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Exact Classical Nonequilibrium Statistical-Mechanical Analysis of the Finite Ideal Gas*

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A system consisting of N noninteracting point particles bouncing elastically from the walls of a rectangular box is studied. The macroscopic observables are assumed to be the center of mass, total energy, and total momentum. The initial N-particle probability distribution $P(0)$ corresponding to these observables is set up. Liouville's equation is solved exactly and analytically for $P(t)$, and exact expressions are obtained for various reduced distributions and moments and for the time dependence of the macroscopic observables. It is shown that the expected value of any analytic phase function relaxes to equilibrium. The evolution of the nonequilibrium entropy $S(t)$ is investigated. It is found that $S(t)$ undergoes a nonmonotonic increase from a minimum at $t=0$ to a maximum at $t \to \infty$, and that $S(t \to \infty)$ is the usual canonical entropy. It is shown that statistical irreversibility occurs for arbitrary N, but that predictability occurs only for large (but not necessarily infinite) N.

I. INTRODUCTION

The purpose of this paper is to study and to illustrate certain general principles of nonequilibrium statistical mechanics by means of an exact analysis of a particular N-particle system. The system chosen is the N-particle Knudsen gas (i.e., a gas in which the mean free path is much longer than the container, so that collisions between particles may be neglected) enclosed in a rectangular box with perfectly reflecting walls.

The spirit of this paper is that the Knudsen gas provides a useful "model" system, for which exact calculations can be carried out, and which may illustrate some of the important characteristics of the statistical mechanics of more complicated systems (i.e., systems in which interactions are important). Of course, certain effects not obtained in the present study will show up in more complicated systems. For instance, the only relevant time parameter in the present problem is the "hydrodynamic time," which is related to the length of the container. In systems with interparticle interactions, the "kinetic time" (related to the interaction length) is also expected to be important.

Model systems have been widely used for the study of the principles of nonequilibrium statistical mechanics. Such systems have been especially popular for the study of the question of the origin of irreversibility. Most of the systems (e.g., the Ehrenfest dog-flea model,[1] the Kac ring model,[2] the moving markers model[3]) have been nonmechanical; that is, nonmechanical probabilistic concepts have been more or less arbitrarily introduced into the system. An important characteristic of these nonmechanical models is that probability is introduced *at all times*, rather than only at the initial instant.

Several studies of truly mechanical models have been carried out in the past[4–12]; these studies are based on the use of Liouville's equation, so that probability is introduced into the theory only at the initial time, this probability being then propagated in time by Liouville's equation. As has been pointed out previously,[13] the element of probability which is introduced at the initial time

in statistical mechanics is crucial; in fact, this element of probability is sufficient to introduce irreversibility into the theory. Thus, the study of a mechanical system by means of Liouville's equation should not be called a "mechanical analysis"; it is, rather, a "statistical-mechanical analysis of a mechanical system."

To the authors' knowledge, the present work is the only statistical-mechanical study of an N-particle mechanical system in which the wall forces are included in an approximately realistic way, and in which Liouville's equation is solved exactly and analytically for all time. A complete discussion of previous work in this field will be given in Sec. VII.

In Sec. II, the initial N-particle probability distribution is set up. The authors take the point of view that statistical mechanics arises due to the observer's lack of complete information about the mechanical system, and that the initial distribution should be set up in such a way as to reflect, as accurately as possible and with no unwarranted assumptions, the initial information which the observer *does* possess. This point of view is sometimes called the "information-theory point of view."[8, 14–18]. If the reader does not subscribe to this point of view, then he should omit Eqs. (2.1)–(2.6) of Sec. II and simply consider (2.7) to be the assumed initial distribution, with no justification being given for that distribution. It is assumed, in Sec. II, that the given initial information consists of the expected values of the center of mass, total energy, and total momentum; these quantities are thus the "macroscopic observables." The choice of these particular quantities as observables may seem unduly restrictive, i.e., the use of the particular initial distribution (2.7) may seem unduly restrictive. However, these three quantities are the only simple, global (i.e., dependent on the state of the entire N-body system) mechanical quantities possessing much direct physical significance. Another possibility is the total angular momentum, but this quantity is quite complicated to deal with when the system is confined to a rectangular box. Thus, as long as the observables are restricted to global quantities, the given initial informa-

tion (and consequently the given initial distribution) is actually quite general. For simplicity, nonglobal quantities (such as the expected density) will not be considered.

In Sec. III the exact, analytic solution for arbitrary time of Liouville's equation is obtained. In Sec. IV, this solution is used to obtain exact analytic expressions for various reduced distributions, all of the moments of the N-particle distribution, and the time dependence of the macroscopic observables. It is found that the expected value of any analytic phase function approaches equilibrium as $t \to \infty$. In Sec. V, the time dependence of the nonequilibrium entropy $S(t)$ (as defined by Robertson[18]) is studied. It is found that $S(t)$ undergoes a nonmonotonic increase to its asymptotic value $S(t \to \infty)$, and that the asymptotic value agrees with the conventional equilibrium expression for the entropy. In Sec. VI, it is shown that the present analysis is also applicable to a one-dimensional gas of N particles which interact elastically with each other and with the walls. Detailed comparison of the present work with the work of others is given in Sec. VII, and further discussion is given in Sec. VIII.

II. INITIAL DISTRIBUTION

Consider a Knudsen gas of N identical particles of mass m which bounce elastically from the walls of a rectangular box. The walls are located at $x = 0$, $x = L_1$, $y = 0$, $y = L_2$, $z = 0$, and $z = L_3$. Suppose that the available measuring instruments are capable of making rough (i.e., macroscopic) measurements of the center of mass $\vec{R}$, total energy H, and total momentum $\vec{P}$. Since the information furnished by these measuring instruments is less than complete, it is necessary to use a statistical, rather than a mechanical, description of the system[8, 13-18]

An initial measurement of $\vec{R}$, H, and $\vec{P}$ yields the following information:

$$\langle \vec{R} \rangle_0, \langle H \rangle_0, \langle \vec{P} \rangle_0 . \tag{2.1}$$

Here, $\langle \; \rangle_t$ means "expected value at time t," i.e.,

$$\langle g(X) \rangle_t = \int g(X) P(X, t) dX, \tag{2.2}$$

where X represents a point in the $6N$-dimensional phase space, and $P(X, t)$ is the N-particle probability distribution function for the phase point X. The only general prescription for finding the initial distribution corresponding to given initial information appears to be Jaynes' principle of maximum uncertainty.[14] According to this principle, the initial distribution is that function maximizing the uncertainty

$$- \int P(X,0) \ln P(X,0) dX \tag{2.3}$$

with respect to those distributions satisfying the given information. Applying this principle to the initial information (2.1), the initial distribution is found to be [14]

$$P(X,0) = A^{-1} \exp(-N\vec{\alpha} \cdot \vec{R} - \beta H - \vec{\gamma} \cdot \vec{P}), \tag{2.4}$$

where A is chosen to normalize P,

$$\int P(X,0) dX = 1, \tag{2.5}$$

and the coefficients $N\vec{\alpha}$, β, $\vec{\gamma}$ are chosen to satisfy the given information (2.1). Equation (2.4) gives $P(X,0)$ for any phase point such that all the particles are inside the box; P is zero if any particle is outside the box. Using

$$\vec{R} = N^{-1} \sum \vec{r}_i ,$$

$$H = (2m)^{-1} \sum \vec{p}_i \cdot \vec{p}_i, \quad \vec{P} = \sum \vec{p}_i , \tag{2.6}$$

the distribution (2.4) may be written in the more convenient form

$$P(X,0) = Z^{-1}$$
$$\times \exp[-\vec{\alpha} \cdot \sum \vec{r}_i - (\beta/2m) \sum (\vec{p}_i - \vec{p}_0)^2]. \tag{2.7}$$

Here the partition function Z is given by

$$Z = \int \exp[-\vec{\alpha} \cdot \sum \vec{r}_i$$
$$- (\beta/2m) \sum (\vec{p}_i - \vec{p}_0)^2] dX, \tag{2.8}$$

the new coefficient $\vec{p}_0$ is defined by $\vec{p}_0 = -m\vec{\gamma}/\beta$, the particles are labeled by i, and the sums run from from $i = 1$ to N.

