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Violation of Boltzmann's H Theorem in Real Gases*

E. T. Jaynes
Arthur Holly Compton Laboratory of Physics, Washington University, St. Louis, Missouri 63130
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The well-known variational (maximum-entropy) property of the Maxwellian velocity distribution is used to shed some light on the range of validity of the Boltzmann transport equation. It permits a characterization of the initial states for which the Boltzmann H theorem is violated. In particular, it is shown that: (a) Any monatomic system for which the equilibrium potential energy exceeds the minimum possible value possesses a continuum of initial states for which the approach to equilibrium takes place through an increase, rather than a decrease, in Boltzmann's H. (b) If the initial distribution of particles is spatially homogeneous and Maxwellian, the approach to equilibrium will take place through an increase (decrease) in the Boltzmann H, according as the initial potential energy is less (greater) than the equilibrium value. (c) A necessary condition for the H-theorem-violating phenomenon is that the approach to equilibrium takes place through a conversion of kinetic energy into potential energy; a sufficient condition requires also that the initial velocity distribution be sufficiently close to Maxwellian. (d) These H-theorem-violating conditions are readily attained experimentally; for example, the free expansion of oxygen gas at 160 °K and 45-atm pressure produces an experimentally realizable violation of the Boltzmann H theorem.

I. INTRODUCTION

Ever since the famous *Umkehreinwand* and *Wiederkehreinwand* of Zermelo and Loschmidt, it has been clear that the Boltzmann H theorem, and therefore the Boltzmann transport equation, cannot be of universal validity, even for a dilute gas. Any system possesses certain initial states for which the H theorem is violated. In one sense, these H-theorem-violating states can be characterized at once, as those in which the particle positions and velocities are so correlated that *Stosszahlansatz* fails to hold. However, this is very abstract, and gives no hint as to how, or whether, such states could be produced experimentally.

It is often supposed that these H-theorem-violating states are in some way exceptional, so that they may be disregarded in practice. While this conclusion is undoubtedly correct in many cases, we show below that when the system has an appreciable potential energy, there is a class of initial conditions for which interparticle forces automatically produce and maintain H-theorem-violating states, with the result that $\dot{H}$ remains positive, on the average, throughout the approach to equilibrium. These conditions are, moreover, in no way exceptional; they can be (and undoubtedly have been) produced experimentally.

The existence of this H-theorem-violating phenomenon was pointed out briefly at the end of the writer's Brandeis lectures[1] on statistical mechanics; however, the class of states for which it occurs was described incompletely, in terms of the average force acting on a particle. We obtain below a simpler description, in terms of the kinetic and potential energy of the system.

II. DERIVATIONS

Consider a monatomic fluid consisting of N particles of mass m, confined to a box of volume V,

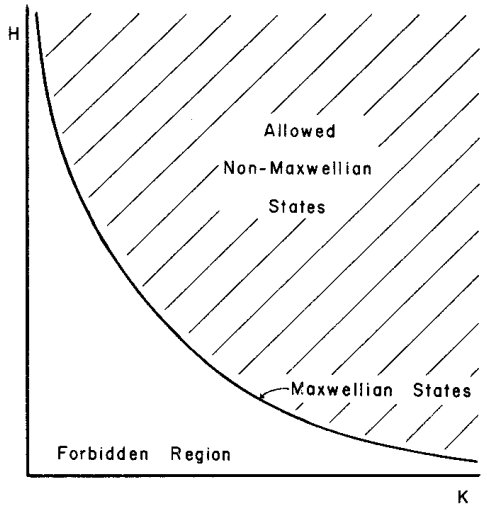

FIG. 1. Possible states in the K-H plane, allowed by Eq. (2.4).

interacting through a potential energy $U(x_1 \cdots x_N)$ which is a symmetric function of the coordinates x_i. All integrations over the coordinates and velocities, d^3x, d^3v, are understood to be over the volume V, and all of velocity space, respectively. The Boltzmann distribution function $f(x, v, t)$ is normalized so that the number of particles, total kinetic energy, and Boltzmann H are given, respectively, by

$$N = \int f(x, v, t)\, d^3x\, d^3v, \tag{2.1}$$

$$K = \int \tfrac{1}{2} m v^2 f(x, v, t)\, d^3x\, d^3v \ , \tag{2.2}$$

$$H = \int f \ln f\, d^3x\, d^3v \ . \tag{2.3}$$

The basic variational property is

$$H \geq N\left[\left(\ln\left(\frac{N}{V}\right) - \frac{3}{2} + \frac{3}{2}\ln\left(\frac{3Nm}{4\pi K}\right)\right]\right. \ , \tag{2.4a}$$

