

Citation:

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We suppose that the molecules are perfectly rigid and elastic and that they attract each other with forces acting at distances so great that we may consider the sphere of action as uniformly filled with matter.

For this case the value of Ψ is given by the equation

$$e^{-\frac{\Psi}{\theta}} = (2\pi\theta m_1)^{\frac{3}{2}n_1} (2\pi\theta m_2)^{\frac{3}{2}n_2} \int e^{-\frac{\epsilon_q}{\theta}} dx_{11} \dots dz_{2n_2} \dots \quad (2)$$

I shall represent the coordinates of the molecule k of the first kind by x_{1k} , y_{1k} and z_{1k} , and those of the molecule l of the second kind by x_{2l} , y_{2l} and z_{2l} .

The integration has to be extended to a $3(n_1 + n_2)$ -dimensional space, the notion of which is obtained if we take the $3(n_1 + n_2)$ coordinates of the centres of the molecules as cartesian coordinates of a single point, and give all possible positions to the molecules of the gas.

We must exclude from the space all those points at which a condition of one of the forms

$$\left. \begin{aligned} (x_{1k} - x_{1l})^2 + (y_{1k} - y_{1l})^2 + (z_{1k} - z_{1l})^2 < \sigma_1^2 \\ (x_{1k} - x_{2l})^2 + (y_{1k} - y_{2l})^2 + (z_{1k} - z_{2l})^2 < \sigma^2 \\ (x_{2k} - x_{2l})^2 + (y_{2k} - y_{2l})^2 + (z_{2k} - z_{2l})^2 < \sigma_2^2 \end{aligned} \right\} \dots \quad (3)$$

is fulfilled.

I have proved ¹⁾ in my dissertation that the large majority of the systems of a canonical ensemble may be considered as identical in all properties that are accessible to our means of observation. For all these equivalent or identical systems the value of the potential energy of the attractive forces is equal.

The sphere of action being uniformly filled, this quantity (ϵ_{q_0}) can be represented by

$$\epsilon_{q_0} = - \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2V} \dots \dots \quad (4)$$

As to the potential energy of the repulsive forces, we need not speak of it when we take into account the conditions (3).

We shall obtain a good approximation, if, in the equation (2), we write ϵ_{q_0} instead of ϵ_q (which differs from ϵ_{q_0} only in a small part of the systems). By this, the exponential factor becomes a constant and we may put it before the sign of integration.

The quantity Ψ is thus expressed by the equation

¹⁾ l. c. p. 14

$$e^{-\frac{\psi}{\theta}} = (2\pi\theta m_1)^{\frac{3}{2}n_1} (2\pi\theta m_2)^{\frac{3}{2}n_2} e^{-\frac{\epsilon_{q_0}}{\theta}} \int dx_{11} \dots dz_{2n_2} \dots \quad (5)$$

and its determination is reduced to the calculation of the integral on the right-hand side. Let the function $\chi(n_1, n_2)$ represent this integral.

In my dissertation I have determined this function to the degree of exactitude indicated above. Before proceeding to the determination of the terms of higher order I shall repeat the former calculation which now only wants further extension.

The $3(n_1 + n_2)$ -dimensional space of integration can be decomposed into $n_1 + n_2$ threedimensional spaces, each corresponding to one of the molecules. We shall divide these spaces into elements which are small in comparison with the volume of a molecule.

In order to determine the integral defining the function $\chi(n_1, n_2)$ we decompose it into a sum of products of $n_1 + n_2$ elements chosen in the spaces in question, each space being represented in the product by one and only one element.

In order clearly to see the way in which the products are formed with the restrictions imposed by (3), we proceed as follows: We number the spaces corresponding to the molecules of the first kind from 1 to n_1 , those corresponding to the molecules of the second kind from $n_1 + 1$ to $n_1 + n_2$, and we choose the elements in the order indicated by these numbers.