By direct integration, one obtains the following relations:

$$Z = Z_1^N$$
$$\text{where } Z_1 = \left(\frac{2\pi m}{\beta}\right)^{3/2} \prod_\mu \frac{1 - e^{-\alpha_\mu L_\mu}}{\alpha_\mu} \tag{2.9}$$

$$\langle \vec{p}_i \rangle_0 = \vec{p}_0, \tag{2.10}$$

$$\langle \vec{P} \rangle_0 = N\vec{p}_0, \tag{2.11}$$

$$\langle (\vec{p}_i - \vec{p}_0)^2/2m \rangle_0 = 3/2\beta, \tag{2.12}$$

$$\langle H \rangle_0 = 3N/2\beta + N\vec{p}_0^2/2m, \tag{2.13}$$

$$\langle R_\mu \rangle_0 = \langle r_{i\mu} \rangle_0$$
$$= 1/\alpha_\mu - L_\mu / [\exp(\alpha_\mu L_\mu) - 1], \tag{2.14}$$

where μ runs over the integers 1, 2, and 3 corresponding to the directions x, y, and z. Equations (2.11), (2.13), and (2.14) determine $\vec{\alpha}$, β, and $\vec{p}_0$ in terms of the given information. [It follows from (2.14) that $\langle R_\mu \rangle_0$ is a monotonic decreasing function of α_μ, with

$$\langle R_\mu \rangle_0 \to L_\mu \quad \text{as } \alpha_\mu \to -\infty ,$$
$$\langle R_\mu \rangle_0 \to L_\mu/2 \quad \text{as } \alpha_\mu \to 0 ,$$
$$\langle R_\mu \rangle_0 \to 0 \quad \text{as } \alpha_\mu \to +\infty .$$

Thus, for any given $\langle R_\mu \rangle_0$ in the permitted range $0 \le \langle R_\mu \rangle_0 \le L_\mu$, (2.14) determines a unique α_μ in the range $-\infty \le \alpha_\mu \le \infty$.] Equation (2.10) shows that $\vec{p}_0$ is the expected momentum of each particle Equation (2.12) shows that $3/2\beta$ is the "mean ran-

dom kinetic energy" (i. e. , the mean kinetic energy as seen in a frame moving with the mean velocity $\vec{p}_0/m$) of each particle.

The initial distribution (2. 7) may be written as a product of distributions for each degree of freedom $(r_{i\mu}, p_{i\mu})$ as follows:

$$P(X, 0) = \prod_{i=1}^{N} \prod_{\mu=1}^{3} P(r_{i\mu}, p_{i\mu}, 0), \qquad (2.15)$$

$$P(r_{i\mu}, p_{i\mu}, 0) = Z_{i\mu}^{-1}$$
$$\times \exp\left[-\alpha_\mu r_{i\mu} - (\beta/2m)(p_{i\mu} - p_{0\mu})^2\right], \quad (2.16)$$

$$Z_{i\mu} = \left(\frac{2\pi m}{\beta}\right)^{1/2} \frac{1 - \exp(-\alpha_\mu L_\mu)}{\alpha_\mu} \qquad (2.17)$$

According to (2.15), the degrees of freedom (and hence also the particles) are statistically independent at $t = 0$.

III. TIME DEPENDENCE OF $P(X,t)$

A. Reduction to One Degree of Freedom

The distribution $P(X, t)$ obeys Liouville's equation

$$i\, \partial P(X, t)/\partial t = \hat{L} P(X, t), \qquad (3.1)$$

where the Liouville operator $\hat{L}$ is defined by[19]

$$\hat{L}g(X) = i[H, g(X)], \qquad (3.2)$$

where $[\ ,\ ]$ is the Poisson bracket. The formal solution of (3. 1) is

$$P(X, t) = \exp(-i\hat{L}t)P(X, 0). \qquad (3.3)$$

The Hamiltonian for the Knudsen gas is $H = \sum H_{i\mu}$, where $H_{i\mu} = p_{i\mu}^2/2m + V_\mu(r_{i\mu})$, and where $V_\mu(r)$ is the wall potential (zero for $0 < r < L_\mu$, infinite for $r < 0$ or $r > L_\mu$). Thus, the Liouville operator may be written $\hat{L} = \sum \hat{L}_{i\mu}$, where $\hat{L}_{i\mu}$ operates only on the variables $(r_{i\mu}, p_{i\mu})$. Thus (3. 3) and (2. 15) imply

$$P(X, t) = \prod_{i=1}^{N} \prod_{\mu=1}^{3} P(r_{i\mu}, t), \qquad (3.4)$$

$$P(r_{i\mu}, p_{i\mu}, t) = \exp(-i\hat{L}_{i\mu}t)P(r_{i\mu}, p_{i\mu}, 0). \quad (3.5)$$

Thus the time evolution of $P(X, t)$ may be obtained by finding the distribution $P(r_{i\mu}, p_{i\mu}, t)$ for a single particle in a one-dimensional square well $0 < r_{i\mu} < L_\mu$, subject to the initial distribution $P(r_{i\mu}, p_{i\mu}, 0)$ given by (2. 16).

B. Solution of the One-Dimensional Problem

In this sub-section, the subscripts i and μ will be omitted.

An extension of the method used by M. Born[4] to solve a one-dimensional problem similar to the present problem will be used to obtain an exact analytic expression for the one-dimensional distribution $P(r, p, t)$. The method used by Born is as follows: Replace the initial condition $P(r, p, 0)$ by the extended initial condition $\bar{P}(r, p, 0)$ which is identical to $P(r, p, 0)$ in the region $0 < r < L$ and is defined for r outside this region by

$$\bar{P}(-r, -p, 0) = \bar{P}(r, p, 0), \qquad (3.6)$$

$$\bar{P}(r + 2L, p, 0) = \bar{P}(r, p, 0), \qquad (3.7)$$

while at the same time replacing the actual Hamiltonian [containing the wall potential $V(r)$]

$$H = p^2/2m + V(r) \qquad (3.8)$$

by the free-particle Hamiltonian

$$\bar{H} = p^2/2m. \qquad (3.9)$$

The new problem, with initial condition $\bar{P}(r, p, 0)$, Hamiltonian $\bar{H}$, and range $(-\infty < r < \infty)$, is much simpler than the original problem. However, as shown by Born,[4] the solution $\bar{P}(r, p, t)$ of the new problem is, for $0 < r < L$, the same as the solution $P(r, p, t)$ of the original problem, i.e.

$$P(r, p, t) = \bar{P}(r, p, t) \text{ for } 0 < r < L. \qquad (3.10)$$

A proof of this statement is given in the Appendix.

