac{\Psi}{\Theta} = Const. + \sum_1^k o n_r \left( \log \frac{\omega_r}{n_r} - \frac{\epsilon_r}{\Theta} \right) dz_r = \\ = Const. + o \int_0^Z n \left( \log \frac{\omega}{n} - \frac{\epsilon}{\Theta} \right) dz \dots \dots (15)$$

The average component, corresponding to the parameter  $o$ , of the force exerted by the systems of the ensemble is given — as GIBBS showed — by the relation

$$\bar{K}_o = -\frac{d\Psi}{do} \dots \dots \dots (XIV)$$

The force  $K_o$ , exerted by the systems of maximum frequency, is equal to the average force  $\bar{K}_o$ . Therefore equation (XIV) may be used to determine the force in a real system. Before I use (15) to

<sup>1)</sup> The function  $\omega$  is connected with this number.

<sup>2)</sup> In this examination the function  $\mathfrak{S}(n, dz)$  introduced in my dissertation will have to play a part.



determine  $K_0$ , I shall put this equation in a new form by means of (VI) namely

$$-\frac{\Psi}{\Theta} = \text{Const.} + \int_0^Z \left( \mu n - n^2 \frac{d \log \omega}{dn} - \frac{an^2}{\Theta} + \frac{n\epsilon_c}{\Theta} \right) dz =$$

$$= \text{Const.} + (\mu-1)n + \int_0^Z \left( (n-n^2) \frac{d \log \omega}{dn} - \frac{an^2}{\Theta} + \frac{n\epsilon_c}{\Theta} \right) dz.$$

with the aid of (10) we can replace this formula by

$$-\frac{\Psi}{\Theta} = C' + \int_0^Z p_h dz + \frac{1}{\Theta} \int_0^Z \left( -n\epsilon_c + 2 \int_{z_h}^z \frac{dn}{dz} \epsilon_c dz \right) dz \quad (XI')$$

For  $K_0$  we get finally

$$K_0 = p_h Z + \int_0^Z \left( -n\epsilon_c + 2 \int_{z_h}^z \frac{dn}{dz} \epsilon_c dz \right) dz \quad \dots \quad (XV)$$

An approximate value for  $K_0$  can be found, by putting  $\epsilon_c = -\frac{C_2}{2} \frac{d^2 n}{dz^2}$ ,

This value for  $K_0$  amounts to

$$K_0 = p_h Z + \frac{C_2}{2} \int_0^Z \left( n \frac{d^2 n}{dz^2} - \left( \frac{dn}{dz} \right)^2 \right) dz =$$

$$= p_h Z - C_2 \int_0^Z \left( \frac{dn}{dz} \right)^2 dz$$

$$= p_h Z + C_2 \int_0^Z n \frac{d^2 n}{dz^2} dz \quad \dots \quad (16)$$

When the surface of the capillary layer increases by unit of area the free energy (so far as it depends on capillary action) decreases by

$$\int_0^Z \left( -n\epsilon_c + 2 \int_{z_h}^z \frac{dn}{dz} \epsilon_c dz \right) dz \quad \dots \quad (17)$$

or, if we use the approximate values by

$$- C_2 \int_0^Z \left( \frac{dn}{dz} \right)^2 dz =$$

$$+ C_2 \int_0^Z n \frac{d^2 n}{dz^2} dz, \dots \dots \dots (18)$$

i. e. the free energy increases proportionally to the surface. Only the elements of the capillary layer contribute to the integrals, for it is only in these elements that  $\epsilon_c$  and  $\frac{dn}{dz}$  differ from zero. The quantities expressed by (17) and (18), taken with the negative sign, agree with what is commonly called the capillary energy. In this form they also represent the so called surface tension.

The quantity

$$p_h - n_c \epsilon_c + 2 \int_{z_h}^{z_r} \frac{dn}{dz} \epsilon_c dz,$$

or the corresponding approximate quantity (c. f. (16))

$$pZ + \frac{C_2}{2} \left( n_r \frac{d^2 n_r}{dz^2} - \left( \frac{dn_r}{dz} \right)^2 \right),$$

may be called the horizontal pressure in the element  $dz_r$  at the height  $z_r$ . I shall represent it by  $p_{hr}$ . As we can see from (10), the connection between  $p_r$  and  $p_{hr}$  is given by the formula

$$p_{hr} - p_r = n_r \epsilon_{cr} \dots \dots \dots (XVI)$$

The term  $\epsilon_{cr}$  being 0 in the homogeneous layer, we have

$$p_{hr} = p_r = p_{h1} = p_{h2}.$$

We can determine the sign of  $\epsilon_{cr}$ , and therefore that of  $p_{hr} - p_r$ , by means of the equations (VI) and (10). We then come to a discussion exactly analogous to that which VAN DER WAAALS has given on p. 19 of his paper<sup>1)</sup>.

If one goes upward from the liquid phase,  $\epsilon_c$  is first 0, then positive, then 0 again, after that negative and finally 0 in the gaseous phase.

By means of the foregoing considerations, we can obtain all the results formerly found by VAN DER WAAALS and the above method may also be applied to a spherical mass, whose density is distributed symmetrically around the centre.

<sup>1)</sup> C.f. VAN DER WAAALS—KOHNSTAMM p. 239.