

An Approach to Equilibrium

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In this paper the concept of statistical equilibrium of an isolated mechanical system chosen from a Gibbsian ensemble of such systems is modified to mean a state in which the observable local macroscopic properties such as the local density of particles, mean energy, temperature, entropy, etc., have attained their equilibrium values, i.e., the values which would be obtained from the density in phase space which corresponds to the appropriate stationary solution of Liouville's equation. The approach to equilibrium in time in this sense (i.e., for the local properties which are suitable averages over the action variables of the system) of a wide class of multiply periodic systems, etc., is demonstrated under the condition that a local property exist initially. Certain characteristics of such a weak convergence as monotonicity of

approach after a sufficiently long time has passed and the asymptotic magnitudes of the local properties are investigated. The question of extension of this ergodic result to less restricted mechanical systems has been discussed and the relationship to ergodic theory and coarse graining indicated.

On the basis of the above result the general transport theory and the approach to spatial uniformity of a sufficiently ideal gas is investigated, by using as a model a gas of elastic hard-sphere molecules with vanishing diameter. In particular it is shown that under suitable conditions the diffusion in density satisfies Fick's laws and the conduction of heat satisfies Fourier's law, albeit with time-dependent transport coefficients.

1. INTRODUCTION

THE fundamental desideratum of statistical mechanics asserts that in general a statistical ensemble of isolated mechanical systems approaches in time statistical equilibrium unless at the outset this state has already been attained.¹ The precise sense in which this desideratum is to be understood as well as the specification of necessary and sufficient conditions under which it may be demonstrated has been the subject of considerable interest (and incidentally controversy) for the past fifty years or more.^{2,3} In particular, for systems of material particles under the influence of forces which depend only on the spatial coordinates, the Poincaré cycle theorem⁴ precludes the possibility that (in the usual sense of function theory) the ensemble density of the systems converges to the stationary ensemble density as the time $t \rightarrow \pm \infty$ starting from an arbitrarily given initial ensemble density. Such a strong mode of convergence, though, is in general not necessary to explain the observed approach to equilibrium of actual physical systems. This approach is observed rather in the study of any of the local macroscopic properties of the physical systems satisfying a suitable phenomenological transport equation such as a local density, mean velocity, temperature, mean energy, pressure, entropy, etc. These quantities approach in time the same value they would have in a state of statistical equilibrium. These local macroscopic properties can in general be exhibited as incomplete phase averages over the ensemble density of a

sufficiently "smooth" function of some or all of the canonical coordinates of the system.⁵

The purpose of the present investigation will be the demonstration and study of certain characteristics of such a weak convergence to equilibrium (i.e., in the local properties) for certain mechanical systems, including a wide class of multiply or conditionally periodic Hamilton-Jacobi systems. This complements a previous investigation on multiply periodic Hamilton-Jacobi systems which led to estimates of the Poincaré recurrence time and the asymptotic fraction of the time spent by a system in a recurrence.⁶ It will turn out that the appropriate incomplete phase averages which exhibit the desired convergence will be with respect to a suitable set of action variables. The simplest example of the class of physical systems we shall be concerned with is afforded by a gas composed of hard-sphere molecules of vanishingly small diameter, i.e., one satisfying the equilibrium equation of state $p = nkT$ where p is the pressure, n the number density, T the temperature, and k Boltzmann's constant. Since this example already illustrates the general features of the mode of convergence of the wider class of mechanical systems we are interested in, we shall deal with it first. Without undue restriction in generality for our purposes, we need consider only the case where the gas is one-dimensional and is restricted to move along the circumference of a circle of unit radius.

What we hope to accomplish in this paper is the following: First, we wish to point out that a plausible, though perhaps not always totally satisfactory, definition of an equilibrium state of an ensemble of systems need be associated only with the weak convergence with increasing time of the sequence of ensemble densities in phase space. Each member of this sequence corre-

¹ J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Yale University Press, New Haven, 1914), Chap. XII in particular.

² For general reviews see P. and T. Ehrenfest, *Encykl. math. Wiss.* 4, No. 32 (1911); S. Chandrasekhar, *Revs. Modern Phys.* 15, 1 (1943); D. ter Haar, *Revs. Modern Phys.* 27, 289 (1955).

³ A. J. F. Siegert, *Phys. Rev.* 76, 1708 (1949).

⁴ H. Poincaré, *Acta Math.* 13, 67 (1890).

⁵ Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954); see also H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, Inc., New York, 1952), pp. 130 ff.

⁶ H. L. Frisch, *Phys. Rev.* 104, 1 (1956).

sponds to some arbitrary choice of the initial complexions of the systems in the ensemble. In the specific examples discussed below, we show that this process corresponds to a special kind of coarse graining. Next we consider three categories of systems: (1) systems in which the interaction between the degrees of freedom of the system can somehow be shown to imply the existence of macroscopic dissipative effects over reasonable times of observation; (2) systems with interactions about which nothing can be said as to whether they exhibit macroscopic dissipative effects or not, and finally (3) systems in which the interaction can be transformed away. We consider only very special classes of mechanical systems belonging to the second and third categories and show that these exhibit an approach to equilibrium which has features formally resembling certain of the main features of the particular approach to equilibrium exhibited by a class of systems belonging to category one which have been investigated. Besides exhibiting explicitly by this the existence of another mode of approach to equilibrium which is independent of any dissipative mechanism, we wish to argue the plausibility that at least certain arbitrary systems other than those considered below may still approach equilibrium in our sense even though the more usual approach to equilibrium, depending on the dissipative mechanisms of the system, fails to function or is incapable of being shown to function. Whether anything is gained by this description depends on whether or not the features of this approach to equilibrium possess only a superficial resemblance to the desired features of a physically acceptable approach to equilibrium. We bias the remainder of the discussion towards the second eventuality.

Needless to say, this does not dispose of the first eventuality, in which case the calculations of Secs. 2, 3, and 4 of this paper merely demonstrate the fact that the models introduced with the kind of interactions exhibited below are "bad" models. They are "bad" models in the sense that they lead to only a pseudo-equilibrium state and an approach to this pseudo-equilibrium whose properties are physically unrealistic even in limit cases of real systems. If one adopts this point of view, then much of the discussion of Secs. 3 and 5 becomes irrelevant.