According to (2. 16) and (3. 6), the new initial condition $\bar{P}(r, p, 0)$ is, for $-L < r < L$,

$$\bar{P}(r, p, 0) = Z_1^{-1} \exp\{-\alpha |r| - (\beta/2m)[p - \theta(r)p_0]^2\} \text{ for } -L < r < L, \qquad (3.11)$$

where $\theta(r) = -1$ for $-L < r < 0$ and $\theta(r) = +1$ for $0 < r < L$. The partition function Z_1 is given by (2. 17). Outside of the region $-L < r < L$, $\bar{P}(r, p, 0)$ is given by the periodicity condition (3. 7). It follows from the free-particle Hamiltonian (3. 9) that the distribution $\bar{P}$ at the time t is

$$\bar{P}(r, p, t) = \bar{P}(r - pt/m, p, 0). \qquad (3.12)$$

Since $\bar{P}(r, p, 0)$ is periodic in r with period $2L$, it can be written as a Fourier series in r:

$$\bar{P}(r, p, 0) = a_0(p) + \sum a_n(p) \cos(n\pi r/L) + \sum b_n(p) \sin(n\pi r/L). \tag{3.13}$$

Evaluating the coefficients with the help of (3.11) and then using (3.12) and (3.10), the following expression is found for $P(r, p, t)$ in the region $0 < r < L$:

$$P(r, p, t) = Z_1^{-1} s_0(p) \left(\frac{1 - e^{-\alpha L}}{2\alpha L} \right) + Z_1^{-1} s_0(p) \sum_{n=1}^{\infty} \frac{\alpha L}{\alpha^2 L^2 + n^2 \pi^2} [1 - (-1)^n e^{-\alpha L}] \cos\left[\frac{n\pi}{L} \left(r - \frac{pt}{m} \right) \right]$$
$$+ Z_1^{-1} s_1(p) \sum_{n=1}^{\infty} \frac{n\pi}{\alpha^2 L^2 + n^2 \pi^2} [1 - (-1)^n e^{-\alpha L}] \sin\left[\frac{n\pi}{L} \left(r - \frac{pt}{m} \right) \right], \tag{3.14}$$

where $s_0(p)$ and $s_1(p)$ are defined by

$$s_j(p) = \exp\left[-\beta(p - p_0)^2 / 2m \right] + (-1)^j \exp\left[-\beta (p + p_0)^2 / 2m \right]. \tag{3.15}$$

Equation (3.14) is the exact, analytic expression for the one-dimensional distribution for a particle in a box $0 < r < L$ subject to the initial condition (2.16).

C. Solution of the N-Particle Problem

The solution to the original problem (3.1) with initial condition (2.7) [i.e., with the initial information (2.1)] is given by (3.4), where the one-dimensional distribution $P(r_{i\mu}, p_{i\mu}, t)$ is given by (3.14) and (3.15), and the one-dimensional partition function is given by (2.17). Note that $P(X, t)$ does not, strictly speaking, relax to equilibrium. According to (3.4) and (3.14), $P(X, t)$ undergoes an oscillatory behavior at any fixed phase point X. However, as will be seen in the following section, the system approaches equilibrium in a certain "weak" sense.

IV. APPROACH TO EQUILIBRIUM

In this section, various reduced distributions, moments, and expected values will be calculated.

Integrating (3.14) over all momenta, the reduced distribution for the configuration $(\vec{r}_1, \cdots \vec{r}_N)$ is found to be

$$P(\vec{r}_1, \cdots \vec{r}_N, t) = \prod_{i=1}^{N} \prod_{\mu=1}^{3} P(r_{i\mu}, t), \tag{4.1}$$

where the one-dimensional distribution for $r_{i\mu}$ alone is given by

$$P(r, t) = L^{-1} + \frac{2\alpha}{1 - e^{-\alpha L}} \sum_{n=1}^{\infty} \frac{1 - (-1)^n e^{-\alpha L}}{(\alpha^2 L^2 + n^2 \pi^2)^{1/2}} \cos\left(\frac{n\pi r}{L} \right) \exp\left(\frac{-n^2 \pi^2 t^2}{2L^2 m\beta} \right) \cos\left(\frac{n\pi p_0 t}{Lm} + \Phi_n \right), \tag{4.2}$$

and where the phase angle for the nth term is defined by

$$\Phi_n = \cos^{-1} [\alpha L / (\alpha^2 L^2 + n^2 \pi^2)^{1/2}]. \tag{4.3}$$

In (4.2) and (4.3), the subscripts i and μ have been omitted. According to (4.2), $P(r_{i\mu}, t)$ relaxes to the equilibrium value $P(r_{i\mu}, t \to \infty) = L^{-1}$, with a relaxation time τ_μ (for relaxation in the μ direction) given by

$$\tau_\mu = (2m\beta)^{1/2} L_\mu / \pi \quad \text{where} \quad \mu = x, y, z. \tag{4.4}$$

Similarly, the reduced distribution for the momenta $(\vec{p}_1, \cdots \vec{p}_N)$ may be obtained by integrating (3.14) over all coordinates. The result will not be written down here. It is found that $P(\vec{p}_1, \cdots \vec{p}_N, t)$ does not relax to equilibrium, but instead undergoes an oscillatory behavior [at a fixed point $(\vec{p}_1, \cdots \vec{p}_N)$] similar to the behavior found in Sec. III for the N-particle distribution. However, as will be seen, the momentum distribution relaxes to equilibrium in a certain "weak" sense.

It is possible to carry out an exact calculation of all the moments of $P(X, t)$. Since, by (3.4), the degrees of freedom are statistically independent, it suffices to consider only the moments of the one-dimensional distribution $P(r_{i\mu}, p_{i\mu}, t)$. Omitting the subscripts i and μ, these moments are defined by

$$\langle r^j p^k \rangle_t = \int r^j p^k P(r, p, t) dr dp \quad \text{where} \quad j, k = 0, 1, 2, \ldots \tag{4.5}$$

Using (3.14), it is possible to do the integral explicitly, for arbitrary j and k. The result is

$$\langle r^j p^k \rangle_t = \langle r^j p^k \rangle_{eq} + F_{jk}(t), \tag{4.6}$$

where $\langle r^j p^k \rangle_{eq} = \int r^j p^k P_{eq}(r, p) dr dp, \tag{4.7}$

$$P_{eq}(r,p) = (2L)^{-1}(\beta/2\pi m)^{1/2}s_0(p),\tag{4.8}$$

with $s_0(p)$ given by (3.15). The distribution $P_{eq}(r,p)$ is an equilibrium distribution, i.e., P_{eq} satisfies the time-independent Liouville equation. The distribution $P_{eq}(r,p)$ is independent of r, and is an even function of p with maxima near $p = \pm p_0$. Thus $P_{eq}(r,p)$ differs from the canonical distribution; this may be traced to the fact that any even power p^{2n} of the momentum is a constant of the motion, so that the system "remembers" all initial even moments of the momentum: $\langle p^{2n}\rangle_t = \langle p^{2n}\rangle_0$. If the initial mean momentum is zero, then by (2.11), (4.18), and (3.15), it is seen that $P_{eq}(r,p)$ is the canonical distribution. The time-dependent part $F_{jk}(t)$ of the j-k^{th} moment may be calculated explicitly, but will not be written down here since the expression is rather lengthy. For all moments except the even moments of p, (i.e., for all cases except $j = 0$, $k = 2n$), the dominant term of $F_{jk}(t)$ (for large t) has a time dependence given by