We have to consider that, if we have chosen for the centre of the k^{th} molecule ($k < n_1$) an element lying at a point x_{1k}, y_{1k}, z_{1k} , we must exclude from the $k + 1^{\text{th}}$ up to the n_1^{th} space those elements which are situated in spheres described with the radius σ_1 around the points of these spaces whose coordinates are equal to x_{1k}, y_{1k} and z_{1k} . Similarly we must exclude those elements from the spaces from $n_1 + 1$ up to $n_1 + n_2$, which lie within the spheres of radius σ described around the points of the spaces having for coordinates x_{1k}, y_{1k} and z_{1k} . If, further, in the space $n_1 + v_2$ an element has been chosen at a point with the coordinates $x_{2n_1+v_2}, y_{2n_1+v_2}, z_{2n_1+v_2}$ we must exclude in all following spaces the elements of spheres with radius σ_2 described around the points of those spaces having their coordinates equal to $x_{2n_1+v_2}, y_{2n_1+v_2}, z_{2n_1+v_2}$.

The elements in the spaces 1 to $n_1 + n_2 - 1$ having been chosen, there remains in the last space $n_1 + n_2$ a region $g_{n_1+n_2}$ for the choice of the $(n_1 + n_2)^{\text{th}}$ element.

In determining the sum we can first take together all those cases in which the elements of the spaces 1 to $n_1 + n_2 - 1$ are the same.

Considering that n_1 and n_2 are very great numbers, and that the

elements have been chosen quite arbitrarily, we easily see that the quantity $g_{n_1+n_2}$ must be the same for the greater majority of the possible ways of choosing the elements in the spaces up to the $(n_1 + n_2 - 1)^{\text{th}}$, and that we may therefore write

$$\chi(n_1, n_2) = g_{n_1+n_2} \chi(n_1, n_2 - 1) \dots \dots \dots (6)$$

$g_{n_1+n_2}$ being now a quite definite quantity, which it remains to determine.

It is very easy to find a first approximation to its value. For this purpose we have only to neglect the fact that the above mentioned spheres in the $(n_1 + n_2)^{\text{th}}$ space intersect. Doing so, we find

$$g_{n_1+n_2} = V - n_1 \frac{4}{3} \pi \sigma^3 - (n_2 - 1) \frac{4}{3} \pi \sigma_2^3 \dots \dots (7)$$

From (6) and (7) we deduce by successive reductions

$$\chi(n_1, n_2) = \chi(n_1) \prod_1^{n_2} \left(V - n_1 \frac{4}{3} \pi \sigma^3 - (v_2 - 1) \frac{4}{3} \pi \sigma_2^3 \right), \dots (8)$$

where we have affixed to the sign of the product the highest value that we have to give to the number denoted by the corresponding Greek letter. A similar notation will be used in later formulae.

It is easily seen that, with the degree of exactitude to which we have now confined ourselves, the value of $\chi(n_1)$ is given by

$$\chi(n_1) = \prod_1^{n_1} \left(V - v_1 \frac{4}{3} \pi \sigma_1^3 \right) \dots \dots \dots (9)$$

In order to push our approximation further, we have to determine $g_{n_1+n_2}$ more accurately. We must take into account that the spheres mentioned above intersect, and that we have therefore subtracted too much from the total volume.

Now three cases are to be distinguished.

1. Intersection between the spheres of radius σ described around the points corresponding to the centres of the molecules of the first kind. The distance x of the centres cannot be less than σ_1 and must be less than 2σ .

2. Intersection between the spheres of radius σ_2 described around the points corresponding to the molecules of the second kind. The distance of the centres must lie between σ_2 and $2\sigma_2$.

3. Intersection between the spheres of radius σ and σ_2 described around the points corresponding to the centres of molecules of the first and second kinds respectively. The distance x of the centres must lie between σ and $\sigma_2 + \sigma$.

I shall determine the parts corresponding to these three kinds of

intersections, which have been subtracted too much from V . These parts are equal for by far the majority of the possible combinations of elements in the spaces from the first up to the $(n_1 + n_2 - 1)^{\text{th}}$. We may suppose that the distribution of the points corresponding to the centres of molecules from 1 tot $n_1 + n_2 - 1$ is uniform in the $(n_1 + n_2)^{\text{th}}$ space.