or more briefly,

$$H \geq A - B\, \ln K \ , \tag{2.4b}$$

where, for fixed N, V, the constants A and B are independent of the microstate. The equality applies in (2.4) if and only if $f(x, v, t)$ is equal "almost everywhere" to the Maxwellian distribution

$$f_M(x, v, t) \equiv (N/V)(\lambda/\pi)^{3/2} e^{-\lambda v^2} \ , \tag{2.5}$$

with

$$\lambda \equiv 3Nm/4K \ . \tag{2.6}$$

Proof. On the positive real axis, $\ln z \leq (z - 1)$, with equality if and only if $z = 1$. Therefore,

$$\int f \ln(f_M/f) d^3x\, d^3v \leq \int f\left[(f_M/f) - 1\right] d^3x\, d^3v = 0 \ , \tag{2.7}$$

with equality if and only if $f = f_M$ almost everywhere. The inequality (2.7) is equivalent to

$$H \geq \int f \ln f_M\, d^3x\, d^3v, \tag{2.8}$$

and on evaluating the right-hand side of (2.8), we have the result (2.4).

The above assertions now follow from the graphical interpretation of (2.4). Figure 1 represents the plane whose coordinates are the Boltzmann H and the total kinetic energy K. Any microstate determines a point on this plane; a given point corresponds, of course, to many different microstates. According to (2.4), the possible microstates are all mapped onto the shaded region lying above the curve $H = A - B \ln K$, which represents the locus of all spatially homogeneous Maxwellian velocity distributions; the Maxwellian states thus form the boundary between allowed and forbidden regions of the plane.

Starting from any initial state, represented by a point P, the approach to equilibrium is represented by some trajectory in this plane. We assume that, for an isolated system with a fixed total energy E, there is a unique final equilibrium point P_{eq} which (i) depends only on E, and not on the particular initial state, and (ii) lies on the Maxwellian boundary.[2]

If the system is a nearly ideal gas, so that the potential energy is negligible, then the kinetic energy is a constant of the motion, and this trajectory can only be a vertical line terminating at the Maxwellian boundary, in agreement with the Boltzmann H theorem. If there is an appreciable potential energy of interaction, the image point may move laterally, representing an interconversion of kinetic and potential energy.

In Fig. 2, we show the locus of possible initial states corresponding to a given total energy E. The potential energy is assumed to have a unique minimum possible value U_{min}, and so the kinetic energy must be bounded by $0 \leq K \leq K_{max}$, where $K_{max} \equiv E - U_{min}$. If the equilibrium kinetic energy

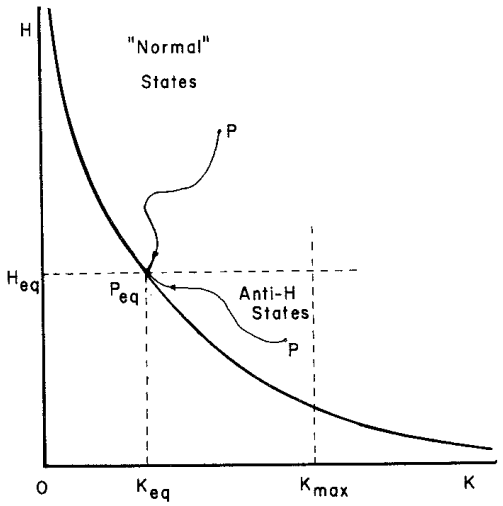

FIG. 2. Location of H-theorem-violating states.

is less than K_{max}, there is a triangular region of H-theorem-violating states, from which the approach to the equilibrium point necessarily requires an average increase, rather than a decrease in H.

It is seen that a necessary condition for the H-theorem-violating phenomenon is that the initial kinetic energy be greater than K_{eq}, so that kinetic energy is converted into potential energy in going to equilibrium. The other statements (a)–(c) made in the abstract are equally evident from inspection of Fig. 2. It is interesting that the Maxwellian initial velocity distribution represents a "maximally H-theorem-violating" condition, in the sense that for a given amount of kinetic-potential-energy conversion, one obtains the maximum possible increase in H.

III. DISCUSSION

In spite of implications to the contrary sometimes found in the literature, the Boltzmann H theorem is not a demonstration of the second law of thermodynamics.[3] The H-theorem-violating phenomenon therefore in no way represents a violation of the second law. As we have shown elsewhere,[4] in systems with an appreciable potential energy the entropy is not determined by the Boltzmann H, but by the Gibbs H, which is appreciably different and does not increase. These points are perhaps emphasized most strongly by citing definite experiments in which, if we attempted to define the entropy in terms of the Boltzmann H, we would be forced to conclude that the second law had been violated.

In order to realize the H-theorem-violating phenomenon experimentally, one must produce an initial nonequilibrium state in which the kinetic energy is greater than its final equilibrium value. This might be accomplished by suddenly adding kinetic energy to a system; thus in the initial stages of an explosion, particles acquire a high kinetic energy, and the subsequent hydrodynamic motion separates them against attractive forces; in some cases it might be possible to produce the H-theorem-violating condition in this way.

