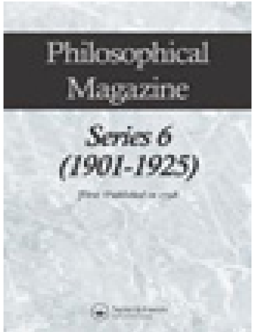

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Hence
$$\bar{r}_s'' = \frac{2p}{m} = 2\text{K}.$$

If we take Drude's values of n and nK, we obtain the following values of $\bar{r}_s''$:—

Metal.	n.	nK.	r_s''.
Silver	0·18	3·67	41
Gold	0·37	2·82	15
Sodium	0·005	2·61	1043

If n were zero, and nK not zero (Lord Kelvin's "ideal silver"), $\bar{r}_s''$ would be infinitely great! If we had a very thin film of sodium, and a ray of light were repeatedly reflected within the film at the proper angle, its intensity would be very much increased. This would be contrary to the conservation of energy. The explanation of course, is, that in such thin films the geometrical laws of reflexion and refraction do not hold.

The observations recorded in this and the preceding article were carried out in the Physical Institute of the University of Göttingen at the suggestion, and under the continual advice of Prof. W. Voigt.

IV. *Lord Rayleigh on the Virial Equation.*

By S. H. Burbury, *F.R.S.**

In his paper on this subject in the Philosophical Magazine for April 1905, Lord Rayleigh considers a system of molecules, elastic spheres, which also exert on each other finite forces. And concerning these forces he assumes that within the effective range of any type sphere there are many others, and that the forces which the type sphere exerts on the more distant molecules within this range are not inappreciably small compared with those which it exerts on its immediate neighbours. In his own language, the forces are "of the character considered in the theory of capillarity, that is extending to a range which is a large multiple of molecular distances, and not increasing so fast with diminishing distance as to make the total effect sensibly dependent upon the positions occupied by neighbours." Then he goes on to say: "Under these restrictions symmetry ensures that the resultant force upon a sphere, situated in the interior and not undergoing collision, is zero; and the whole effect of such forces is represented (Young, Laplace, Van der Waals)

* Communicated by the Author.

by an addition to the pressure of a quantity independent of the temperature and inversely proportional to the square of the volume."

By this he means one of two things, namely, (1) the resultant force on a molecule is zero on average of time; or (2) the resultant force is actually zero at every instant for a sphere not at that instant undergoing collision. If he means the first alternative, the resultant force must be zero on average of time if the motion be stationary. If, then, X, Y, Z be the component forces on a molecule, $\overline{X}$, $\overline{Y}$, $\overline{Z}$ their values on average of time, $\overline{X}=\overline{Y}=\overline{Z}=0$. But it does not follow that $\overline{Xx+Yy+Zz}=0$ on average of time, that is that the time average of the Virial for molecules in the interior is zero.

In fact, as admitted in Lord Rayleigh's paper, it is not true for the collision forces between elastic spheres. Neither then can it be true if the molecules are centres of repulsive force, becoming evanescent at distances very small compared with molecular distances. There is in fact no proof that $\overline{Xx+Yy+Zz}=0$ for molecules in the interior, and therefore no proof that the whole effect "can be represented by an addition to the pressure of a term independent of the temperature and proportional to $\frac{1}{v^2}$."

If we take the second alternative, that at every instant the resultant force is actually zero for every sphere not at that instant undergoing collision, Lord Rayleigh must mean by "symmetry," that his spheres, although in motion relatively to each other, are at every instant in some symmetrical arrangement such, to take an example, as at the angles of cubes or regular tetrahedrons. Is a motion possible in which this shall be the case at every instant? Without going so far as to say that no such motion is possible, we may say, I think, with confidence that it cannot be motion in accordance with Maxwell's law. Lord Rayleigh's system, then, is not a rare gas. Perhaps it may be a liquid, or a dense gas, to which Maxwell's law is inapplicable.

In order to form a theory of the motion of a system of mutually acting molecules, to which we cannot apply the ever recurring assumption of infinite rarity, we require to know what part is to be played by the potential, χ, of the intermolecular forces. In a statical system in stable equilibrium χ is minimum. What is the corresponding law for stationary motion in a dynamical system? I think Lord Rayleigh is the man to answer that question, if he could be induced to do so.

In the silence of the authorities, I have myself suggested that Boltzmann's $e^{-2h\chi}$ law supplies the necessary guidance. The chance that any group or system of molecules shall be in a configuration in which the potential of their mutual forces, and of the external forces if any, is χ, is proportional to $e^{-2h\chi}$. Or, if you prefer so to state it, the time during which on the average of any very long time they will be in that configuration is proportional to $e^{-2h\chi}$. That gives the minimum χ for a statical system as a particular case. For if χ_0 be the potential in the configuration A_0, and χ_1 in the configuration A_1, and if $\chi_0 < \chi_1$, A_0 is more probable than A_1 in the ratio $e^{2h(\chi_1-\chi_0)}$, that is in an infinite ratio in the statical system, for which h is infinite. The statical system must therefore be in minimum potential. Also if there be only external forces acting, Boltzmann's law gives $e^{-2h\chi}$ as *the density* at the point where the potential is χ, as in Maxwell's vertical column of air. I worked out the consequences of the application of the law to the general case in a former paper (Phil. Mag. for October 1901), and I think my conclusions were in the main right. If so, the law would be inconsistent with Lord Rayleigh's symmetry, and with its consequences. In fact it seems to me that Lord Rayleigh's symmetry and Boltzmann's law cannot both be true for one and the same system in the same state.

It may be said perhaps that Boltzmann's law holds only for external, and not for intermolecular forces. Some English writers, notably Dr. Watson, while not expressing their disagreement with the law as applied to intermolecular forces, prefer to let it alone. That I think arises from excess of caution, or perhaps because the law, if so applied, leads to results inconsistent with some favourite doctrines of the orthodox theory of gases. The proof of the law given by Boltzmann at p. 134 of his *Vorlesungen*, Part I., is formally applicable to intermolecular forces. Why may we not so apply it?

V. *Actinium and its Successive Products.*

By T. Godlewski, *Ph.D.* (*Cracow*)*.

RUTHERFORD and Soddy, in their well-known investigations† on the activity of thorium, have shown that it is possible to separate from it a very active constituent

* Communicated by Prof. E. Rutherford, F.R.S. Presented before the Academy of Sciences in Cracow, April 3, 1905.

† Rutherford and Soddy, Phil. Mag. Sept. and Nov. 1902; Trans. Chem. Soc. lxxxi. pp. 321 & 807 (1902).