external field, represented by $f_{ext}(t)$, then the Langevin Equations (2.14) are modified to

$$\dot{q} = p/m, \quad \dot{p} = -2\kappa p - m\omega^2 q + f(t) + f_{ext}(t).$$

[20]This result also holds good in presence of an external field but with $\langle q(t) \rangle$ and $\langle p(t) \rangle$ replaced by

$$\langle q(t) \rangle + \int_0^t d\tau\, f_{ext}(t-\tau)\,(\sin\omega_0\tau/m\omega_0)\, e^{-\kappa\tau},$$

$$\langle p(t) \rangle + \int_0^t d\tau\, f_{ext}(t-\tau)[\cos\omega_0\tau - (\kappa/\omega_0)\sin\omega_0\tau]e^{-\kappa\tau},$$

respectively.

[21]Since $\mathfrak{F}(t)$ is a *complex* Gaussian random process with zero mean, its characteristic functional $\xi[\lambda(\cdot)]$ defined by

$$\xi[\lambda(\cdot)] \equiv \langle \exp\{i\int [\lambda^*(t)\mathfrak{F}(t) + \lambda(t)\mathfrak{F}^*(t)]dt\}\rangle$$

is given by

$$\xi[\lambda(\cdot)] = \exp\left\{-\tfrac{1}{2}\int\int [\lambda^*(t)\lambda^*(\tau)\langle \mathfrak{F}(t)\mathfrak{F}(\tau)\rangle \right.$$
$$+ \lambda(t)\lambda(\tau)\langle \mathfrak{F}^*(t)\mathfrak{F}^*(\tau)\rangle + \lambda^*(t)\lambda(\tau)\langle \mathfrak{F}(t)\mathfrak{F}^*(\tau)\rangle$$
$$\left. + \lambda(t)\lambda^*(\tau)\langle \mathfrak{F}^*(t)\mathfrak{F}(\tau)\rangle]\,dt\,d\tau\right\}.$$

[22]G. S. Agarwal, Phys. Rev. A **3**, 828 (1971).

[23]These identities are easily proved by making use of the general theory developed in Refs. 8(a) and 8(b).

[23a]We may also eliminate the rapidly oscillating terms directly from the stochastic equation (2.6) and then in the weak-coupling limit, we obtain the Fokker-Planck equation (3.2). For an excellent discussion of this elimination procedure, see, for example, R. L. Stratonovich, Ref. 5, Vol. II, p. 113.

[24]We have made use of the identity (1.18) given in V. Bargmann, Commun. Pure Appl. Math. **14**, 187 (1961).

Violation of Boltzmann's *H* Theorem in Real Gases*

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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 ap-

preciable 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

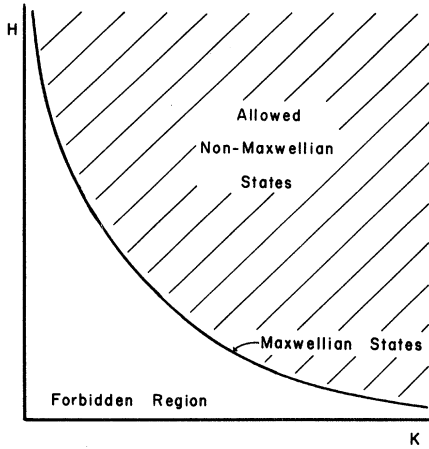Consider a monatomic fluid consisting of N particles of mass m, confined to a box of volume V,

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 ve-
locities, 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, re-
spectively, by

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

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

$$H = \int f \ln f \, d^3x \, d^3v \ . \qquad (2.3)$$

The basic variational property is

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

or more briefly,

$$H \geq A - B \ln K \ , \qquad (2.4b)$$

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

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

with

$$\lambda \equiv 3Nm/4K \ . \qquad (2.6)$$

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

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

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

$$H \geq \int f \ln f_M \, d^3x \, d^3v, \qquad (2.8)$$

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

The above assertions now follow from the graph-
ical 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 cor-
responds, 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 dis-
tributions; 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 repre-
sented 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 Max-
wellian 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 tra-
jectory 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 interconver-
sion 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
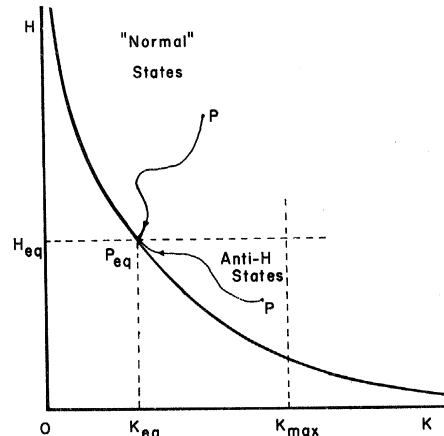$K_{max} \equiv E - U_{min}$. If the equilibrium kinetic energy

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 ap-
proach to the equilibrium point necessarily re-
quires 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 "maxi-
mally *H*-theorem-violating" condition, in the sense
that for a given amount of kinetic-potential-energy
conversion, one obtains the maximum possible in-
crease in *H*.