$$t^k \exp(-\pi^2 t^2/2\beta L^2 m).\tag{4.9}$$

As already mentioned, the even momentum moments $\langle p^{2n}\rangle$ are constant in time. Thus, all moments $\langle r^j p^k\rangle_t$ of the one-dimensional distribution $P(r,p,t)$ [and hence all moments of $P(X,t)$] relax toward equilibrium, with the equilibrium values being given by (4.7) and (4.8). It follows that the expected value $\langle g(X)\rangle$ of any analytic N-particle phase function $g(X)$ relaxes to the equilibrium value $\langle g(X)\rangle_{eq}$:

$$\langle g(X)\rangle_t \to \langle g(X)\rangle_{eq} = \int g(X)P_{eq}(X)dX ,\tag{4.10}$$

where $P_{eq}(X) = \prod_{i=1}^{N}\prod_{\mu=1}^{3}P_{eq}(r_{i\mu},p_{i\mu})$ \tag{4.11}

with $P_{eq}(r_{i\mu},p_{i\mu})$ given by (4.8). Thus, although the exact N-particle distribution $P(X,t)$ does not possess a limit as $t\to\infty$ [i.e., $P(X,t)$ does not relax to equilibrium], the system still "effectively" approaches equilibrium in the sense that the expected value of any analytic phase function approaches the equilibrium value given by (4.10). The effective asymptotic distribution is $P_{eq}(X)$, given by (4.11). This behavior has been termed a "weak" approach to equilibrium.[10] This seems to be the type of behavior which Gibbs[20] had in mind in his discussion of the relaxation of $P(X,t)$. Thus, this behavior may also be called "Gibbs phase mixing."

It is interesting to investigate the relaxation times associated with the various moments. For long t, the predominant term in $F_{jk}(t)$ is proportional to the expression (4.9). For $k = 0$ (i.e., for any moment $\langle r_\mu^j\rangle$ of r_μ alone), the time for relaxation of (4.9) is $(2m\beta)^{1/2}L_\mu/\pi$, in agreement with the relaxation time (4.4) found for $P(r_\mu,t)$. For $k \neq 0$, the function (4.9) has a maximum at $t = (km\beta)^{1/2}L_\mu/\pi$, and it then falls off exponentially with the relaxation time $(2m\beta)^{1/2}L_\mu/\pi$. Thus, the moment $\langle r_\mu^j p_\mu^k\rangle$ has the relaxation time $(\sqrt{2} + \sqrt{k})(m\beta)^{1/2}L_\mu/\pi$ for $k = 0, 1, 2, \cdots$. Thus, higher-momentum moments fall off more slowly. Generally speaking, one may say that phase functions having a simple momentum dependence (i.e., whose expansions in powers of r and p contain only low powers of p) relax rapidly, whereas phase functions having a complicated momentum dependence relax slowly. The reason for this is that Gibbs phase mixing implies a stretching out of the initial distribution into finer and finer filaments,[20] where the filaments (for the particle in a box) are nearly parallel to the r_μ axis.[8] The condition for a phase-function to be relaxed is that the function must vary only a small amount when the phase point varies from one filament to another. Thus, a function with a smooth momentum dependence will approach equilibrium more rapidly than one with a complicated momentum dependence.

The meaning of the fundamental relaxation time τ_μ, given by (4.4), is that τ_μ is on the order of the time required for a particle moving at the initial "random root mean square" speed $\sigma(v_\mu) \equiv [\langle(v_\mu - v_{0\mu})^2\rangle_0]^{1/2}$, $v_{0\mu} \equiv p_{0\mu}/m = \langle p_\mu\rangle/m$ to cross the container in the μ direction. To show this, use (2.12) and (4.4). At $t = 0$,

$$\langle(v_\mu - v_{0\mu})^2\rangle = m^{-2}\langle(p_\mu - p_{0\mu})^2\rangle = (\beta m)^{-1} = 2L_\mu^2/\pi^2\tau_\mu^2, \quad \sigma(v_\mu) = \sqrt{2}L_\mu/\pi\tau_\mu \sim L_\mu/\tau_\mu.$$

Thus, the relaxation time is dependent on the probabilistic spread of the initial velocities.

Explicit expressions for a few of the moments will now be given. Subscripts i and μ will be omitted. The expected position of the ith particle is

$$\langle r\rangle_t = \frac{L}{2} - \frac{4\alpha L^2}{\pi^2\tanh(\alpha L/2)}\sum_{n\,\text{odd}}\frac{1}{n^2(\alpha^2 L^2 + n^2\pi^2)^{1/2}}\exp\left(\frac{-n^2\pi^2 t^2}{2m\beta L^2}\right)\cos\left(\frac{n\pi p_0 t}{Lm} + \Phi_n\right),\tag{4.12}$$

where the Φ_n are defined by (4.3). The expected position is seen to oscillate with decreasing amplitude around $L/2$. The second moment of r is

$$\langle r^2\rangle_t = \frac{L^2}{3} + \frac{4\alpha L^3/\pi^2}{1 - e^{-\alpha L}}\sum_n\frac{(-1)^n[1-(-1)^n e^{-\alpha L}]}{n^2(\alpha^2 L^2 + n^2\pi^2)^{1/2}}\exp\left(\frac{-n^2\pi^2 t^2}{2L^2 m\beta}\right)\cos\left(\frac{n\pi p_0 t}{Lm} + \Phi_n\right).\tag{4.13}$$

Equations (4.12) and (4.13) may be obtained by integration beginning with (4.2). According to (4.12) and (4.13), the asymptotic value (for long times) of the variance of r is

$$\sigma^2(r) = \langle r^2 \rangle_\infty - \langle r \rangle_\infty^2 = L^2/12, \tag{4.14}$$

in agreement with the variance found directly from the asymptotic reduced distribution $P(r, t \to \infty) = L^{-1}$. The expected momentum of the i th particle may be calculated from (3. 14). The result is

$$\langle p \rangle_t = \frac{4\alpha L}{\tanh(\alpha L/2)} \sum_{n \text{ odd}} \frac{1}{\alpha^2 L^2 + n^2 \pi^2} \exp\left(\frac{-n^2 \pi^2 t^2}{2L^2 m \beta}\right) \left[\sin\left(\frac{n \pi p_0 t}{Lm}\right)\left(\frac{n \pi t}{\beta L} - \frac{\alpha L p_0}{n \pi}\right) + \cos \frac{n \pi p_0 t}{Lm}\left(\frac{\alpha t}{\beta} + p_0\right)\right]. \tag{4.15}$$

It is seen that $\langle p \rangle_t$ exhibits an oscillatory relaxation to $\langle p \rangle_\infty = 0$, and that the predominant time dependence (for long times) is $t \exp(-\pi^2 t^2/2L^2 \beta m)$, in agreement with (4. 9).

The expected values of the macroscopic observables $\langle \vec{R} \rangle$, $\langle H \rangle$, and $\langle \vec{P} \rangle$ will now be calculated. The expected value of the μ component of the center of mass is

$$\langle R_\mu \rangle_t = \langle N^{-1} \sum_{i=1}^{n} r_{i\mu} \rangle_t = \langle r_{1\mu} \rangle_t, \tag{4.16}$$

since the distributions for the $r_{i\mu}$ ($i = 1, 2, \cdots N$) are identical. Thus $\langle R_\mu \rangle_t$ is given by the right-hand side of (4. 12) (with the subscript μ placed on α, L, and p_0). The variance of R_μ at time t is

$$\sigma^2 \langle R_\mu \rangle = \langle R_\mu^2 \rangle_t - \langle R_\mu \rangle_t^2 = N^{-1} \sigma^2(r_{1\mu}), \tag{4.17}$$

as may be shown by using $R_\mu = N^{-1} \sum r_{i\mu}$ and the statistical independence of the $r_{i\mu}$ Thus, although by (4. 14) the dispersion (i.e., the square root of the variance) of $r_{i\mu}$ increases to $L/(12)^{1/2}$ as $t \to \infty$, the dispersion of R_μ increases only to $L/(12N)^{1/2}$. The small dispersion of R_μ is, of course, due to the fact that R_μ is a sum function.

