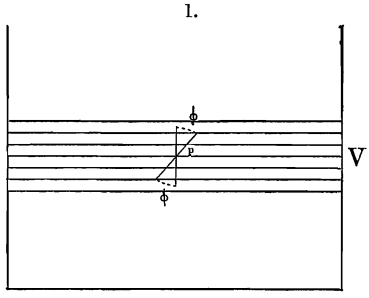
ART. XXIX.—*On the Mean Free Path of a Molecule;* by N. D. C. HODGES.

THE free path of a molecule is dependent on the amount of obstruction it meets with, on the density of the medium. Meyer gives for the mean free path on page 308 of his Kinetische Theorie der Gase, $L=\frac{1}{\pi\sqrt{2}N\xi^2}$. Here N is the number of molecules in the unit volume.

I consider the length of path in a medium of variable density. At the surface of a liquid, if there is no sharp transition from the liquid to the gaseous state, we shall have a succession of less and less dense vapors from where there is liquid to the surrounding atmosphere. The layers V (fig. 1) are what I refer to. The depth of these vapors, is of course, much magnified.

1.



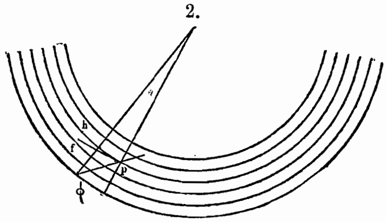
I propose to find the pressure upon the particle, p, when the surface of the liquid is plain and when it is spherical. Taking molecules moving with any definite velocity, they will reach p and give it an impulse, when they are at a distance from p less than their mean free path. Now, the particles from below come from denser layers than those from above. A greater number will come from below than from above; there will be a tendency to drive p upward. To find this tendency, we must find how much denser the lower layers, from which molecules impinging on p come, are than those above, from which particles come to p. If $\delta\rho$ is the obstruction met by a molecule in passing vertically upward through a single layer, $\frac{\delta\rho}{\cos\varphi}$ will be that met in the direction at an angle φ with the vertical. The integral $\frac{1}{\cos\varphi}\int_{\rho_0}^{\rho_1} d\rho$ gives the obstruction met by the molecule from one end to the other of its path. This integral must be constant, for the length of path is independent of the direction. As the differential of the obstruction is the same as the differential of the density,

$$\frac{1}{\cos\varphi}\int_{\rho_0}^{\rho_1} d\rho = \frac{\rho_1 - \rho_0}{\cos\varphi}$$

when ρ_0 is the density at the point p and ρ_1, that at the other end of the path. As $\frac{\rho_1 - \rho_0}{\cos\varphi} = \varkappa$, the numerator $\rho_1 - \rho_0$ must be proportional to $\cos\varphi$. The pressure on p is proportional to this difference, and the resultant component in the upward direction to $\cos^2\varphi$.

When the surface is spherical (fig. 2), each element of the path offers an obstruction expressed by $\frac{\delta\rho}{\cos(\varphi - \frac{1}{2}\alpha)}$ for the parts below p, and by $\frac{\cos(\varphi + \frac{1}{2}\alpha)}{\delta\rho}$ for those above p, α is the angle between the radius of curvature at the point p and that to the

2.



other end of the path. $\varphi - \frac{1}{2}\alpha$ is the mean value of the angle between the direction of the path and the normals to the surfaces of equal density for the parts below p, and $\varphi + \frac{1}{2}\alpha$ the corresponding angle for those above p.

Integrating, $\frac{\rho_1' - \rho_0'}{\cos(\varphi - \frac{1}{2}\alpha)} = \varkappa = \frac{\rho_0' - \rho_2'}{\cos(\varphi + \frac{1}{2}\alpha)}$. This shows that, whereas the difference in density above and below was the same for a plane surface, in the case of curved surfaces the pressure from below is greater, and that upward less. Or the pressure from below is greater, and that from above greater. This must cause a greater density at p.

The tendency for a particle to move from the liquid into the surrounding atmosphere is due to the difference in density of its liquid and of its vapor. For small changes in the density, the change in this tendency may be assumed as proportional to the change of density. It must be found what change in density takes place at p. As the change in density is due to an increase of pressure on p, this increase must be equal in all directions. So it is only necessary to consider one direction. Take the direction tangent to the curved surface at p. The increase in pressure is, therefore, proportional to the difference in density of the layer through f and that through h, or to the length fh. It is evident that $\frac{fh}{L} = \frac{\frac{1}{2}L}{r}$, when r is the radius of curvature, and L the length of the mean free path.

Hence we have $\frac{\text{the change of tension}}{\text{the tension of the vapor at plane surface}} = \frac{\frac{1}{2}L}{r}$

Sir William Thomson has shown that the change in tension at a curved surface is equal to the pressure of a column of the vapor of the height to which the liquid would rise in a capillary tube of a diameter of twice the radius of curvature of the surface.

In a tube of diameter $1{\cdot}294^{mm}$ water rises to a height of $23{\cdot}379^{mm}$. The data for the calculation are:

Weight of a liter of water vapor (at 100° C.)	·80357 grams
" " mercury	13·579 "
Tension of water vapor at 20° C.	$18{\cdot}495^{mm}$

The height of a column of mercury equivalent to the column of water vapor of height $23{\cdot}379^{mm}$ is

$$\frac{\cdot 80357}{13{,}579},\ 100,\ \frac{18{\cdot}495}{760},\ \frac{23{\cdot}379}{100}$$

The first factor is the fraction of a liter of mercury which a liter of water equals. The second reduces the height of this to millimeters. The third gives the result at 20° C., supposing the vapors to follow Boyle's law. The fourth is the fraction of a liter there was to be considered.

The expression for the mean free path in these surface vapors is then

$$\tfrac{1}{2}L = \cdot 647\frac{\cdot 80357}{13{,}579},\ 100,\ \frac{18{\cdot}495}{760},\ \frac{1}{18{\cdot}495}\ \frac{23{\cdot}379}{100}\ r = \cdot 647.$$

This gives $L = \cdot 0000024^{mm}$.

If the law according to which the density of the vapors vary with the depths was known, the free path of a molecule in a gas at the ordinary pressure could be found.

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