1. The number of pairs of points (corresponding to molecules of the first kind) with mutual distance lying between x and $x + dx$ amounts to

$$2\pi n_1^2 \frac{x^2 dx}{V} \dots \dots \dots (10)$$

The common part of two spheres of radius σ having a central distance x is given by

$$\pi \left(\frac{4}{3} \sigma^3 - \sigma^2 x + \frac{x^3}{12} \right) \dots \dots \dots (11)$$

Hence, the total part subtracted too much on account of these intersections is equal to

$$\frac{2\pi^2 n_1^2}{V} \int_{\sigma_1}^{2\sigma_1} \left(\frac{4}{3} \sigma^3 x^2 - \sigma^2 x^3 + \frac{x^5}{12} \right) dx = \frac{\pi^2 n_1^2}{V} \left(\frac{8}{9} \sigma^6 - \frac{8}{9} \sigma^4 \sigma_1^2 + \frac{1}{2} \sigma^2 \sigma_1^4 - \frac{\sigma_1^6}{36} \right) \quad (12)$$

2. The number of pairs of points (corresponding to the centres of molecules of the second kind) with a mutual distance between x and $x + dx$ is

$$2\pi (n_2 - 1)(n_2 - 2) \frac{x^2 dx}{V} \dots \dots \dots (13)$$

The common part of the spheres is found for this case, if in (11) we replace σ by σ_2 , so that we find for the part subtracted too much from V

$$2\pi^2 \frac{(n_2 - 1)(n_2 - 2)}{V} \int_{\sigma_2}^{2\sigma_2} \left(\frac{4}{3} \sigma_2^3 x^2 - \sigma_2^2 x^3 + \frac{x^5}{12} \right) dx = \frac{17(n_2 - 1)(n_2 - 2)}{16} \frac{2}{V} \left(\frac{2}{3} \pi \sigma_2^3 \right)^2 \quad (14)$$

3. The number of pairs of points such that one point corresponds to the centre of a molecule of the first kind and one to that of a molecule of the second kind, the mutual distance lying between x and $x + dx$, amounts to

$$4\pi n_1 (n_2 - 1) \frac{x^2 dx}{V} \dots \dots \dots (15)$$

The common part of the spheres is now given by

$$\pi \left[\frac{2}{3} \sigma_1^3 + \frac{2}{3} \sigma^3 - \frac{\sigma_1^2 (x^2 + \sigma_1^2 - \sigma^2)}{2x} - \frac{\sigma^2 (x^2 + \sigma^2 - \sigma_1^2)}{2x} + \frac{(x^2 + \sigma_1^2 - \sigma^2)^2}{24x^3} + \frac{(x^2 + \sigma^2 - \sigma_1^2)^2}{24x^3} \right] \dots (16)$$

and the total part subtracted too much from V by

$$4 \pi^2 \frac{n_1 (n_1 - 1)}{V} \int \left[\frac{2}{3} (\sigma^3 + \sigma_1^3) x^2 - \frac{1}{2} (\sigma^2 + \sigma_1^2) x^3 - \frac{1}{4} (\sigma^2 - \sigma_1^2)^2 x + \frac{1}{12} x^5 \right] dx = \pi^2 \frac{n_1 (n_1 - 1)}{V} \left(-\frac{1}{18} \sigma_1^6 + \sigma_1^4 \sigma^2 \right) (17)$$

The value of $g_{n_1+n_2}$ is found by adding (12), (14) and (17) to (7) and substituting the obtained value in (8). By successive reductions we get

$$\chi(n_1, n_2) = \chi(n_1) \prod_1^{n_2} \left[V - n_1 \frac{4}{3} \pi \sigma^3 - (v_2 - 1) \frac{4}{3} \pi \sigma_1^3 + \frac{n_1^2}{V} \pi^2 \left(\frac{8}{9} \sigma^6 - \frac{8}{9} \sigma^3 \sigma_1^3 + \frac{1}{2} \sigma^2 \sigma_1^4 - \frac{1}{36} \sigma_1^6 \right) + \frac{17(v_2 - 1)(v_2 - 2)}{36} \pi^2 \sigma_1^6 + \frac{n_1(v_2 - 1)}{V} \pi^2 \left(-\frac{1}{18} \sigma_1^6 + \sigma_1^4 \sigma^2 \right) \right] (18)$$

It is easily seen that to the degree of approximation now required, $\chi(n_1)$ is represented by

$$\chi(n_1) = \prod_1^{n_1} \left(V - (v_1 - 1) \frac{4}{3} \pi \sigma_1^3 + \frac{17(v_1 - 1)(v_1 - 2)}{36} \pi^2 \sigma_1^6 \right) (19)$$