The expected energy is constant, since H is a constant of the motion:

$$\langle H \rangle_t = \langle H \rangle_0, \tag{4.18}$$

where $\langle H \rangle_0$ is given by (2. 13). The expected value of the μ component of the total momentum is

$$\langle P_\mu \rangle_t = \langle \sum_{i=1}^{N} p_{i\mu} \rangle_t = N \langle p_{1\mu} \rangle_t, \tag{4.19}$$

where $\langle p_{1\mu} \rangle_t$ is given by (4. 15) (with the subscript μ placed on L, α, and p_0). Equations (4. 16), (4. 18), and (4. 19), coupled with (4. 12) and (4. 15), give the time dependence of the macroscopic observables $\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$. It is interesting to note that the macroscopic observables approach the values they would have in the *canonical* distribution having expected energy $\langle H \rangle_0$ (i.e., $\langle \vec{R} \rangle \to L/2$ and $\langle \vec{P} \rangle \to 0$), even though the equivalent asymptotic distribution given by (4. 11) and 4. 8) is not the canonical distribution.

V. NONEQUILIBRIUM ENTROPY

Robertson[18] has given a useful general definition of the nonequilibrium entropy. As applied to the present problem, Robertson's definition of the entropy $S(t)$ is

$$S(t) = -k \int dX \rho(X, t) \ln \rho(X, t), \tag{5.1}$$

where k is Boltzmann's constant and $\rho(X, t)$ is *defined* by
$$\rho(X, t) = A^{-1}(t)$$
$$\times \exp[-N \vec{\alpha}(t) \cdot \vec{R} - \beta(t)H - \vec{\gamma}(t) \cdot \vec{P}]. \tag{5.2}$$

Here $A(t)$ is determined by the normalization condition $\int \rho(X, t) dX = 1$, and the defining equations for the time-dependent coefficients $N\vec{\alpha}(t)$, $\beta(t)$, and $\vec{\gamma}(t)$ are

$$\langle \vec{R} \rangle_t = \int dX \vec{R} \rho(X, t), \tag{5.3}$$

$$\langle H \rangle_t = \int dX H \rho(X, t), \tag{5.4}$$

$$\langle \vec{P} \rangle_t = \int dX \vec{P} \rho(X, t). \tag{5.5}$$

Note the important distinction between the *con-*

stants $\vec{\alpha}$, β, and $\vec{\gamma}$, which are determined by the initial information (2. 1), and the time-dependent multipliers $\vec{\alpha}(t)$, $\beta(t)$, and $\vec{\gamma}(t)$, which are determined by the values of the macroscopic observables at time t. Comparing (2. 4) and (5. 2), it is seen that

$$\vec{\alpha}(t = 0) = \vec{\alpha}, \quad \beta(t = 0) = \beta, \quad \vec{\gamma}(t = 0) = \vec{\gamma}. \tag{5.6}$$

The definition (5. 2) of $\rho(X, t)$ involves no assumptions; in particular, it is not assumed that the system is at or near equilibrium.[18] The entropy defined by (5. 1) has the following properties:[18] It agrees with the usual equilibrium entropy whenever the system is represented by the equilibrium canonical distribution; $S(t)$ increases (but not necessarily monotonically) in a nonequilibrium process; $S(t)$ depends only on the instantaneous values of the macroscopic observables, i.e., $S(t)$ is a thermodynamic-state variable.

The meaning of $S(t)$ is as follows[21]: Let the values at time t of the macroscopic observables [as predicted by $P(X, t)$ determined from Liouville's equation] be $\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$; the entropy $S(t)$ is then the value of the observer' s *uncertainty*[14,15] about the underlying phase point X at time t, when the only information available to the observer is

$\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$. Thus, an increasing entropy implies loss of information (i.e., increasing uncertainty) about the underlying phase point X.

Replacing the multiplier $\vec{\gamma}(t)$ by the new coefficient $\vec{p}_0(t) = -m\vec{\gamma}(t)/\beta(t)$, $\rho(X, t)$ becomes

$$\rho(X, t) = Z^{-1}(t) \exp\{-\vec{\alpha}(t) \cdot \sum \vec{r}_i - [\beta(t)/2m]$$

$$\times \sum [\vec{p}_i - \vec{p}_0(t)]^2\}, \tag{5.7}$$

where the time-dependent partition function is

$$Z(t) = \int dX \exp\{-\vec{\alpha}(t) \cdot \sum \vec{r}_i$$

$$- [\beta(t)/2m] \sum [\vec{p}_i - \vec{p}_0(t)]^2\}. \tag{5.8}$$

The relationship between the observables $\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$ and the quantities $Z(t)$, $\vec{\alpha}(t)$, $\beta(t)$, and $\vec{\gamma}(t)$ is the same as that between $\langle \vec{R} \rangle_0$, $\langle H \rangle_0$, and $\langle \vec{P} \rangle_0$ and the quantities Z, $\vec{\alpha}$, β, and $\vec{\gamma}$. Thus, using (2.9) – (2.14) along with (4.16), (4.18), and (4.19),

$$Z(t) = Z_1^N(t)$$

where $Z_1(t) = \left[\frac{2\pi m}{\beta(t)}\right]^{3/2} \prod_\mu \frac{1 - e^{-\alpha_\mu(t)L_\mu}}{\alpha_\mu(t)}$ (5.9)

$$\vec{p}_0(t) = N^{-1} \langle \vec{P} \rangle_t = \langle \vec{p}_i \rangle_t, \tag{5.10}$$

$$3/2\beta(t) = \langle [\vec{p}_i - \vec{p}_0(t)]^2/2m \rangle_t \tag{5.11}$$

$$3/2\beta(t) + \vec{p}_0^2(t)/2m = N^{-1} \langle H \rangle_t = N^{-1} \langle H \rangle_0, \tag{5.12}$$

$$\alpha_\mu^{-1}(t) - L_\mu/[e^{\alpha_\mu(t)L_\mu} - 1]$$

$$= \langle R_\mu \rangle_t = \langle r_{i\mu} \rangle_t. \tag{5.13}$$

Using (5.1), (5.7), (5.9), (5.11), and (5.13), it is a a straightforward matter to show that the entropy is given in terms of $\vec{\alpha}(t)$, $\beta(t)$, and $\vec{p}_0(t)$ by

