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P. M. HEIMANN

**MOLECULAR FORCES, STATISTICAL
REPRESENTATION AND MAXWELL'S**

DEMON

I

THIS paper is concerned with Maxwell's discussion of the nature of molecular forces and of the use of statistical methods in gas theory, and with some epistemological and methodological aspects of his work on the kinetic theory of gases. His discussion of these problems arose from his two classic papers on gas theory: Maxwell used a statistical distribution function to describe the velocities of gas molecules and—it will be argued—his work on the theory of gases was governed by his interest in the nature of matter. In his first attempt to formulate a theory of gases, in 'Illustrations of the Dynamical Theory of Gases' (1860), he used an elastic-sphere model for the molecules and described collisions between such molecules.¹ He subsequently abandoned this molecular model in his paper 'On the Dynamical Theory of Gases' (1867), where he used a 'centre of force' molecule. In this paper he did not consider collisions, the impact of elastic spheres, but intermolecular encounters, the interactions between 'centres of force'.² In his later work on gas theory he further considered the problem of the nature of molecular forces and came to question the principle that the same laws applied to micro- as to macro-phenomena; I will suggest that he implicitly questioned the transference of the laws of dynamics to the motions of individual molecules.

His use of statistical representation to describe the velocities of gas molecules was fundamental to his theory of gases. Maxwell did not consider that this method was a temporary mode of representation which would be replaced by a treatment of the motions of individual molecules, but regarded it rather as a method imposed by the phenomena, that is, by experiments on sensible aggregates of molecules. He nevertheless argued that individual, insensible molecules were not subject to 'chance and change', for their behaviour was 'certain and immutable';³ the statistical method was not applicable to the motions of individual molecules. Here I

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