Studies in History and Philosophy of Modern Physics 57 (2017) 53–65

Contents lists available at ScienceDirect

Studies in History and Philosophy of Modern Physics

journal homepage: www.elsevier.com/locate/shpsb

Maxwell and the normal distribution: A colored story of probability, independence, and tendency toward equilibrium

Balázs Gyenis

Institute of Philosophy, HAS RCH, 4 Tóth Kálmán Str Budapest, Hungary

ARTICLE INFO

Article history:
Received 4 January 2015
Received in revised form
21 November 2016
Accepted 16 January 2017
Available online 4 February 2017

Keywords:
Maxwell
Kinetic theory
Statistical mechanics
Normal distribution
Independence
H-theorem
Second law of thermodynamics
Condition A

ABSTRACT

We investigate Maxwell's attempt to justify the mathematical assumptions behind his 1860 Proposition IV according to which the velocity components of colliding particles follow the normal distribution. Contrary to the commonly held view we find that his molecular collision model plays a crucial role in reaching this conclusion, and that his model assumptions also permit inference to equalization of mean kinetic energies (temperatures), which is what he intended to prove in his discredited and widely ignored Proposition VI. If we take a charitable reading of his own proof of Proposition VI then it was Maxwell, and not Boltzmann, who gave the first proof of a tendency towards equilibrium, a sort of H-theorem. We also call attention to a potential conflation of notions of probabilistic and value independence in relevant prior works of his contemporaries and of his own, and argue that this conflation might have impacted his adoption of the suspect independence assumption of Proposition IV.

When citing this paper, please use the full journal title *Studies in History and Philosophy of Modern Physics*

1. Introduction

James Clerk Maxwell's early work on the kinetic theory of gases was a major step-stone in the introduction of probabilistic methods into physics. Proposition IV of Maxwell's (1860) *Illustrations of the Dynamical Theory of Gases*, his first derivation of the velocity distribution law, is frequently cited as “one of the most important passages in physics” (Truesdell, 1975, p. 34) and as such had been thoroughly investigated in the works of Brush (1958, 1971, 1976, 1983); Dias (1994); Brush, Everitt, and Garber (1986a); Garber (1970); Gillispie (1963); Heimann (1970); Porter (1981); Truesdell (1975); Uffink (2007) and other historians of science. Proposition IV shows that, given certain assumptions, the three velocity components of molecules of a box of gas follow the normal distribution and the speed (the magnitude of velocity) follows what nowadays is called the Maxwell-Boltzmann distribution.

This paper provides a new conceptual and historical analysis of Maxwell's derivation. We make four contributions to the literature. First, the paper sheds new light on the logical structure of Proposition IV and gives the first detailed analysis of how Maxwell attempted to physically justify the three main mathematical assumptions on which it rests. This allows us to show, second, that contrary to the common historical wisdom molecular collisions did play an essential role in establishing the conclusion of Proposition IV: one of its three mathematical assumptions requires a prior lemma showing that collisions among particles of the same mass bring about an equilibrium velocity distribution, and we argue that Maxwell indeed made an attempt to lend credence to such an approach to equilibrium on the basis of his Propositions I–III.

To substantiate this claim we take a look at Maxwell's remarks preceding Proposition IV as well as at his attempt to arrive at a proof of tendency towards equilibrium in his discredited and widely ignored Proposition VI. We present a surprisingly simple proof of tendency towards equilibrium that rests on Propositions I–III, both in the relevant special case when all particles have the same mass and in the general case when masses differ. Although this proof of equalization of temperatures is interesting in its own right and is not known by experts, we argue that it is not novel since its general case is nothing but a charitable reconstruction of Maxwell's Proposition VI. Since the charitable reading of Proposition VI provides a proof of tendency towards equilibrium in the general case, and since the special case of this proof is really

E-mail address: gyepi@hps.elte.hu
URL: http://hps.elte.hu/~gyepi

http://dx.doi.org/10.1016/j.shpsb.2017.01.001
1355-2198/

simple, it is reasonable to assume that Maxwell's brief remarks preceding Proposition IV are at least partially motivated by this special case. Additionally, if the charitable reading is tenable then Maxwell preceded Ludwig Boltzmann by at least 6 years in providing a mechanical argument for tendency towards equilibrium, and this priority of Maxwell should be more widely recognized.

Fourth, the paper contributes to the scholarly discussion of the crucial and arguably unjustified probabilistic independence assumption of Proposition IV. The conflation of different interpretations of probability have already been pointed out in the literature as a potential source of Maxwell's mistake in accepting this independence assumption; besides furthering this analysis we also provide a novel interpretation according to which Maxwell, instead of conflating different interpretations of probability, might have conflated different notions of independence. We distinguish two notions – probabilistic independence and value (or parameter) independence –, argue that their difference was not clear in the relevant works of Clausius and Herschel, and point out that in fact Herschel mistakenly emphasized that it is the satisfaction of value independence that is crucial for the proof that Maxwell allegedly have adapted as his Proposition IV. Thus if Maxwell indeed adapted the proof from Herschel's review article then he also likely to have accepted Herschel's assessment of the assumption on which “the whole force of the proof turns.” This in turn could explain why Maxwell was content with the physical justification of the independence assumption since value independence of the velocity components would have appeared immediately clear. Although there seems to be no conclusive evidence deciding which of these two conflations were committed by Maxwell (maybe both), we point out that in his prior and contemporaneous work Maxwell means value independence when he is discussing “independence”.