Substituting these values in (5), taking the logarithm of the result, and developing this logarithm in ascending powers of $\frac{1}{V}$, we find

$$-\frac{\Psi}{\theta} = C + \frac{a_1 n_1^2 + 2a_2 n_1 n_2 + a_3 n_2^2}{2\theta V} + \sum_1^{n_1} \left[\log V - \frac{v_1 - 1}{V} \frac{4}{3} \pi \sigma_1^3 - \frac{(v_1 - 1)(v_1 - 2)}{V^2} \frac{15}{36} \pi^2 \sigma_1^6 \right] + \sum_1^{n_2} \left[\log V - \frac{n_1}{V} \frac{4}{3} \pi \sigma^3 - \frac{(v_2 - 1)}{V} \frac{4}{3} \pi \sigma_1^3 - \frac{(v_2 - 1)(v_2 - 2)}{V^2} \frac{15}{36} \pi^2 \sigma_1^6 - \frac{8}{9} \frac{n_1^2}{V^2} \pi^2 \sigma_1^3 \sigma^3 + \frac{1}{2} \frac{n_1^2}{V^2} \pi \sigma^2 \sigma_1^4 - \frac{1}{36} \frac{n_1^2}{V^2} \pi^2 \sigma_1^6 - \frac{16}{9} \frac{n_1 (v_2 - 1)}{V^2} \pi^2 \sigma_1^3 \sigma^3 + \frac{n_1 (v_2 - 1)}{V^2} \pi^2 \sigma_1^4 \sigma^2 - \frac{1}{18} \frac{n_1 (v_2 - 1)}{V^2} \pi^2 \sigma_1^6 \right] (20)$$

C being the part which is independent of V .

Since n_1 and n_2 are very large numbers, we easily see that the expression (20) can be transformed to

$$\begin{aligned}
 -\frac{\Psi}{\theta} = C + \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V} + (n_1 + n_2) \log V - n_1^2 \frac{\beta_1}{V} - \frac{5}{16} n_1^3 \frac{\beta_1^2}{V^2} \\
 - n_2^2 \frac{\beta_2}{V} - \frac{5}{16} n_2^3 \frac{\beta_2^2}{V^2} \\
 - 2n_1 n_2 \frac{\beta}{V} \\
 - \frac{8}{9} \frac{n_1^2 n_2}{V^2} \pi^2 \sigma_1^3 \sigma^3 + \frac{1}{2} \frac{n_1^2 n_2}{V^2} \pi^2 \sigma_1^4 \sigma^2 - \frac{1}{36} \frac{n_1^2 n_2}{V^2} \pi^2 \sigma_1^6 \\
 - \frac{8}{9} \frac{n_1 n_2^2}{V^2} \pi^2 \sigma_2^3 \sigma^3 + \frac{1}{2} \frac{n_1 n_2^2}{V^2} \pi^2 \sigma_2^4 \sigma^2 - \frac{1}{36} \frac{n_1 n_2^2}{V^2} \pi^2 \sigma_2^6 \dots (21)
 \end{aligned}$$

where β_1 has been put for $\frac{2}{3} \pi \sigma_1^3$, β_2 for $\frac{2}{3} \pi \sigma_2^3$ and β for $\frac{2}{3} \pi \sigma^3$.

Finally, differentiating Ψ with respect to V , we find the following equation for the pressure

$$\begin{aligned}
 \frac{p}{\theta} = \frac{n_1 + n_2}{V} + \frac{n_1^2 \beta_1}{V^2} + \frac{5}{8} \frac{n_1^3 \beta_1^2}{V^3} + \frac{n_2^2 \beta_2}{V^2} + \frac{5}{8} \frac{n_2^3 \beta_2^2}{V^3} + \frac{2 n_1 n_2 \beta}{V^2} \\
 - \frac{n_1^2 n_2}{V^3} \beta_1^2 \left(-4 \frac{\beta}{\beta_1} + \frac{9}{4} \frac{\beta \sigma}{\beta_1 \sigma_1} - \frac{1}{8} \right) \\
 - \frac{n_1 n_2^2}{V^3} \beta_2^2 \left(-4 \frac{\beta}{\beta_2} + \frac{9}{4} \frac{\beta \sigma}{\beta_2 \sigma_2} - \frac{1}{8} \right) \\
 - \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V^2}.
 \end{aligned}$$

The quantity θ is proportional to the absolute temperature.

The expression for p is of course symmetrical in the quantities relating to the two kinds of molecules, and it would have been possible to find the same result by arranging the spaces in a different order. Our result agrees with that of HAPPEL, the only difference being in the notations.