An easier method is to remove suddenly a volume constraint (for example, by opening a valve), thus allowing a gas to expand freely into a vacuum. From (2.4) and the relation $K=\frac{3}{2}NkT$, the Boltzmann H for a system in thermal equilibrium at temperature T may be written as

$$H=C-N\ln V-\tfrac{3}{2}N\ln T \quad , \tag{3.1}$$

where C is independent of the thermodynamic state. If the gas is allowed to expand freely from volume V to an infinitesimally greater one $V+\delta V$, the condition that H will increase in going to the new equilibrium state is thus

$$\left(\frac{\partial T}{\partial V}\right)_E < -\frac{2T}{3V} \quad , \tag{3.2}$$

from which it appears that the substances commonly used as refrigerants would be the best candidates; however, this condition is readily attained with almost any gas, as the following argument shows.

Using well-known thermodynamic identities, the condition (3.2) may be written in terms of the equation of state as

$$T\left(\frac{\partial P}{\partial T}\right)_V - P > \frac{2C_v T}{3V} \quad , \tag{3.3}$$

where P is the pressure, and C_v the specific heat at constant volume. For a gas obeying the van der Waals equation of state $(P+aV^{-2})(V-b)=NkT$, (3.3) reduces to $2C_vTV<3a$, which can always be satisfied above the critical temperature by sufficiently high pressure.

In terms of the enthalpy, $h\equiv E+PV$, (3.3) becomes

$$\left(\frac{\partial h}{\partial T}\right)_V - \frac{PV}{T} > \tfrac{5}{3}C_v \quad , \tag{3.4}$$

in which form the left-hand side can be read off from the published Mollier charts for various substances. From the Mollier chart of oxygen[5] we find that for 1 mole at $T=160\ ^\circ$K, $P=45$ atm, $(\partial h/\partial T)_V=12$ cal deg^{-1}, and $V=200$ cm^3, from which $PV/T=1.3$ cal deg^{-1}, making the left-hand side of (3.4) equal to 10.7 cal deg^{-1}. Since $C_v=\frac{5}{2}Nk=5.0$ cal deg^{-1}, the right-hand side of (3.4) is 8.3 cal deg^{-1}. The inequality is thus well satisfied, and we conclude that free expansion of oxygen gas at 160 °K and 45 atm would produce a violation of the Boltzmann H theorem. (Although in Sec. II we had in mind the case of a monatomic gas, the analysis is valid for polyatomic ones, provided we interpret K as representing only the translational kinetic energy.)

It has, of course, been recognized from the start that the original derivation of the Boltzmann transport equation, from which the H theorem follows, is valid only for a dilute gas. This in itself does not prove that the transport equation is necessarily incorrect in other cases; and indeed it has been used extensively in treatments of transport phenomena in imperfect gases, liquids, plasmas, and solids, while many attempts have been made to derive it under less restrictive assumptions than used by Boltzmann. To the best of the writer's knowledge, these analyses have not led previously to the discovery of specific experimental situations in which the Boltzmann equation can be shown to give a qualitatively incorrect result. In the case of oxygen at 160 °K and 45 atm, the mean free path estimated from the kinetic theory cross sections is

still about 15 Å; so one might have expected Boltzmann's assumptions to be more nearly justified than in many applications to plasmas and solids. Our results suggest that, instead of seeking to characterize the *physical systems* for which the Boltzmann transport equation is valid, it may be more appropriate to seek, for a given physical system, to characterize the *initial states* for which it is valid. The analysis given here, of course, is very far from answering this question.

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[1]E. T. Jaynes, in *Statistical Physics*, edited by K. W. Ford (Benjamin, New York, 1963), Vol. 3, Chap. 4.

[2]This assumption appears to be one of the "fundamental" propositions of statistical mechanics; i. e., one which has never been proved or doubted; and we do neither here. We have, of course, the well-known fact that the Maxwellian distribution with a particular partitioning of total energy between kinetic and potential, corresponds to an overwhelmingly greater phase volume than any other disposition of the energy; this makes it highly plausible, but does not prove, that a physical system will go to this equilibrium condition. In addition, we have excellent experimental evidence that the assumption is correct for all systems; otherwise it is very hard to see how the propositions of elementary thermodynamics (existence of a definite, reproducible equation of state, heat capacity, etc.) could be valid.

[3]For a particularly clear explanation of this point, see T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), pp. 91–96.

[4]E. T. Jaynes, Am. J. Phys. 33, 391 (1965).

[5]R. B. Scott, *Cryogenic Engineering* (van Nostrand, Princeton, N. J., 1959).