$$S(t) = \tfrac{3}{2} Nk \{\ln [2\pi m V^{3/2} \beta^{-1}(t)] + 1\}$$

$$+ Nk \sum h_\mu(t), \tag{5.14}$$

where $V = L_1 L_2 L_3$ and where h_μ ($\mu = 1, 2, 3$) is given by

$$h_\mu(t) = \ln \frac{1 - e^{-\alpha_\mu(t)L_\mu}}{\alpha_\mu(t)L_\mu}$$

$$+ 1 - \frac{\alpha_\mu(t)L_\mu}{e^{\alpha_\mu(t)L_\mu} - 1} \tag{5.15}$$

The time dependence of the quantities $\vec{\alpha}(t)$, $\beta(t)$, and $\vec{p}_0(t)$ will now be investigated. According to (5.10) and (4.15), $p_{0\mu}(t)$ oscillates with decreasing amplitude about $p_{0\mu}(t \to \infty) = 0$. It thus follows, from (5.12), that $\beta^{-1}(t)$ exhibits the behavior shown in Fig. 1. [In order to simplify matters, Fig. 1 is drawn for the case that $L_1 = L_2 = L_3$, so that the period of oscillation of $p_{0\mu}(t)$ is the same for all μ. In case the three sides are not of equal length, the "nodes" in Fig. 1 at t_0, $3t_0$, $\cdots$ will
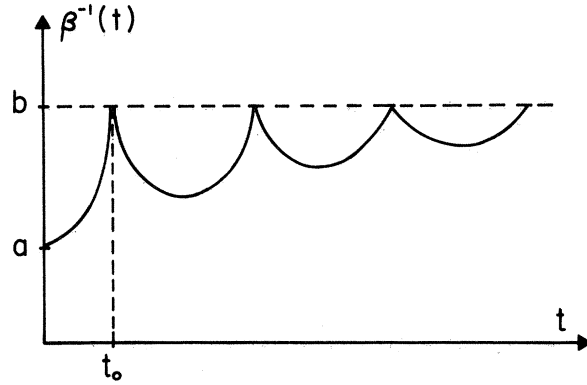

FIG. 1. Time dependence of $\beta^{-1}(t)$. The initial and final values of β^{-1} are: $a = 2\langle H \rangle/3N - p_0^2/3m$, $b = 2\langle H \rangle/3N$.

not occur, and the approach of $\beta^{-1}(t)$ to its asymptotic value will be somewhat smoother than the behavior shown in Fig. 1.] According to (5.10) and (5.11), $3/2\beta(t)$ is the mean random kinetic energy [i. e., the mean value of the kinetic energy as seen in a frame whose velocity is $\vec{p}_0(t)/m$] per particle at time t. Thus $\beta^{-1}(t)$ may be interpreted as $kT(t)$, where $T(t)$ is the instantaneous, nonequilibrium temperature of the system. The increase in temperature shown in Fig. 1 is a result of the conversion of "nonrandom" kinetic energy into "random" kinetic energy. According to (4.12), $\langle r_{i\mu} \rangle_t$ oscillates with decreasing amplitude about $\langle r_{i\mu} \rangle_\infty = 0$. It is not difficult to show, from (5.13), that this implies that $\alpha_\mu(t)$ oscillates with decreasing amplitude about α_μ $(t \to \infty) = 0$.

The time dependence of $S(t)$ will now be investigated. According to Fig. 1, the first term on the right-hand side of (5.14) undergoes a nonmonotonic increase from a minimum at $t = 0$ to a maximum as $t \to \infty$. Using (5.15), the function h_μ, considered as a function of α_μ, may be shown to have the following properties: $h_\mu(\alpha_\mu) = 0$ when $\alpha_\mu = 0$; $h_\mu(\alpha_\mu)$ is monotonic decreasing as $|\alpha_\mu|$ increases. It has just been seen that $\alpha_\mu(t)$ undergoes a damped oscillatory motion about $\alpha_\mu(t \to \infty) = 0$. It follows that $h_\mu(t)$ undergoes the behavior shown in Fig. 2. Thus, the second term on the right-hand side of (5.14) undergoes a nonmonotonic increase from a minimum at $t = 0$ to a maximum as $t \to \infty$. It follows that $S(t)$ undergoes a nonmonotonic increase from the initial minimum value $S(0)$ [given by (5.14) and (5.15) with $\vec{\alpha}(0) = \vec{\alpha}$, $\beta(0) = \beta$] to the final maximum value

$$S(t \to \infty) = \tfrac{3}{2} Nk \ln \left(\frac{2\pi m V^{\frac{2}{3}}}{\beta(\infty)}\right) + \frac{3Nk}{2}, \tag{5.16}$$

where $\beta^{-1}(\infty) = kT(\infty)$ and, by Fig. 1, $T(\infty)$ is the conventional equilibrium temperature:

$$kT(\infty) = 2\langle H \rangle/3N. \tag{5.17}$$

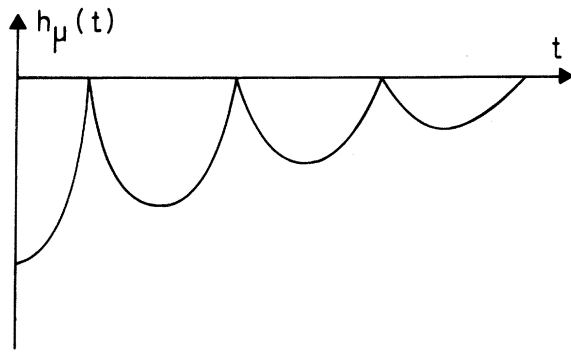Equation (5.16) is just the conventional expression

FIG. 2. Time dependence of $h_\mu(t)$.

for the entropy of an ideal gas [except that the factor $-k \ln N!$, which should be added to (5.1) if the system is composed of identical particles, has been omitted here for simplicity].

VI. ONE-DIMENSIONAL GAS WITH ELASTIC INTERACTIONS

Consider a system of N identical point particles constrained to lie on the x axis, and colliding elastically with each other and with the walls at 0 and L. When two particles collide, they simply exchange velocities. Thus, the mechanical evolution of any phase function $f(X)$ which doesn't depend on the labeling of the particles [i.e., which is symmetric in the one-particle phase points (r_i, p_i)] may be found by neglecting the collisions and treating the system as a one-demensional gas of noninteracting particles.

As in Sec. II, let the initial information for the one-dimensional gas be $\langle R \rangle_0$, $\langle H \rangle_0$, and $\langle P \rangle_0$. The initial distribution $P(X, 0)$ is then the initial distribution given in Sec. II (suitably restricted for the one-dimensional case), and $P(X, t)$ is the distribution given in Sec. III. Since $P(X, t)$ is symmetric in the one-particle phase points, the expected values of the symmetric phase functions $R(X)$, $H(X)$, and $P(X)$ may be found by neglecting all collisions between particles. Thus the evolution of the macroscopic observables $\langle R \rangle$, $\langle H \rangle$, and $\langle P \rangle$ is as given in Sec. IV (suitably restricted for the one-dimensional case), and the evolution of the entropy $S(t)$ is as given in Sec. V.

It is thus seen that, at least in the one-dimensional case, the results of the present paper carry over to systems in which elastic collisions occur.

VII. COMPARISON WITH THE WORK OF OTHERS

As was mentioned in Sec. I, there have been several previous nonequilibrium statistical-mechanical studies of model mechanical systems. Many of these studies were carried out on systems having only one degree of freedom,[4-8] while some have been carried on N-particle systems.[9-12]

Born[4] considers a single one-dimensional particle bouncing back and forth in a perfectly reflecting box. Beginning with a rather unphysical initial condition $P(r, p, 0)$ (chosen for mathematical convenience), Born finds exact, analytic expressions for $P(r, p, t)$ and for the reduced distribution $P(r, t)$. As in the present paper, Born shows that $P(r, t)$ approaches equilibrium as $t \to \infty$. Born does not investigate the moments of $P(r, p, t)$.

Synge[5] studies phase mixing in a single one-dimensional oscillator. Synge shows that phase mixing (i.e., an approach to equilibrium in the "weak" sense defined in Sec. IV) occurs for every one-dimensional oscillator with the exception of the perfect harmonic oscillator; no analytic expressions are given for $P(r, p, t)$ or its moments.

