Physics. — "*The variability with time of the distributions of Emulsion-particles*". By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

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SMOLUCHOWSKI discussed this problem in different papers and gave a complete survey of his work in three lectures ad Göttingen.[1])

He deduced a formula for the average change of the number of particles in an element, which at the moment zero contains n particles. This formula is:

$$\overline{\Delta}_n = (\nu - n) P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P is the probability that a particle which lies in the element at the time zero. may have come outside in the moment t; whilst ν is the number of particles which at a homogeneous distribution over the whole volume would come to lie in the element in consideration.

Also for the average square with a given number of particles n at the time zero SMOLUCHOWSKI gives a formula, viz.

$$\overline{\Delta}^2 n = [(n - \nu)^2 + n] \; P^2 + (n + \nu) P, \quad . \quad . \quad . \quad . \quad (2)$$

from which follows — if the average also is determined according to n —

$$\overline{\Delta}^2 = 2 \, \nu \, P.$$

These relations are deduced by SMOLUCHOWSKI with the help of calculations of probability, which "nach Ausführung recht komplizierter Summationen (yield) merkwürdigerweise das einfache Resultat".

It goes without saying, that it must be possible to attain such a simple result also by a less complicated method. That this is indeed the case I want to demonstrate in this paper. At the same time it will be possible to give some extension to the result.

1. Let us think the space divided into a great number of equal elements, which we shall mark by the indices $1 \, . \, . \, \varkappa \, . \, . \, k$. Let there be at a given moment $t = 0$ $n_1 \, . \, . \, n_\nu \, . \, . \, n_k$ particles in

[1]) Cf. Phys. Zeitschr. 1916, p. 557 and also Phys. Zeitschrift XVI. 1915. p. 323.

these elements. After a time t has passed these numbers have become changed. Let $p_{1\varkappa}$ then represent the chance that a particle which at the time $t=0$ is in the element 1, is found at the time t in the element $\varkappa$, and let $p_{\varkappa 1}$ represent the probability of the reversed transition. Then, if there is no predilection for any direction in the movement of the particles, it goes without saying that $p_{1\varkappa}=p_{\varkappa 1}$.

Further $\sum_{\lambda=1}^{\lambda=k} p_{\varkappa\lambda}=P$ if the sum is taken according to all values λ except $\varkappa=\lambda$, for the sum represents the probability that the particle has come after the time t in one of the $k-1$ other elements, i.e. outside the element $\varkappa$.

If an element λ contains n_λ particles the number of particles having passed from λ to $\varkappa$ in a given case will be $\Delta_{\lambda\varkappa}$. I shall now calculate first the average values of $\Delta_{\lambda\varkappa}$, $\Delta^2_{\lambda\varkappa}$ and $\Delta_{\lambda\varkappa}\,\Delta_{\mu\varkappa}$. The number of cases where $\Delta_{\lambda\varkappa}$ has the value s and thus $n_\lambda - s$ particles have remained in the element, amounts to:

$$\frac{n_\lambda\,!}{n_\lambda-s\,!\,s\,!}\,p_{\lambda\varkappa}^{\,s}\,(1-p_{\lambda\varkappa})^{\,n_\lambda-s} \quad . \;.\;.\;.\;.\;.\;. \quad (3)$$

as is easily seen; to determine the three average-values this expression must be multiplied by s resp. s^2 and summed from zero to n_λ. Then after quite an elementary calculation of these finite sums, we find

$$\overline{\Delta_{\lambda\varkappa}^{\,2}}=p_{\lambda\varkappa}^{\,2}\,(n_\lambda^{\,2}-n_\lambda)+p_{\lambda\varkappa}\,n_\lambda \quad .. \;.\;.\;.\;.\;.\;. \quad (5)$$

and

$$\overline{\Delta_{\lambda\varkappa}}=p_{\lambda\varkappa}\,n_\lambda \quad .\;.\;.\;.\;.\;.\;.\;.\;. \quad (4)$$

To determine the average of a double product we need only replace (3) λ by μ and s by t (where t represent the number of emitted particles in a definite case).