III. DISCUSSION

In spite of implications to the contrary some-
times 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 vio-
lation of the second law. As we have shown else-
where,[4] in systems with an appreciable potential
energy the entropy is not determined by the Boltz-
mann *H*, but by the Gibbs *H*, which is appreciably
different and does not increase. These points are
perhaps emphasized most strongly by citing def-
inite experiments in which, if we attempted to de-
fine 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 $K=\tfrac{3}{2}NkT$, the Boltz-
mann *H* for a system in thermal equilibrium at
temperature *T* may be written as

$$H = C - N\ln V - \tfrac{3}{2}N\ln T , \qquad (3.1)$$

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 con-
dition that *H* will increase in going to the new
equilibrium state is thus

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

from which it appears that the substances common-
ly used as refrigerants would be the best candi-
dates; 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

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

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 $2C_v TV < 3a$, which can always be
satisfied above the critical temperature by suf-
ficiently high pressure.

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

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

in which form the left-hand side can be read off
from the published Mollier charts for various sub-
stances. From the Mollier chart of oxygen[5] we
find that for 1 mole at $T = 160\,°K$, $P = 45$ atm,
$(\partial h/\partial T)_V = 12\,\text{cal deg}^{-1}$, and $V = 200\,\text{cm}^3$, from which
$PV/T = 1.3\,\text{cal deg}^{-1}$, making the left-hand side of
(3.4) equal to $10.7\,\text{cal deg}^{-1}$. Since $C_v = \tfrac{5}{2}Nk = 5.0$
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 trans-
port 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 phenom-
ena 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 Boltz-mann'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 Max-wellian 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).

Theory of Superfluidity

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The generator-coordinate method, well known in nuclear physics, is employed to derive the Bogoliubov theory of superfluidity of a boson system. The treatment is fully number conserving. Analogies to a *normal* Fermi system (especially to the random-phase approximation for that system) are pointed out, and some further insight into the nature of superfluidity is gained. Possible generalizations are mentioned.

I. INTRODUCTION

The generator-coordinate method[1-4] is well known as a powerful means of treating nuclear systems, and is especially useful for describing collective properties of nuclei. One of its virtues is a simul-taneous treatment of both the ground state and the low-lying states of the system. One of its applica-tions was an alternative derivation, by Jancovici and Schiff,[5] of the random-phase approximation (RPA) for a normal Fermi system. Extensions of the Jancovici-Schiff treatment to a derivation of a higher RPA[6] as well as to a pairing Fermi system[7] have been suggested. There is nothing in the meth-od which would limit its usefulness to the realm of nuclear physics only. In fact, it may find applica-tions in various other many-body systems. The purpose of the present paper is to call attention to the applicability of the method to a many-boson system and, in particular, to show that a fully number-conserving application of the method, in a form closely analogous to the Jancovici-Schiff derivation of the RPA, yields a number-conserving version of the Bogoliubov theory of superfluidity.[8-11]

The relation between the Bogoliubov transformation in a boson system and the *summation* of the RPA *diagrams* has been known for a long time.[9,12] How-ever, up to now it has been derived within the con-text of a particle number nonconserving formalism, which keeps only the *average* number of particles fixed. It is interesting to note that the Jancovici-Schiff derivation of the RPA for a Fermi system does *not* yield the pairing effects. The BCS and Bogoliubov-Valatin results in the theory of super-conductivity are derived only at the expense of in-troducing states which do not conserve the number of particles. Usually, the Bogoliubov-Valatin quasiparticles in the theory of superconductivity are considered the analogs of the quasiparticles representing the low-lying states of a superfluid boson system. However, the present formalism implies that the latter states are rather the analogs of the RPA collective particle-hole modes of a *normal* Fermi system. Although we will not carry it out in the present publication, it is tempting to include number nonconservation in the present formalism, in the manner used in Ref. 7 for the discussion of the so-called "pairing vibrations"