Brillouin[6] gives a qualitative analysis of various one-dimensional oscillators; again, no attempt is made to obtain an analytic solution.

Andrews[7] studies the single one-dimensional particle in a box. Andrews shows that the time-correlation function $\langle \alpha(t)\alpha(0) \rangle$, where $\alpha(t)$ represents the departure from equilibrium of the arbitrary observable α at time t, approaches zero as $t \to \infty$. It follows that the system effectively approaches equilibrium as $t \to \infty$. Andrews does not study $P(r, p, t)$ or its moments.

Hobson[8] studies the one-dimensional particle in a box, using a rather unphysical initial distribution which permits the use of geometrical methods for the investigation of the evolution of $P(r, p, t)$. The qualitative features of the phase mixing of $P(r, p, t)$ are studied, as is the approach to equilibrium of $\langle r \rangle_t$. No attempt is made to study $P(r, p, t)$ or its moments analytically.

In the present work, the simplifying feature which makes it possible to obtain an exact solution is the fact that the N-body problem is separable into $3N$ one-dimensional problems. Thus, the irreversibility which is exhibited in the present work is already exhibited in the one-dimensional problems considered by Born,[4] Synge,[5] Brillouin,[6] Andrews,[7] and Hobson.[8]

Turning now to studies of N-particle systems, Teramoto and Suzuki[9] consider a one-dimensional gas of N particles in a box, where the particles collide elastically with each other and with the walls (this is the system discussed in Sec. VI of the present paper). Beginning with an initial distribution $P(X, 0)$ which places all N particles in the left half of the box at $t = 0$, the authors examine the expected number of particles $\langle n \rangle_t$ in the left half of the box at time t. Exact, analytic results are obtained for $\langle n \rangle_t$ for the cases $N = 1$, $N = 2$, and $N \gg 1$. As expected, $\langle n \rangle_t \to N/2$ as $t \to \infty$. Teramoto and Suzuki do not examine the behavior of $P(X, t)$ or of its moments.

An important paper by Frisch[10] gives what appears to be the first clear statement of the concept of the weak approach to equilibrium. Frisch considers a one-dimensional system of point particles which are distributed on a unit circle and collide elastically with each other. This system is similar to the system discussed in Sec. VI of the present paper, with the following important distinction: by distributing the particles in a circle, Frisch throws out the effects of the walls; the result is that the momentum is a constant of the motion, and the momentum distribution is time-independent. By neglecting the walls, the

problem is of course considerably simplified. Furthermore, this procedure for getting rid of the walls is only meaningful for the one-dimensional gas. Frisch gives an exact, analytic expression for the N-particle distribution $P(X, t)$, and shows that the expected value of any phase function must approach equilibrium as $t \to \infty$. Thus, Frisch shows that the system approaches equilibrium in the weak sense. Frisch studies the detailed time-dependence of a few expectation values of physical interest, obtaining, for instance, an expression quite similar to (4.2) for the expected particle density. Frisch does not study the entropy $S(t)$.

J. Ford[11] studies a one-dimensional chain of N particles in which nearest neighbors are coupled by anharmonic (but approximately harmonic) forces. A certain "linear approximation"[11] to the exact mechanical motion is used. The ends of the chain are left free, so that wall forces are not considered. The weak approach to equilibrium is shown to occur for this system, and the equivalent asymptotic distribution is studied. No study is made of the time dependence of $P(X, t)$ or its moments.

Jepsen[12] studies a one-dimensional system of N point particles distributed on a circle and colliding elastically (this system is identical with the system studied by Frisch[10]). Since wall forces are neglected, the momentum distribution is time-independent. Jepsen studies the expected value of one-particle phase functions in the limit $N \to \infty$. No explicit, analytic results are obtained for $P(X, t)$ or its moments for finite N.

It may be worthwhile to compare the spirit of the present work (and of Refs. 4–12) with the work of Blatt[22] and others.[23–26] In Refs. 22–26, irreversible behavior is obtained by introducing a stochastic interaction between the surroundings and the system of interest. Blatt[22] defines an irreversible process as a process in which the entropy increases, and he defines the entropy as $-k \int P(X, t) \ln P(X, t) dX$ or its quantum statistical-mechanical equivalent $-k \, \mathrm{Tr}[\hat{P}(t) \ln \hat{P}(t)]$ where $\hat{P}(t)$ is the density operator. (Note the important distinction between Blatt's definition of the entropy and the definition given in Sec. V.) It is well-known that $-k \int P \ln P dX$ is constant in time, so Blatt argues that in order to obtain irreversible behavior we are forced to choose one of the following alternatives:

1. Replace the exact distribution $P(X, t)$ with a "coarse-grained" distribution $\tilde{P}(X, t)$.[27] It may be shown[27] that the coarse-grained entropy $-k \int \tilde{P} \ln \tilde{P} dX$ increases.

2. Consider the effect of the surroundings on the evolution of $P(X, t)$ by including a stochastic interaction between the system and the environment.

Blatt argues that the coarse-graining procedure is arbitrary and not physically justified, so that the second alternative must be accepted. The following remarks are pertinent to Blatt's point of view:

1. It has been shown in Ref. 10 and in the present work that even completely closed systems behave irreversibly, in the sense that all expectation values $\langle g(X) \rangle_t$ settle down to a constant

value as $t \to \infty$.

2. It has been seen that Blatt's definition of the entropy is not the only acceptable one, but that on the contrary Robertson's definition[18] is nonarbitrary and yields an increasing entropy even in closed systems.

3. Despite the above two remarks, interactions between the system and the surroundings may be important in determining the final equilibrium state of the system. It has been seen in Sec. IV that, for noninteracting clsosed systems, the effective asymptotic distribution $P_{eq}(X)$ is not necessarily the canonical distribution. This is due to the fact that the system "remembers" the distribution of all constants of the motion $p_{i\mu}^2$. Suppose now that a weak interaction between the particles were included in the problem. It seems likely that the only remaining constant of the motion would then be the total energy $H(X)$, since all other constants of the motion should be destroyed by the interaction. However, the effective asymptotic distribution $P_{eq}(X)$ would still be noncanonical, since the system would "remember" the initial energy distribution. If we desire the theory to describe an approach to the *canonical* distribution, it then becomes necessary to introduce interactions with the surroundings in order to alter the energy distribution.

VIII. DISCUSSION

Exact, analytic expressions have been found for the evolution of the N-particle probability distribution $P(X, t)$, for various moments of the distribution, and for the macroscopic observables $\langle \vec{R} \rangle$, $\langle H \rangle$, and $\langle \vec{P} \rangle$ for the N-particle Knudsen gas. Even though N is finite, the system exhibits an approach to equilibrium in the weak sense, i.e., the expected value of any analytic phase function settles down to a constant value as $t \to \infty$. As has been pointed out many times by various authors,[7, 8, 10, 11, 13] this in no way contradicts such *mechanical* theorems as Poincaré's recurrence theorem. The relaxation time is the "hydrodynamic time" σ/L, where σ^2 is the variance of the velocity. It is not surprising that the hydrodynamic time is the relevant time parameter in this problem, since the walls of the system (rather than the interactions between particles) are the cause of relaxation. The effective asymptotic distribution $P_{eq}(X)$ has been found, where $P_{eq}(X)$ is defined to be that distribution which yields the correct asymptotic (as $t \to \infty$) properties of the system. The distribution $P_{eq}(X)$ satisfies the time-independent Liouville equation, i.e., $P_{eq}(X)$ is an equilibrium distribution. Due to the fact that any even power of any single-particle momentum is a constant of the motion, the system never "forgets" the initial values of the even moments of the one-particle momenta; thus $P_{eq}(X)$ is not the canonical distribution. However, the observables $\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$ approach the asymptotic values $L/2$, $\langle H \rangle_0$, and 0 respectively; these asymptotic values agree with the values calculated from the canonical distribution having energy $\langle H \rangle_0$.