2. ONE-DIMENSIONAL GAS

Consider N identical molecules (point particles), each of mass m , distributed on a unit circle. Let the angular position and velocity of the i th particle be θ_i and ω_i . Since the collisions between the molecules are elastic and the particles indistinguishable, we can allow the colliding molecules to move as if they passed through one another without collision.⁶ The solution of the Hamilton canonical equations can then immediately be written down:

$$\begin{aligned} \omega_i &= \omega_i^0, \\ \theta_i &= \theta_i^0 + \omega_i t \pmod{2\pi}, \quad i = 1, \dots, N \end{aligned} \quad (1)$$

where θ_i^0 and ω_i^0 are the values of the angular position and velocity of the i th particle at time $t=0$. The density in phase space of a Gibbsian ensemble of such systems, $\mu = \mu(\theta_1, \dots, \theta_N; \omega_1, \dots, \omega_N; t)$, which satisfies Liouville's equation $d\mu/dt=0$, is thus given by

$$\mu = \mu^0(\theta_1 - \omega_1 t, \dots, \theta_N - \omega_N t; \omega_1, \dots, \omega_N), \quad (2)$$

where $\mu^0(\theta_1^0, \dots, \theta_N^0; \omega_1^0, \dots, \omega_N^0)$, the initial density, is a symmetric function in the sets of variables $\theta_1^0, \dots, \theta_N^0$ and $\omega_1^0, \dots, \omega_N^0$. We choose to normalize μ over the whole phase space to the total number density $n = N/2\pi$.

In what follows, we can assume without undue restriction that μ^0 can be written as a convergent infinite sum of N -fold products of jointly normalizable functions $f_e^0(\theta_i^0; \omega_i^0)$, viz.,

$$\int_{-\infty}^{\infty} \int_0^{2\pi} f_e^0(\theta_i^0; \omega_i^0) d\theta_i^0 d\omega_i^0 = \text{constant} = \gamma(e) < \infty.$$

Hence

$$\mu = \sum_{e=0}^{\infty} \alpha_e \prod_{i=1}^N f_e^0(\theta_i - \omega_i t; \omega_i), \quad (3)$$

with α_e suitable constants and $f_e^0(\theta_i - \omega_i t; \omega_i)$ periodic in $\theta_i - \omega_i t$ with period 2π [see (1)] and uniformly continuous in its arguments. Later we shall need, in order to discuss adequately the transport theory of this fluid, the existence of third-order moments of μ^0 as well as continuous derivatives of the first two. The relevant local macroscopic properties of our gas can be expressed as averages over an angular velocity of the one-molecule distribution function (O.M.D.F.) $f(\theta, \omega; t)$,

$$\begin{aligned} f(\theta, \omega; t) &= \int_{-\infty}^{\infty} \dots \int_0^{2\pi} \dots \int_0^{2\pi} \mu^0(\theta - \omega t, \theta_2 - \omega_2 t, \dots, \theta_N - \omega_N t; \\ &\quad \omega_1 \omega_2, \dots, \omega_N) \prod_{i=2}^N d\theta_i \prod_{i=2}^N d\omega_i = f^0(\theta - \omega t; \omega) \\ &= \sum_{e=0}^{\infty} \alpha_e \gamma^{N-1}(e) f_e^0(\theta - \omega t; \omega), \end{aligned} \quad (4)$$

by virtue of (3), where f^0 is periodic with period 2π in $\theta - \omega t$. If we assume furthermore that the initial O.M.D.F. is representable by a Fourier series in θ which is uniformly continuous in θ and ω , we have for all time⁷

$$\begin{aligned} f(\theta, \omega; t) &= f^0(\theta - \omega t; \omega) \\ &= n[\psi_0(\omega) + \sum_{k=1}^{\infty} \{\psi_k(\omega) \cos[k(\theta - \omega t)] \\ &\quad + \bar{\psi}_k(\omega) \sin[k(\theta - \omega t)]\}]. \end{aligned} \quad (5)$$

⁷ The conclusion that $f(\theta, \omega; t) = f^0(\theta - \omega t; \omega)$ follows directly from (2); we have introduced (4) only to set up a correspondence with the more general case; see Eq. (25).

The Fourier coefficients satisfy

$$\int_{-\infty}^{\infty} \psi_0(\omega) d\omega = 1, \int_{-\infty}^{\infty} \psi_k(\omega) d\omega < \infty, \int_{-\infty}^{\infty} \bar{\psi}_k(\omega) d\omega < \infty, \quad (6)$$

and

$$\int_{-\infty}^{\infty} f(\theta, \omega; t) d\omega \geq 0. \quad (7)$$

Since f is as usual normalized to n in the kinetic theory of gases, we have

$$\int_{-\infty}^{\infty} \int_0^{2\pi} f(\theta, \omega; t) d\theta d\omega = n, \quad (8)$$

and the initial local density of molecules is

$$\rho_0(\theta) = \int_{-\infty}^{\infty} f^0(\theta; \omega) d\omega \geq 0.$$

In view of (3) and (5), we can immediately conclude that neither μ nor f approach in the usual sense a stationary distribution characteristic of statistical equilibrium: i.e., μ a solution of the time-independent Liouville equation and f the time-independent (one-particle) molecular velocity distribution $n\psi_0(\omega)$. Unless the velocities ω_i are rationally dependent, μ is a multiply periodic function whose value, although never becoming equal to $\mu(t=0)$, approaches it to any desired degree of approximation infinitely often with probability one, i.e., Poincaré recurrences occur.⁶ Even more explicitly, we can see from (5) that $f(\theta, \omega; t)$ is a periodic function taking on its initial value $f^0(\theta; \omega)$ whenever $t = 2\pi n/\omega$ ($n=0, \pm 1, \pm 2, \dots$). Thus, in the usual sense neither μ nor f approach an equilibrium distribution in time.