The paper is organized as follows. Section 2 starts with a reconstruction of Maxwell's proof of Proposition IV and identifies the three mathematical assumptions (of existence, independence, and symmetry) that are required for the proof to work. We work backwards from here, first historically, then conceptually. We recall Maxwell's own wording of his proof of Proposition IV and contrast it with a proof of Herschel that has been identified by historians as its likely source. Section 3 also briefly reviews the existing historical literature regarding Maxwell's attempt to justify the mathematical assumptions of Proposition IV. Section 4 reviews the particle collision model of Maxwell's Proposition I–III and identifies a crucial assumption (Condition M) that is needed for Proposition II to work. Section 5 shows how Proposition I–III and Condition M can be used to argue for the equalization of mean kinetic energies and contrasts the argument with Maxwell's Proposition VI. Section 6 distinguishes between two independence notions and calls attention to the conflation of these two notions in the works of Herschel, Clausius, and Maxwell. Section 7 puts the pieces back together by analyzing the extent to which the three aforementioned mathematical assumptions of Proposition IV – that of existence (Section 7.1), independence (Section 7.2), and symmetry (Section 7.3) – could be physically justified by Maxwell's collision model (Table 1).

2. Proposition IV – Maxwell's derivation

As we know from a 1859 letter to George Gabriel Stokes (Maxwell, 1859, p. 277), Maxwell's interest in the kinetic theory of gases was aroused by the papers of Rudolf Clausius. Clausius was mainly interested in explaining heat in terms of molecular motion, and in his 1857 article he used an elastic sphere model to establish a connection between the average kinetic energy and the pressure of the gas. This treatment met the criticism of a Dutch meteorologist, Buys-Ballot (1858): if, as calculations suggest, the molecules of a gas move at speeds of several hundreds meters per second, odors released in one corner of a room should almost instantly be noticed in the other corner. To answer the objection, Clausius (1858); (1859) attempted to show that repeated collisions prevent molecules from traveling for great distances in straight lines. These considerations led him to introduce the notion of the mean free path (for further historical details see Brush et al., 1986a; 1986b). Maxwell developed the approach further in his *Illustrations of the Dynamical Theory of Gases* (Maxwell, 1860).

Table 1
Linear structure of the beginning of the Illustrations of the Dynamical Theory of Gases (1860) with the sections where they are analyzed in this paper.

Illustrations locus	Content	Section(s)
Proposition I–III	Analysis of particle collisions; *Condition M* appears as a hidden assumption of Proposition II.	4, 6, 7
'If a great many equal spherical particles were in motion […]'	Claim that collisions would lead to a stable kinetic energy (temperature) and velocity distribution.	5, 7
Proposition IV	Derivation of velocity distribution.	2, 3, 6, 7
Proposition V	Derivation of relative velocity distribution.	(2)
Proposition VI	Collisions lead to an equalization of temperatures of a mix of gases.	5, 7

The main goal of Herapath, Waterston, Krönig and Clausius was to establish the kinetic theory as a bridge between thermodynamics and atomic theory. However, the focus of the *Illustrations* is on problems of viscosity, diffusion and heat conduction: Maxwell attempted to treat these as special cases of a general process in which momentum or energy is transported by molecular motion. To investigate these transport properties he relied on results he derived about the velocity distribution of a gas in his Proposition IV.

Proposition IV aims to show that in a box of gas the number of particles whose velocity component in a particular direction lies between v_x and $v_x + dv_x$ is proportional to $e^{-\frac{v_x^2}{a^2}}$ and that the number of particles whose speed lies between v and $v + dv$ is proportional to $v^2 e^{-\frac{v^2}{a^2}}$, where a is a parameter which gets determined later. In essence the proof relies on the fact that the only solution of the functional equation

$$f^2(0)\cdot f(|\vec{v}|) = f(v_x)\cdot f(v_y)\cdot f(v_z) \tag{1}$$

is the Gaussian

$$f(v_x) = C\cdot e^{A\cdot v_x^2}. \tag{2}$$

Eq. (1) arises from three assumptions: that

(A1) a stationary velocity distribution exists;
(A2) the components of velocity in an orthogonal coordinate system are independent;
(A3) the velocity distribution only depends on the magnitude of the velocity.

If we denote the stationary velocity distribution of (A1) with $\mathbf{f}(\vec{v})$ and if by “independence” we mean probabilistic independence (treating the velocity components as random variables) then (A2) translates to $\mathbf{f}(\vec{v}) = \mathbf{f}_x(v_x)\mathbf{f}_y(v_y)\mathbf{f}_z(v_z)$ and (A3) translates to rotational symmetry of $\mathbf{f}$, namely that there exists a function g for which $\mathbf{f}(\vec{v}) = g(|\vec{v}|)$. Noting that $\mathbf{f}_x$, $\mathbf{f}_y$, and $\mathbf{f}_z$ are distributions it is easy to show that $f \doteq \mathbf{f}_x = \mathbf{f}_y = \mathbf{f}_z$ and that $g(.) = f^2(0)\cdot f(.)$, leading to Eq. (1).