Possibly the most important feature of the pres-

ent analysis is the following result: *irreversibility* (i. e., a weak approach to equilibrium) occurs for arbitrary N, and is not dependent on the assumption of large N; however, *predictability* occurs only for large N. To make this statement more concrete, consider the behavior of the observable $\langle R_\mu \rangle_t$. According to (4.16) and (4.12), $\langle R_\mu \rangle_t$ settles down to equilibrium as $t \to \infty$. This occurs for arbitrary N, and in fact the behavior of $\langle R_\mu \rangle_t$ is entirely independent of N. Physically, $\langle R_\mu \rangle_t$ represents the observer's *best prediction* about the position of the center of mass of the system at time t, where that prediction is based on the initial data $\langle \vec{R} \rangle_0$, $\langle H \rangle_0$, and $\langle \vec{P} \rangle_0$ available to the observer. In any statistical prediction, there is always some chance of error. To investigate the chance of making a significant error, it is necessary to examine the variance of R_μ at time t. This variance is given by (4.17), and is seen to be strongly dependent on N. According to (4.17) and (4.14), for small N the dispersion (i. e., the square root of the variance) of R_μ becomes comparable to the length of the box as $t \to \infty$, whereas for large N the dispersion of R_μ remains small compared to the length of the box. Thus statistical predictions behave irreversibly for arbitrary N, but these predictions have a good chance of being in error unless N is large. For large N, and for sum functions (such as R_μ), predictions behave irreversibly and are not likely to be in error. Note that it is not necessary to let $N \to \infty$ to obtain high predictability; it is only necessary to let N be large. For instance, according to (4.17), predictions about R_μ for $t \to \infty$ should be valid to within a distance $0.01 L_\mu$ if $N = 10^4$.

The nonequilibrium entropy $S(t)$ undergoes a nonmonotonic increase at t increases. The increase of $S(t)$ is a reflection of the fact that if the observer knows only the instantaneous predicted values $\langle \vec{R} \rangle_t$, $\langle H \rangle_t$, and $\langle \vec{P} \rangle_t$ of the observables at time t, then the observer will know less and less about the underlying state $X(t)$ of the system as time increases. The asymptotic value $S(t \to \infty)$ of the entropy agrees with the value calculated from the canonical distribution having mean energy $\langle H \rangle_0$.

ACKNOWLEDGMENT

APPENDIX: PROOF OF EQUATION (3.10)

Consider the initial distribution

$$P(r, p, 0) = \delta(r - r_0)\delta(p - p_0) \qquad (A.1)$$

corresponding to exact knowledge of the initial phase point of the particle. The solution to Liouville's equation for the initial distribution (A.1) is simply

$$P(r, p, t) = \delta(r - r_t)\delta(p - p_t), \qquad (A.2)$$

where (r_t, p_t) is the phase point at time t corresponding to the initial phase point (r_0, p_0). If it can be shown that the replacement of the "old" problem [particle in a box with initial distribution $P(r, p, 0)$ for $0 < r < L$] by the "new" problem [free particle with initial distribution $\bar{P}(r, p, 0)$ defined for all r by (3.6) and (3.7)] is valid for the special initial distribution (A.1), then (by superposition) the proof is complete for arbitrary initial distributions

According to (3.6) and (3.7), the "new" initial conditions place a particle not only at (r_0, p_0), but also at the points $(r_0 + 2nL, p_0)$ and $(-r_0 - 2nL, p_0)$ for $(n = 0, \pm 1, \pm 2, \ldots)$ (see Fig. 3). In the "new" problem, each particle moves with constant momentum, with no reflections from the walls. An examination of Fig. 3 should convince the reader that the "new" problem yields, at any time t, exactly one particle in the region $0 < r < L$, and that the position and momentum of this particle are precisely the position and momentum of the particle in the "old" problem. Thus, the "new" problem gives the correct distribution $P(r, p, t)$ inside the box $0 < r < L$.
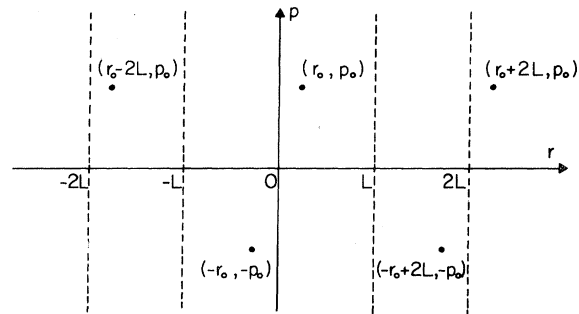

FIG. 3. The initial condition $\bar{P}(r, p, 0)$ corresponding to the distribution given by (A.1).

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Relativistic Thermodynamics of Moving Systems

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Thermodynamics is extended to systems moving with relativistic velocities. It is shown that one is led naturally, although not necessarily, to the thermodynamics of Ott, if one maintains the first and second law in their original form. The classical theory of Planck *et al.* can also be obtained in the case of a homogeneous fluid; the difference with Ott's theory is that the fluid alone is regarded as the thermodynamic system, rather than the fluid together with the box in which it is enclosed. Subsequently, a third form of relativistic thermodynamics is obtained by replacing the first law with a covariant equation expressing conservation of both energy and momentum. This leads to a formulation in which not only S but also T and $đQ$ are scalars. The discussion of heat transfer between systems with different velocities is thereby simplified. It is shown that such processes are irreversible even for equal temperatures, unless the velocities are equal too.

1. INTRODUCTION

The problem is to extend the laws of thermodynamics to a system moving with relativistic velocity $\vec{u}$. If $\vec{u}$ is taken to be a constant, this is simply the problem of transforming the thermodynamic properties of the system to a different frame of reference. However, *one wants to treat $\vec{u}$ as an additional thermodynamic variable* subject to adiabatic variations. That amounts to extending the usual space of thermodynamic variables by adding three dimensions, corresponding to the three components of $\vec{u}$. Thermodynamics of moving systems is therefore more than simply an exercise in Lorentz transformations.

The first law of thermodynamics is affected, because the work $đA$ now consists of the usual term representing the work done by expanding, $đA_V$, plus an additional term $đA_u$, representing the work involved in varying $\vec{u}$, that is, in accelerating or decelerating the whole system.

The second law is affected because Kelvin's principle, "No cyclic engine can convert heat into work," receives an extended meaning: "not even when the engine employs acceleration and deceleration of the system (to relativistic velocities)."

2. THE NONRELATIVISTIC CASE

The above remarks also apply to the nonrelativistic case, but that case is trivial. One has $đA_u = -M\vec{u} \cdot d\vec{u}$, where M is the mass of the system and is constant.[1] For the "internal energy" U one simply takes

$$U = U^0 + M\vec{u}^2,$$

where U^0 is the internal energy of the system at rest. The first law then states

$$đQ = dU + đA,$$
$$= dU + đA_u + đA_V,$$
$$= dU^0 + đA_V. \tag{1}$$

Thus the two additional terms cancel and everything reduces to the usual thermodynamics of systems at rest.

Incidentally, we note for future use that, for a homogeneous system, (1) may be written in the form