Let us now consider the local macroscopic properties of our fluid in terms of which we can formulate its phenomenological transport theory. The relevant properties are the density of the fluid at any point, $\rho(\theta; t)$; its mean velocity, $\omega_0(\theta; t)$ (this is related to the peculiar velocity of the kinetic theory $\Omega = \omega - \omega_0$); the mean energy $E(\theta; t)$; the pressure $p(\theta; t)$ ⁸; the temperature $T(\theta; t)$; etc. These are defined, if they exist, by

$$\rho(\theta; t) = \int_{-\infty}^{\infty} f(\theta, \omega; t) d\omega = \int_{-\infty}^{\infty} f^0(\theta - \omega t; \omega) d\omega, \quad (9)$$

$$\omega_0(\theta; t) \rho(\theta; t) = \int_{-\infty}^{\infty} \omega f^0(\theta - \omega t; \omega) d\omega, \quad (10)$$

$$E(\theta; t) \rho = \frac{1}{2} m \int_{-\infty}^{\infty} \omega^2 f^0(\theta - \omega t; \omega) d\omega, \quad (11)$$

$$p(\theta; t) = m \int_{-\infty}^{\infty} \omega(\omega - \omega_0) f^0(\theta - \omega t; \omega) d\omega, \quad (12)$$

$$kT(\theta; t) = \frac{m}{\rho} \int_{-\infty}^{\infty} (\omega - \omega_0)^2 f^0(\theta - \omega t; \omega) d\omega, \text{ etc.}, \quad (13)$$

⁸ For this fluid the pressure tensor reduces to the scalar pressure.

respectively. Now (9)–(13) show that the relevant uniformly continuous local properties $A(\theta; t)$ are all averages over f with respect to ω (an action variable) of a smooth-function (i.e., continuous) $h(\omega; \theta)$ which is periodic in θ ; i.e.,

$$A(\theta; t) = \int_{-\infty}^{\infty} h(\omega; \theta) f^0(\theta - \omega t; \omega) d\omega \\ = A_{\infty}(\theta) + \sum_{k=1}^{\infty} \{ [a_k(\theta; t) - \bar{b}_k(\theta; t)] \cos k\theta \\ + [b_k(\theta; t) + \bar{a}_k(\theta; t)] \sin k\theta \}, \quad (14)$$

where

$$A_{\infty}(\theta) = n \int_{-\infty}^{\infty} h(\omega; \theta) \psi_0(\omega) d\omega, \\ a_k(\theta; t) = n \int_{-\infty}^{\infty} h(\omega; \theta) \psi_k(\omega) \cos k\omega t d\omega, \\ \bar{a}_k(\theta; t) = n \int_{-\infty}^{\infty} h(\omega; \theta) \bar{\psi}_k(\omega) \cos k\omega t d\omega, \quad (15) \\ b_k(\theta; t) = n \int_{-\infty}^{\infty} h(\omega; \theta) \psi_k(\omega) \sin k\omega t d\omega, \\ \bar{b}_k(\theta; t) = n \int_{-\infty}^{\infty} h(\omega; \theta) \bar{\psi}_k(\omega) \sin k\omega t d\omega.$$

Now if the local property can be defined for the initial O.M.D.F., i.e.,

$$a_k(\theta; 0), \bar{a}_k(\theta; 0) < \infty,$$

then the Riemann-Lebesgue theorem⁹ assures us that $a_k, \bar{a}_k, b_k, \bar{b}_k \rightarrow 0$ as $t \rightarrow \infty$ and¹⁰

$$A(\theta; t) \rightarrow A_{\infty}(\theta) \text{ as } t \rightarrow \infty. \quad (16)$$

This is our fundamental result. It shows the weak convergence of f to its equilibrium value $n\psi_0(\omega)$ in the sense given by (16). In particular, if h is a function of ω only, $h = h(\omega)$, then (16) shows that $A(\theta; t)$ becomes uniform in space with time; see (9)–(11).

The question that immediately arises is what characterizes the mode of this approach to equilibrium? The answer to this question depends strongly on the nature of our initial distribution. This is easily illustrated by considering a simple initial O.M.D.F. of the form

$$f(\theta, \omega; t) = n\psi_0(\omega) [1 + \varphi_0 \cos(\theta - \omega t)], \quad (17)$$

where φ_0 is a constant, $-1 < \varphi_0 < 1$. Let us consider the local densities corresponding to various choices of the form of the O.M.D.F. in statistical equilibrium,

⁹ E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Clarendon Press, Oxford, 1937), p. 11.

¹⁰ Since $A(\theta, t)$ is uniformly continuous in θ and t and periodic in θ the Fourier series converges uniformly.

$n\psi_0(\omega)$. If $\psi_0(\omega)$ is Maxwellian, i.e.,

$$\psi_0(\omega) = (\beta/\pi)^{\frac{1}{2}} \exp(-\beta\omega^2), \quad (18)$$

we find that

$$\rho(\theta; t) = n[1 + \varphi_0 \exp(-t^2/4\beta) \cos\theta], \quad (19)$$

i.e., the approach to uniformity in space is monotonic in time and incidentally very rapid. On the other hand, if $\psi_0(\omega)$ is chosen to be a step function

$$\psi_0(\omega) = \begin{cases} 0 & \text{for } -\infty < \omega < -\Omega \\ \frac{1}{2}\Omega^{-1} & \text{for } -\Omega \leq \omega \leq \Omega \\ 0 & \text{for } \Omega < \omega < \infty, \end{cases} \quad (20)$$

we find that

$$\rho(\theta; t) = n\{1 + \varphi_0[\sin(\Omega t - \theta) + \sin(\Omega t + \theta)]/2\Omega t\}. \quad (21)$$

In this case the approach to uniformity in the density, etc., is not monotonic but oscillatory. This immediately raises the question of how to characterize the class of initial O.M.D.F.'s whose local properties, e.g., the density, approach their equilibrium values monotonically as $t \rightarrow \infty$. A completely general answer to this question is very difficult to find.¹¹ Indeed, physically it would suffice to find conditions so that representative local properties after an initial transient oscillation approach monotonically their equilibrium values after a sufficiently long time. If we rewrite (5) as a complex Fourier series,

$$f^0(\theta - \omega t; \omega) = n[\psi_0(\omega) + \sum_{\substack{k=-\infty \\ k \neq 0}}^{\infty} \xi_k(\omega) e^{-ik(\theta - \omega t)}], \quad (22)$$

this will certainly be the case if the $\xi_k(\omega)$ can be expressed as Gram-Charlier series in ω , i.e., if

$$\xi_k(\omega) = \sum_{n=0}^{\infty} C_m^{(k)} G_m(\omega),$$

where the $C_m^{(k)}$ are constants and $G_m(\omega) = (-2\pi^{\frac{1}{2}})^m \times \exp(-\pi\omega^2) H_m(2\pi^{\frac{1}{2}}\omega)$, with H_m the Hermite polynomial of order m .

