Citation:

L.S. Ornstein, Determination of the pressure of a gas by means of Gibb's statistical mechanics, in:
KNAW, Proceedings, 13 I, 1910, Amsterdam, 1910, pp. 135-137

Physics. — "*Determination of the pressure of a gas by means of* GIBBS' *statistical mechanics.*" By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of February 27, 1909).

Dr. O. POSTMA has made some remarks on the way in which I have calculated the pressure of a gas by means of GIBBS' statistical mechanics.

The first objection relates to formula (5) of my dissertation

$$\overline{A} = -\frac{\partial \Psi}{\partial a},$$

where $\overline{A}$ is the average in the ensemble of the force corresponding to the parameter a which is exerted by the system, and where Ψ is given by the relation

$$e^{-\frac{\Psi}{\Theta}} = \int e^{-\frac{\varepsilon}{\Theta}} d\lambda_p \, d\lambda_q ;$$

in this equation ε in the energy, $d\lambda_p$ an element of the extension in velocity and $d\lambda_q$ an element of the extension in configuration. The energy ε depends on the momenta, the coordinates and also on the parameter a. The force exerted by a single system is given by the relation

$$A = -\frac{\partial \varepsilon}{\partial a},$$

the coordinates and the momenta being kept constant in the differentiation. Assuming that the kinetic energy does not depend on the coordinates and integrating with respect to the velocities, we obtain:

$$e^{-\frac{\Psi}{\Theta}} = C \int e^{-\frac{\varepsilon_q}{\Theta}} d\lambda_q .$$

The magnitude of the part S of the extension in configuration where systems can be represented and over which therefore the integration has to be extended, depends on the parameter a; this is easily seen in those cases in which a determines the position of walls within which the system is confined. We may say that in the parts of the extension outside S the density of the distribution is zero because ε_q is infinite; and this is also true at the boundary of S.

Let us now consider the increment of $e^{-\frac{\Psi}{\Theta}}$ when a increases by an infinitely small amount da. The integral on the right-hand side changes for two reasons: 1 because ε_q changes in the part S of the extension over which the integral has to be taken when the parameter has the value a; 2 because there must be added an integral taken over a part of the extension S' which surrounds S as an infinitely thin layer. We obtain therefore

$$\delta \int e^{-\frac{\varepsilon q}{\Theta}} d\lambda_q = \int_S \delta e^{-\frac{\varepsilon q}{\Theta}} . d\lambda_q + \int_{S'} e^{-\frac{\varepsilon q}{\Theta}} d\lambda_q .$$

The second integral however is zero because ε_q is infinite everywhere in the layer S'. We obtain finally

$$\frac{\partial \Psi}{\partial a} = C \int_S \left(\frac{\partial \varepsilon_q}{\partial a} \right)_q e^{\frac{\Psi - \varepsilon q}{\Theta}} d\lambda_q = - \bar{A} .$$

Treating the integral, which we found for $e^{-\frac{\Psi}{\Theta}}$ as an ordinary multiple one whose limits depend on the parameter a, and differentiating this integral in the usual way with respect to a, we obtain the same result. There are no objections against this differentiation, as the integrated function has no singularities within the limits of integration. The theorem in question is now proved quite generally and we may immediately apply it to the particular case in which a is the volume v of a gas.

The first objection of Dr. POSTMA being removed in this way, his second objection amounts to this that I should have calculated Ψ by a wrong method. I cannot however, admit the truth of this remark. Dr. POSTMA says that I have limited myself to the most frequent system. It may be that page 62 of my dissertation makes this impression; but in the more detailed calculation which I have given page 111 I have not at all confined myself to the most frequent system. On the contrary, I have considered systems differing greatly from it. It is true that not all the systems of the ensemble have been taken into consideration, but the systems that were neglected fill only a very small part of the extension in configuration and the density of their distribution in the ensemble is very small. The value found for Ψ by formula (131) differs by a factor from that found by (43), but I have shown on page 127 that we may replace this factor by unity. The objection that ε_1 and ε_2 have been supposed to be discontinuous can easily be removed. Indeed, we may begin by considering ε_1 and ε_2 as continuous functions of the coordinates q and the parameter a; the case of discontinuity may then be treated as a limiting case. The validity of this method is shown on page 91 of my dissertation, where I have determined the virial of repulsive forces in this way. The forces on the walls admit of a similar treatment.[1])

It is also possible to calculate ε_1, ε_2, and ε_3 for the most frequent system either directly or by means of the virial, and to determine $\frac{\partial \varepsilon_0}{\partial v}$ $\left(\text{which differs from } \overline{\frac{\partial \varepsilon}{\partial v}}\right)$. The result is A_0 and we find that $A_0 = \overline{A}$. A direct proof of this latter theorem is obtained if after having determined A for each group of equivalent systems (of the number ζ) we calculate the mean value $\overline{A} = \frac{\Sigma_e (A\zeta)}{N}$. The sum must be taken for all possible groups of equivalent systems contained in the ensemble.

I hope to have shown by the above considerations that my determination of the pressure is free from the objections raised by Dr. POSTMA.

Geology. — *"Diluvial boulders from the island of Borkum."* By J. H. BONNEMA. (Communicated by Prof. G. A. F. MOLENGRAAFF).

Some years ago four boulders which had been found by Dr. LORIÉ on the beach of the island of Borkum were sent me with the request to ascertain their age. They excited my interest in a degree that I resolved to go to the island myself with the result that I found 21 pieces more. These 25 boulders are the subject of this short communication.

Both Dr. LORIÉ's boulders and those I have collected are from the northern beach of the middle part of the above-mentioned island, which part is called Tüsskendoor. In accordance with their locality the surface often shows the peculiar gloss produced by flying sand.

They are all of sedimentary origin, and consist of limestone, dolomite, or sandstone.

So far as they consist of one of the two first-mentioned substances they usually show long and narrow holes at the surface somewhat tighter in the middle, so that they resemble the shape of an 8. These holes are mostly about 2 mm. long. Their length, however, varies from 1 to 6 mm.

1) An equation of state may also be established if, without passing to the limiting case of discontinuity, we regard ε_1 and ε_2 as certain given functions of the coordinates and the parameters.