If the result obtained in this way is multiplied by (3) and summed with respect to ν from 0 to n_λ and with respect to t from 0 to n_μ, we find

$$\overline{\Delta_{\lambda\varkappa}\,\Delta_{\mu\varkappa}}=p_{\lambda\varkappa}\,p_{\mu\varkappa}\,n_\lambda\,n_\mu \quad .\;.\;.\;.\;.\;.\;.\;. \quad (6)$$

With the help of the relations (4), (5) and (6) SMOLUCHOWSKI's formulae can now immediately be deduced. The change ${}_n\Delta_\varkappa$, i.e. the total change of the number of particles in the element $\varkappa$ may be represented by

$${}_n\Delta_\varkappa=\Delta_{1\varkappa}+\Delta_{2\varkappa}\ldots+\Delta_{k\varkappa}-(\Delta_{\varkappa 1}+\ldots\Delta_{\varkappa k})\;.\;\;.\;\;. \quad (7)$$

Now we can write $\Delta_\varkappa$ for $\Delta_{\varkappa 1}+\ldots\Delta_{\varkappa k}$, i.e. the total number of particles that leaves the element in the time t.

Then we must determine the average of (7) with constant $n_\varkappa$, while all possible values must be given to the number $n_1 \dots n_\varkappa$ in the other elements. If now we first take the $n_1 \dots n_\nu$ constant and determine the average, we find

$$ {}_n\overline{\Delta}_\nu = p_{1\nu}\, n_1 + \dots p_{k\nu}\, n_k - n_\varkappa\, P . $$

If then we proceed to determine the average according to $n_1 \dots n_\nu$ and keep in mind that $\overline{n_1} = \dots = \overline{n_\nu} = \nu$, we find

$$ {}_n\overline{\overline{\Delta}}_\nu = \nu\,(p_{1\nu} + \dots p_{k\varkappa}) - n_\varkappa\, P = (\nu - n_\varkappa)\, P . $$

In order to find ${}_n\overline{\Delta_\nu^2}$ we proceed in quite an analogous way, we bring (7) into the square. Then we find

$$ \begin{aligned} \Delta_\nu^2 = {} & \Delta_{1\nu}^2 + \dots \Delta_{k\nu}^2 + \Delta_\nu^2 \\ & + 2\,\Delta_{1\nu}\,\Delta_{2\varkappa} + \dots \\ & - 2\,\Delta_\nu\,(\Delta_{1\nu} + \dots \Delta_{k\varkappa}) . \end{aligned} $$

If now we apply (5) and (6) and determine the average with given $n_1 \dots n_k$ and n_ν, we find

$$ \begin{aligned} {}_n\overline{\Delta_\varkappa^2} = {} & (n_1^2 - n_1)\, p_{1\nu}^2 + p_{1\varkappa}\, n_1 + \dots + P^2\,(n_\nu^2 - n_\varkappa) + n_\nu\, P \\ & + 2\, n_1\, n_2\, p_{1\nu}\, p_{2\varkappa} + \dots \\ & - 2\, n\, P\,(p_{1\nu}\, n_1 + \quad p_{k\nu}\, n_k) . \end{aligned} $$

Here the average must be determined keeping constant n_ν with respect to n_1 etc. And we must bear in mind that $\overline{n_1^2} = \overline{n_2^2} = \dots \overline{n_\nu^2} = \nu^2 + \nu$ [1], that further $\overline{n_1} = \nu$ and $\overline{n_1 n_2} = \nu^2$. Consequently we find

$$ \begin{aligned} {}_n\overline{\overline{\Delta}}_\varkappa^2 = {} & (\nu^2 + \nu)\,(p_{1\varkappa}^2 + \dots p_{k\varkappa}^2) \\ & + 2\,\nu^2\,(p_{1\varkappa}\, p_{2\varkappa} + \dots \quad) \\ & - \nu\,(p_{1\varkappa}^2 + \dots \quad) \\ & - 2\, n\, \nu\, P^2 + P^2\,(n^2 - n) + n\, P . \end{aligned} $$

The three first terms together yield $P^2 \nu^2$. The result becomes thus

$$ {}_k\overline{\overline{\Delta^2}}_n = \{ (n-\nu)^2\, P^2 - n^2\, P^2 \} + (n + \nu)\, P_\lambda $$

from which by determining the average according to n the relation

$$ \overline{\Delta^2} = 2\,\nu\, P $$

arises.