Another way of characterizing the approach to equilibrium is by the asymptotic behavior of the local properties, e.g., the density. Two results¹² on the asymptotic behavior of Fourier transforms can be applied immediately. The first (see reference 12, p. 44) assures us that the reduced density $\rho - n$ is $O(e^{-\lambda t})$ as $t \rightarrow \infty$ and $O(e^{+\mu t})$ as $t \rightarrow -\infty$, $\lambda, \mu > 0$, in $\alpha, \beta > 0$, $-\alpha < \text{Im}t < \beta$; as long as the coefficients ξ_k in (22) are integrable $(-\infty, \infty)$ and are analytic within the strip $-\mu < \text{Im}\omega < \lambda$, and as long as within the strip $\xi_k(\omega) = O(e^{-\beta\omega})$ as $\omega \rightarrow +\infty$; $\xi_k(\omega) = O(e^{+\alpha\omega})$ as $\omega \rightarrow -\infty$. Similar results can be obtained for the other local

properties. The second estimate depends on the number of continuous derivatives possessed by ξ_k (see reference 12, pp. 46 ff.). For the reduced density it can be stated as follows: If each ξ_k is N times continuously differentiable in $-\infty < \omega < \infty$, if $\xi^{(N)}(\omega)$ is integrable $(-\infty, \infty)$, and if for each $m=0, 1, \dots, N-1$ the quantity $\xi^{(m)}(\omega) \rightarrow 0$ as $|\omega| \rightarrow \infty$, then

$$\rho - n = o(t^{-N}) \text{ as } t \rightarrow \infty.$$

For analytic $\xi_k(\omega)$ other asymptotic expansions for, say, the reduced density can be obtained by the method of steepest descents. These results should be sufficient to characterize the asymptotic behavior in time of the local properties in most situations of physical interest.

Let us return to the simple example of the approach to equilibrium, i.e., (17)–(19). We note immediately that $\rho \rightarrow n$ irrespective of whether we allow $t \rightarrow +\infty$ or $t \rightarrow -\infty$. This model exhibits no true irreversibility in the sense that the system evolves (in the limit) in a unique sense in time; there is no “time’s arrow” revealed to us. This is to be expected in view of the time-reversal symmetry of the underlying Newtonian dynamics. Still we can speak of a quasi-irreversibility in this sense: Given any initial spatially nonuniform state, in say the density, the system evolves as $t \rightarrow \infty$ to a uniform state; if the system is initially uniform it remains so.

As (19) shows, the rate of attainment of the uniform equilibrium density is essentially governed by the spread of the initial velocity distribution $\psi_0(\omega)$. This spread is conveniently measured by the variance β^{-1} ; the larger β^{-1} , the more rapid is the approach. In this is revealed an important aspect of the physical significance of the weak convergence to equilibrium. The modulation in time of the value of a local property is due to the successive reintroduction in the averaging process of the uncertainty in the specification of the initial velocities of our molecules. If, say in (19), the velocity distribution is completely sharp, i.e.,

$$\psi_0(\omega) = \delta(\omega - \omega_0) = \lim_{\beta^{-1} \rightarrow 0} \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \exp[-\beta(\omega - \omega_0)^2],$$

we find that the conditions for the application of the Riemann-Lebesgue theorem fail¹³ and no convergence, weak or otherwise, can be exhibited. Thus, in this case the density satisfies the relation

$$\rho(\theta; t) = n[1 + \varphi_0 \cos(\theta - \omega_0 t)];$$

i.e., we find sound waves.¹⁴

Before proceeding to a discussion of the transport properties of our fluid, we consider the generalization

¹¹ By comparison with the theory of distribution functions, some results may be derived involving criteria such as the positive definiteness of certain functionals of the ψ 's. Since this hardly yields usable testing procedures, we shall not enlarge on this point.

¹² A. Erdélyi, *Asymptotic Expansions* (Dover Publications, New York, 1956).

¹³ Since $\psi_0(\omega)$ and $h(\omega; \theta)\psi_0(\omega)$ are not in $L(-\infty, \infty)$ [see (15), (16)].

¹⁴ The dependence of the “effective” relaxation time on $\beta^{\frac{1}{2}}$, which is proportional to the reciprocal of the asymptotic rms velocity (and is a parameter of the initial distribution), is clearly unrealistic.

of our fundamental result to other systems. This will reveal more fully that the results obtained for the one-dimensional gas are not due to the weakness of the interaction (if one prefers, the absence of "real" collisions) between the molecules.

3. MULTIPLY PERIODIC SYSTEMS, ETC.

Consider a multiply periodic system whose canonical coordinates are q_i and p_i , $i=1, 2, \dots, N$. We can always introduce a unique set of canonical action and angle variables J_i and θ_i , respectively ($i=1, \dots, N$), which possess the properties: (A) the configuration of the system is periodic in the θ_i 's with period 2π , (B) the Hamiltonian function H transforms into a function of J_i 's only, $H=E(J_1, \dots, J_N)$, and (C) the generator of the transformation from the variables q_i, p_i to the variables J_i, θ_i ($i=1, \dots, N$) is a periodic function of the θ_i 's with the period 2π .¹⁵ The fundamental frequencies of our system, ν_i , are found to be

$$\nu_i = \partial E / \partial J_i = \nu_i(J_1, \dots, J_N).$$

Henceforth we will denote by \mathbf{J} the set of J_i 's, by $\boldsymbol{\theta}$ the set of θ_i 's, and by \mathbf{v} the set of ν_i 's. The solution of Hamilton's equations in terms of these variables is [compare with (1)]

$$\begin{aligned} J_i &= J_i^0, \\ \theta_i &= \theta_i^0 + \nu_i(\mathbf{J})t. \end{aligned} \quad (23)$$

The density in phase space ($\mathbf{J}, \boldsymbol{\theta}$) of a Gibbsian ensemble of systems can be written

$$\begin{aligned} \mu(\theta_1, \dots, \theta_N; J_1, \dots, J_N; t) \\ = \mu^0(\theta_1 - \nu_1(\mathbf{J})t, \dots, \theta_N - \nu_N(\mathbf{J})t; J_1, \dots, J_N) \\ = \mu^0(\boldsymbol{\theta} - \mathbf{v}(\mathbf{J})t; \mathbf{J}), \end{aligned} \quad (24)$$

where the initial density $\mu^0(\theta_1^0, \dots, \theta_N^0; J_1^0, \dots, J_N^0)$ is periodic with period 2π in the $\boldsymbol{\theta}^0$. If the initial density $\mu^0(\boldsymbol{\theta}^0; \mathbf{J}^0)$ is representable by a convergent Fourier series in $\boldsymbol{\theta}^0$, then so is μ in $\boldsymbol{\theta} - \mathbf{v}(\mathbf{J})t$, viz.,

$$\begin{aligned} \mu(\boldsymbol{\theta}; \mathbf{J}; t) &= \mu^0(\boldsymbol{\theta} - \mathbf{v}(\mathbf{J})t; \mathbf{J}) = \Phi(\mathbf{J}) \\ &+ \sum'_{k_1, \dots, k_N} \psi_{k_1, \dots, k_N}(\mathbf{J}) \exp\{-i\mathbf{k} \cdot [\boldsymbol{\theta} - \mathbf{v}(\mathbf{J})t]\}, \end{aligned} \quad (25)$$

where the sum is to be taken over all values of the integers \mathbf{k} except $k_1 = \dots = k_N = 0$.

In what follows we restrict ourselves to the set of all those multiply periodic systems for which the \mathbf{v} span the space $E_N(\mathbf{v})$ defined by $-\infty < \nu_i < \infty$ ($i=1, \dots, N$) as the \mathbf{J} span $E_N(\mathbf{J})$ defined by $-\infty < J_i < \infty$ ($i=1, \dots, N$). This excludes certain trivial cases, for example coupled harmonic oscillators for which the \mathbf{v} are independent of \mathbf{J} . Since the system is assumed to be non-degenerate [see (23)], the Jacobian $\partial \mathbf{v} / \partial \mathbf{J} \neq 0$ everywhere. In complete analogy with the case of the

one-dimensional gas, μ does not converge in time to the solution of the stationary Liouville equation; again we find Poincaré recurrences. Yet if we examine any uniformly continuous local macroscopic property $A(\boldsymbol{\theta}; t)$ which can be formulated as an average of a smooth function $h(\mathbf{v}; \boldsymbol{\theta})$ over μ with respect to the action variables \mathbf{J} , we find that these do converge to the value they have at statistical equilibrium. To see this, we note that

$$\begin{aligned} A(\boldsymbol{\theta}; t) &= \int_{E_N(\mathbf{J})} h(\mathbf{v}; \boldsymbol{\theta}) \mu(\boldsymbol{\theta}, \mathbf{v}; t) d\mathbf{J} \\ &= \int_{E_N(\mathbf{v})} h(\mathbf{v}; \boldsymbol{\theta}) \mu^0(\boldsymbol{\theta} - \mathbf{v}t; \mathbf{J}(\mathbf{v})) \frac{\partial \mathbf{J}}{\partial \mathbf{v}} d\mathbf{v} \\ &= A_\infty(\boldsymbol{\theta}) + \sum'_{k_1, \dots, k_N} a_{k_1, \dots, k_N}(\boldsymbol{\theta}; t) \exp(-i\mathbf{k} \cdot \boldsymbol{\theta}), \end{aligned} \quad (26)$$

by virtue of (25), where

$$\begin{aligned} A_\infty(\boldsymbol{\theta}) &= \int_{E_N(\mathbf{v})} h(\mathbf{v}; \boldsymbol{\theta}) \frac{\partial \mathbf{J}}{\partial \mathbf{v}} \Phi(\mathbf{J}(\mathbf{v})) d\mathbf{v}, \\ a_{k_1, \dots, k_N}(\boldsymbol{\theta}; t) &= \int_{E_N(\mathbf{v})} h(\mathbf{v}; \boldsymbol{\theta}) \frac{\partial \mathbf{J}}{\partial \mathbf{v}} \\ &\quad \times \psi_{k_1, \dots, k_N}(\mathbf{J}(\mathbf{v})) \exp(i\mathbf{k} \cdot \mathbf{v}t) d\mathbf{v}. \end{aligned}$$

If the property exists initially, i.e., $A(\boldsymbol{\theta}; 0) < \infty$, then the Riemann-Lebesgue theorem¹⁶ assures us that it exists and is bounded for all time and

$$A(\boldsymbol{\theta}; t) \rightarrow A_\infty(\boldsymbol{\theta}) \text{ as } t \rightarrow \pm \infty. \quad (27)$$

Again we find the same type of weak convergence to equilibrium, without the true irreversibility that we had found before.

Even if the multiply periodic system is $(N-s)$ -fold degenerate, the preceding theorem goes through if we restrict our integrations to the space of the s incommensurable ν 's, $E_s(\nu)$, the other θ 's being identically zero.¹⁵ A further important property of these systems is the fact that the distribution in \mathbf{J} space is stationary, viz.,

$$\Phi(\mathbf{J}) = \int_0^{2\pi} \dots \int_0^{2\pi} \mu^0(\boldsymbol{\theta} - \mathbf{v}t; \mathbf{J}) d\boldsymbol{\theta},$$

by virtue of (25). The previous considerations concerning the long-time monotonic character of the approach to equilibrium and the asymptotic order of the Fourier coefficients appearing in (26) derived in connection with the one-dimensional gas, can be made to apply here also with only trivial modification.