2. The extension of the given formulae may be obtained to the case that the deviation of density in the various elements of volume are not independent, where however concerning the emission of the particles we must still presuppose independence of the events.

In order to introduce the correlation of the densities I make use of the function g, which was defined by Dr. ZERNIKE and myself. [2]

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[1] We have $n_1 = \nu + \delta$, $\overline{n_1^2} = \nu^2 + 2\,\nu\,\bar{\delta} + \overline{\delta^2} = \nu^2 + \nu$.
$\overline{n_1 n_2} = \overline{(\nu + \delta_1)\,(\nu + \delta_2)} = \nu^2 + \nu\,(\bar{\delta}_1 + \bar{\delta}_2) + \overline{\delta_1\, \delta_2} = \nu^2$.

[2] Chance deviations in density in the critical point of a simple matter. These Proc. XVII, 1914. p. 582.

If δ_0 is the deviation in density in a point $x = 0$, $y = 0$, $z = 0$, then we get for the deviation of density δ in a point x, y, z:

$$\overline{\delta} = g(x, y, z)\, \delta_0\, d v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where dv is the element of volume.

Further

$$\overline{\delta\, \delta_0} = g(x, y, z)\, \overline{\delta_0{}^2}\, dv = g(x\, y\, z)\, \varrho \quad . \quad . \quad . \quad . \quad (9)$$

where ϱ is the number of particles per unit of volume.

We now have

$$\overline{{}_n\Delta_\nu} = n_1\, p_{1\nu} + \ldots n_\nu\, p_{k\nu} - n\, P.$$

Now $\overline{n_1} = \nu + \overline{\delta_1}\, d\, v_1$, if then we introduce (8) and consider $p_{\lambda\nu}$ as function of $x\, y\, z$, bearing in mind that $\delta_0 = \dfrac{\nu - n_\nu}{dv}$, we find

$$\overline{\overline{{}_n\Delta_\nu}} = (\nu - n) \{ P + \int g_{\lambda\nu}\, p_{\lambda\nu}\, d\, v \}$$

The influence of the second part may become considerable with a strong correlation

Also in determining $\overline{\overline{{}_n\Delta^2{}_\nu}}$ the correlation can be taken into consideration. Then in the first place we get the old terms, but moreover (9) yields still new terms in $\overline{n_\lambda{}^2}$, $\overline{n_\lambda}$ and $\overline{n_\lambda\, n_\nu}$, $\overline{n_\lambda\, n_\mu}$. These terms are:

$$2\, \nu\, (\nu - n) \int p_{\lambda\nu}\, g_{\lambda x}\, d\nu$$

$$- (\nu - n) \int p_{\lambda x}{}^2\, g_{\lambda\nu}\, d\, \nu$$

$$- 2\, n\, P\, (\nu - n) \int p_{\lambda\nu}\, g_{\lambda\nu}\, d\, \nu$$

$$+ 2\, \nu \int p_{\lambda\nu}\, p_{\mu x}\, g_{\lambda\mu}\, d\, \nu_\lambda\, d\, \nu_\mu.$$

If then $\overline{\Delta^2{}_n}$ is determined, only the last term remains and a part of the term before last, so that we get

$$\overline{\Delta^2} = 2\, \nu\, (P + \int p_{\lambda\nu}\, p_{\mu\nu}\, g_{\lambda\mu}\, d\, \nu_\mu\, d\, \nu_\lambda$$

$$+ \int p_{\lambda}\, g_{\lambda x}\, d\, \nu).$$

These considerations may also be applied, as least approximately, to the changes, which accidental derivations in density undergo in result of diffusion. Our formulae show then that close to a critical point the deviations in density as a result of their correlation, are not only stronger on the average, but also more strongly changeable.

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