Finally, our result can also be extended to systems which can be separated into an independent multiply

¹⁵ M. Born, *The Mechanics of the Atom* (G. Bell and Sons, Ltd., London, 1927), pp. 86 ff.

¹⁶ H. S. Bochner and K. Chandrasekharan, *Fourier Transforms* (Princeton University Press, Princeton, 1949), p. 57.

periodic part and a nonperiodic part. An example of such a system is the Kepler problem, i.e., a sun surrounded by several small planets, which separates into a perturbed periodic central motion about the center of mass and a nonperiodic motion of the center of mass. We denote the generalized coordinates of the multiply periodic part by J_i, θ_i ($i=1, \dots, s$) and the coordinates of the nonperiodic part by q_j, p_j ($j=s+1, \dots, N$). In terms of these variables the Hamiltonian $H=H(\mathbf{J}, \boldsymbol{\theta}; \mathbf{q}, \mathbf{p})$ separates into a periodic and a nonperiodic part, $H=H_p(\mathbf{J}, \boldsymbol{\theta})+H_n(\mathbf{q}; \mathbf{p})$. The density in phase space, $\mu(\mathbf{J}, \boldsymbol{\theta}; \mathbf{q}, \mathbf{p}; t)$, can be written as a product of densities,

$$\mu = \eta_p(\mathbf{J}, \boldsymbol{\theta}; t) \eta_n(\mathbf{q}, \mathbf{p}; t).$$

If η_n remains bounded for all t , then those local properties $A(\boldsymbol{\theta}; \mathbf{p}, \mathbf{q}; t)$ obtained by averaging some smooth function $h(\mathbf{v}, \boldsymbol{\theta}; \mathbf{p}, \mathbf{q})$ with respect to μ over all J_i 's satisfy (27), as long as the frequencies \mathbf{v} satisfy the previously discussed conditions.

The question of whether these results have any bearing on the behavior of real physical systems needs to be considered. Certainly the preceding results apply to classical gases¹⁷ in the limit of sufficiently high temperature or low pressure where they may be considered to be perfect Knudsen gases. Similarly the preceding theory applies also to the classical limiting case of almost perfect solids insofar as these can be considered to consist of coupled oscillators which are so weakly anharmonic that N normal frequencies still exist albeit being weak functions of the amplitudes (i.e., insofar as they are described by the equivalent linear system in the sense of Krylov and Bogoliubov). But other than these two classes of limiting cases, most real physical systems are probably distinguished by the fact that they possess very much fewer than N analytic time-independent integrals of the motion. Such systems can at best be represented only locally (in phase space) as multiply-periodic systems. In view of this, our model is at best suggestive of the behavior of the far more complex systems with which we deal in practice. Under certain conditions real systems can be approximated sufficiently by a secular perturbation of a multiply periodic system which is constructed so as to destroy most of the N time-independent integrals of the motion (the \mathbf{J}). Brout and Prigogine¹⁸ have developed a formal classical theory for a particular choice of the perturbing potential suggested by the quantum transport theory of Van Hove.¹⁹

We proceed now to give an outline of the transport theory of a typical system for which (27) applies, the one-dimensional (perfect) gas.

¹⁷ The extension of this theory for quantum-mechanical systems is straightforward.

¹⁸ R. Brout and I. Prigogine, *Physica* **22**, 621 (1956).

¹⁹ L. Van Hove, *Physica* **21**, 517 (1955).

4. TRANSPORT THEORY

We note first that (12) and (13) imply the equation of state of our gas,

$$p(\theta; t) = \rho k T(\theta; t). \quad (28)$$

The hydrodynamic transport equations follow from the continuity equation satisfied by $f=f^0(\theta-\omega t; \omega)$,²⁰

$$\frac{\partial f}{\partial t} + \omega \frac{\partial f}{\partial \theta} - \frac{df}{dt} = 0. \quad (29)$$

On multiplying (29) by 1, $m\omega$, and $\frac{1}{2}m\omega^2$ respectively, and integrating over all values of ω , we find after some manipulations the equations of continuity, motion, and energy balance⁶:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \theta}(\omega_0 \rho) = 0, \quad (30)$$

$$m\rho \frac{d\omega_0}{dt} + \frac{\partial p}{\partial \theta} = 0, \quad (31)$$

$$\rho \frac{dE}{dt} + \frac{\partial}{\partial \theta}(q + \omega_0 p) = 0, \quad (32)$$

respectively by virtue of (9)–(13), with the heat flux q given by

$$\begin{aligned} q &= \frac{1}{2}m \int_{-\infty}^{\infty} (\omega - \omega_0)^3 f d\omega \\ &= \frac{1}{2}m \int_{-\infty}^{\infty} (\omega - \omega_0)(\omega^2 - 2\omega\omega_0) f d\omega. \end{aligned} \quad (33)$$

Equations (30)–(32) together with (28) completely determine the macroscopic behavior of the gas.²¹

Our previous considerations would lead us to expect that beside these orthodox transport equations, properties such as the density, etc., would under suitable conditions satisfy equations which are generally thought of as being characteristic of a truly irreversible transport theory, e.g., in the case of the density, Fick's laws. We shall show that in at least two fairly general circumstances the density ρ does satisfy a simple diffusion equation, albeit with a time-dependent diffusion coefficient. In what follows, we shall assume for simplicity that initially there is no mass motion of the fluid as a whole, i.e., $\omega_0(\theta, 0) = 0$. This implies in general that

²⁰ Equation (29) for the O.M.D.F. f is identical in this case with the Boltzmann equation. For, making the usual *Stosszahlansatz*, we find

$$\frac{df}{dt} = \int_{-\infty}^{\infty} d\omega_1 |\omega - \omega_1| \{f(\theta, \bar{\omega}; t) f(\theta, \bar{\omega}_1; t) - f(\theta, \omega; t) f(\theta, \omega_1; t)\},$$

where $\bar{\omega}$ and $\bar{\omega}_1$ are the velocities of the molecules before collision. Noting that for elastic collisions between molecules of the same mass, $\bar{\omega} = \omega_1$ and $\bar{\omega}_1 = \omega$, we regain (29).

²¹ The mean internal energy $U(\theta; t)$ relates E and T ; viz. $U(\theta; t) = E(\theta; t) - \frac{1}{2}m\omega_0^2 = \frac{1}{2}\rho k T$.

$f^0(\theta - \omega t; \omega) = f^0(\theta - \omega t; -\omega)$, i.e., that the Fourier coefficients in (5) are even functions of ω .²²

The first set of circumstances in which we expect that the density satisfies a diffusion equation is when we are initially not far removed from spatial uniformity in the density, i.e., the infinite sum in (5) reduces to a single term, e.g.,

$$f^0(\theta - \omega t; \omega) = n\{\psi_0(\omega) + \psi_1(\omega) \cos(\theta - \omega t)\}; \quad (34)$$

$$\psi_0(\omega) = \psi_0(-\omega), \quad \psi_1(\omega) = \psi_1(-\omega).$$

Let

$$\zeta(\theta, t; m) = \int_{-\infty}^{\infty} \omega^m f^0(\theta - \omega t; \omega) d\omega, \quad (35)$$

$$m = 0, 1, 2, \dots;$$

then by virtue of (34), if $\zeta(\theta, 0; m)$ exists,

$$\zeta(\theta, t; m) = \zeta_\infty(\theta; m) + B_m(t) \cos\theta; \quad m \text{ even} \quad (36)$$

$$\zeta(\theta, t; m) = +\bar{B}_m(t) \sin\theta; \quad m \text{ odd}$$

where

$$\zeta_\infty(\theta; m) = n \int_{-\infty}^{\infty} \omega^m \psi_0(\omega) d\omega,$$

$$B_{2m}(t) = n \int_{-\infty}^{\infty} \omega^{2m} \psi_1(\omega) \cos\omega t d\omega = 2n \int_0^{\infty} \omega^{2m} \psi_1(\omega) \cos\omega t d\omega,$$

$$\bar{B}_{2m+1}(t) = n \int_{-\infty}^{\infty} \omega^{2m+1} \psi_1(\omega) \sin\omega t d\omega$$

$$= 2n \int_0^{\infty} \omega^{2m+1} \psi_1(\omega) \sin\omega t d\omega.$$

From (36), it follows that ζ satisfies the diffusion equation,

$$\partial\zeta(m)/\partial t = D_m(t) \quad \partial^2\zeta(m)/\partial\theta^2, \quad (37)$$

where

$$D_{2m}(t) = [-d \ln B_{2m}(t)/dt]^{-1} = B_{2m}(t)/\bar{B}_{2m+1}(t),$$

$$D_{2m+1}(t) = [-d \ln \bar{B}_{2m+1}(t)/dt]^{-1} = \bar{B}_{2m+1}(t)/B_{2m+2}(t).$$

Particularly interesting are the even ζ since $\zeta(\theta; t; 0) = \rho$, $\zeta(\theta, t; 2) = E\rho$, etc.

The approach to equilibrium of a gas is believed to occur under suitable circumstances by a fairly rapid relaxation to a Maxwellian velocity distribution followed by a much slower approach to spatial uniformity. Since the relaxation to a Maxwellian distribution occurs presumably through the action of the integral term on the right-hand side of Boltzmann's equation, our model of the gas cannot account for it. Still, we can study in our model the subsequent approach to spatial uniformity. We shall find that in this case the density will again satisfy a diffusion equation. Thus, for an arbitrary initial spatial distribution of the molecules, we

²² This implies in turn that when "equilibrium" in our sense is attained, the fluid exhibits no mass flow.

can rewrite (5) as

$$f^0(\theta - \omega t; \omega) = n \left(\frac{\beta}{\pi} \right)^{\frac{1}{2}} \exp(-\beta\omega^2)$$

$$\times \left\{ 1 + \sum_{k=1}^{\infty} (\alpha_k \cos[k(\theta - \omega t)] + \bar{\alpha}_k \sin[k(\theta - \omega t)]) \right\};$$

$$\alpha_k, \bar{\alpha}_k \text{ constants.} \quad (38)$$

This leads to the density

$$\rho(\theta; t) = n \left\{ 1 + \sum_{k=1}^{\infty} \exp(-t^2 k^2 / 4\beta) \right.$$

$$\left. \times [\alpha_k \cos k\theta + \bar{\alpha}_k \sin k\theta] \right\}, \quad (39)$$

which satisfies

$$\partial\rho/\partial t = D(t) \partial^2\rho/\partial\theta^2, \quad (40)$$

with

$$D(t) = t/2\beta. \quad (41)$$

The unrealistic form of this diffusion coefficient again warns us that our analogy with conventional transport theory may be more superficial than real. The disturbing feature is not so much the fact that D is a function of the time but rather that the time-dependent term, instead of decreasing in importance with increasing $|t|$, actually grows.

Whenever the density satisfies (40), we can identify ω_0 with the drift velocity by virtue of (30). Thus, we find

$$\omega_0 = -D(t) \partial \ln\rho / \partial\theta, \quad (42)$$

as expected from diffusion theory. Introducing (41), we can rewrite ω_0 formally as a gradient of a "chemical potential" $\mu = \mu^0 + \beta^{-1} \ln\rho$:

$$\omega_0 = -\gamma(t) \partial\mu / \partial\theta,$$

with a mobility $\gamma(t) = t/2$. For $t > 0$, we are in formal agreement with the thermodynamics of irreversible processes in that $\gamma(t) > 0$, etc.

Finally, to illustrate the importance of β in (38) on the approach to spatial uniformity, we compute the values of the local properties and fluxes. It suffices to take $\alpha_1 = \Phi_0$, $-1 < \Phi_0 < 1$; $\bar{\alpha}_1 = 0$; $\alpha_k, \bar{\alpha}_k = 0$ for $k \geq 2$. We find by virtue of (9)-(13) and (33) that

$$\rho(\theta; t) = n[1 + \Phi_0 \exp(-t^2/4\beta) \cos\theta] \rightarrow n \text{ as } t \rightarrow \infty,$$

$$\omega_0(\theta; t) = \frac{\Phi_0 t \exp(-t^2/4\beta) \sin\theta}{2\beta[1 + \Phi_0 \exp(-t^2/4\beta) \cos\theta]} \rightarrow 0 \text{ as } t \rightarrow \infty, \quad (43)$$

$$T(\theta; t) = \frac{m}{2\beta k} - \frac{m}{k} \frac{\partial \ln\rho}{\partial\beta} - \frac{m\omega_0^2}{k} \rightarrow \frac{m}{2\beta k} \text{ as } t \rightarrow \infty \text{ etc.,}$$

in agreement with (16). The final temperature attained, T_∞ , is identical with the translational temperature of the initial Maxwellian velocity distribution; i.e.,

$$\beta = m/(2kT_\infty). \quad (44)$$

The heat flux q separates as expected into two terms, one describing heat convection (of the temperature

T_∞), the other heat conduction (see Appendix):

$$q = -\omega_0(nm/\beta) + q_{\text{cond}}, \quad (45)$$

where q_{cond} is given by Fourier's law,

$$q_{\text{cond}} = -\frac{1}{2}D(t)k\rho\partial T/\partial\theta, \quad (46)$$

with a thermal conductivity $\lambda = \lambda(t)$ satisfying

$$\lambda = \frac{1}{2}D(t)k\rho,$$

in complete analogy (except for the time dependence) with the results of kinetic theory. By virtue of (43), $q \rightarrow 0$ as $t \rightarrow \infty$.

5. DISCUSSION

The weakening of the usual notion of equilibrium of isolated systems presented in this paper allows us to conclude that a certain very restricted class of mechanical systems approaches in time, in a weak sense, statistical equilibrium. If nothing else, these considerations suggest the plausibility that a much wider class of systems satisfy an ergodic theorem reminiscent of (16) and (27). Such a theorem, implying more than the results of the theory of weak or strong mixing, most probably would use much more direct mathematical tools than those employed by us.²³ The averaging over the action variables in obtaining the local macroscopic properties can of course be interpreted as a kind of coarse graining. Seen in this light, our model comes very close to the original discussion of these questions by Gibbs,¹ who used the example of the stirring of two fluids, one black and one white,²⁴ i.e., $[(N-1)\text{-fold degenerate multiply periodic system}]$.

Our considerations for a finite number of particles (N) refer to averages of observations made on repeated experiments rather than averages of repeated observations on the same system. The distinction between the two interpretations is important. In order to exhibit approach to equilibrium by means of observations on a single system, we must allow N to approach ∞ to prevent Poincaré recurrences. Furthermore, to observe the desired behavior, we require the limits to be taken in the order $N \rightarrow \infty$, first and $t \rightarrow \infty$, second.^{18,23} This observation was already made by Gibbs.¹ Many of these statistical considerations play a role in the formulation of a classical uncertainty relation, as has been shown by Born²⁵ and by Born and Hooton.²⁶

Rather than proceeding with a further discussion of the general points just raised, we wish to focus attention on another physically important element which is lacking in our model. We are able to describe circum-

stances under which systems tend monotonically (or at least monotonically after an initial short transient response) to approach "equilibrium." These circumstances, however, depend on the selection of a suitable class of initial states from which this "generalized relaxation" may commence. In a large class of physical systems, on the other hand, this relaxation appears as a result of certain properties of the dynamical structure of the systems themselves and not of their initial states. An example of such a property is provided by the work of Van Hove.¹⁹ Certainly there also exist exceptions to this behavior; nonetheless, any realistic theory of the approach to equilibrium must be able to account for this behavior and this appears to require more than the modification of the equilibrium definition and the idea of weak convergence.

One local property which we have not discussed is the local entropy; e.g., for our gas, $S = S(\theta; t)$ is given by

$$S = -k \int_{-\infty}^{\infty} f \ln f d\omega.$$

This property is considerably harder to deal with because of its nonlinear dependence on f . If f is positive, integrable (over ω in $[-\infty, \infty]$), bounded from above, and $\partial\rho/\partial t \rightarrow 0$ as $t \rightarrow \infty$, we can at least conclude from the first theorem of the mean that $\partial S/\partial t \rightarrow 0$ as $t \rightarrow \infty$. Much less restrictive theorems can be found.²³

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APPENDIX

By virtue of (13) and (33),

$$\begin{aligned} q &= \frac{1}{2}m \int_{-\infty}^{\infty} (\omega - \omega_0)(\omega - \omega_0)^2 f^0 d\omega \\ &= \frac{1}{2}I(\theta; t) - \frac{1}{2}\omega_0 k T \rho. \end{aligned} \quad (47)$$

To find $I(\theta; t)$, consider

$$\begin{aligned} -\frac{\partial}{\partial\theta} \left[m \int_{-\infty}^{\infty} (\omega - \omega_0)^2 f^0 d\omega \right] &= -\frac{\partial}{\partial\theta} [k T \rho] \\ &= \int_{-\infty}^{\infty} mn\Phi_0 \left(\frac{\beta}{\pi} \right)^{\frac{1}{2}} \exp[-\beta\omega^2(\omega - \omega_0)^2 \sin(\theta - \omega t)d\omega], \end{aligned}$$

by virtue of (43). Integrating by parts and collecting terms, we find

$$\frac{1}{2}I(\theta; t) = -\left(\frac{D(t)k\rho}{2} \right) \frac{\partial T}{\partial\theta} + \frac{\omega_0 k \rho T}{2} - \frac{\omega_0 n m}{\beta}. \quad (48)$$

Substitution of (48) into (47) leads directly to (45) and (46).

²³ H. Grad (private communication). Professor Grad in a forthcoming publication has also treated the gas model much more directly by means of measure theory.

²⁴ P. S. Epstein's article, "Critical Appreciation of Gibbs' Statistical Mechanics," in *Commentary on the Scientific Writings of J. W. Gibbs*, edited by A. Haas (Yale University Press, New Haven, 1936), pp. 509 ff.

²⁵ M. Born, *Physik*. Bl. 11, 49, 314 (1955).

²⁶ M. Born and D. J. Hooton, *Z. Physik* 142, 201 (1955).