

## An Alternative Approach to the Ergodic Problem

J. M. BLATT

*Research Institute for Fundamental Physics, Yukawa Hall,  
Kyoto University, Kyoto, Japan*

and

*Applied Mathematics Department, University of New South Wales,  
Sydney, Australia*

(Received May 19, 1959)

The usual approach to the ergodic problem makes use of the idea of "coarse-graining". That is, a macroscopic observer is supposed to be limited to "coarse-grained" experiments, and the resultant lack of complete information about the system gives rise to the irreversible increase of the (coarse-grained) entropy. It is shown that this approach is untenable, since macroscopic observers are not restricted in principle to coarse-grained experiments, and in fact one "fine-grained" experiment has already been carried out in practice. An alternative approach is presented which avoids these difficulties. The irreversible increase of entropy is due to molecules outside the system proper, which collide with the outside of the box enclosing the system; this leads to a truly random, in principle unpredictable perturbation, which can be treated only stochastically. The number of particles within the system is irrelevant for this purpose, and in particular need not be large.

### § 1. Introduction

In statistical mechanics, we consider ensembles of systems described by a density matrix  $U$ . If each system is enclosed in a perfectly reflecting wall, and has an internal Hamiltonian  $H$ , the time development of the ensemble is given by the Liouville equation

$$\frac{dU}{dt} = \frac{1}{i\hbar} [H, U]. \quad (1.1)$$

The entropy of the typical system of the ensemble is defined by

$$S = -k \operatorname{Tr}(U \ln U), \quad (1.2)$$

where  $k$  is Boltzmann's constant. The *thermal equilibrium state* is that unique density matrix  $U_e$  which leads to the largest entropy  $S$ , subject to whatever macroscopic constraints are imposed on the system (e.g., given average energy, given volume, given number of particles).<sup>1)</sup>

If we start, at time  $t=0$ , from a density matrix  $U_0$ , then the Liouville equation (1.1) leads to the time development

$$U(t) = \exp(-iHt/\hbar) U_0 \exp(+iHt/\hbar). \quad (1.3)$$

This is a unitary transformation, which preserves traces of functions of  $U$ . Hence we obtain immediately:

$$S(t) = S(0). \quad (1.4)$$

That is, the entropy  $S$  fails to increase with time, and the thermal equilibrium distribution  $U_e$  is not approached by the system.

Since actual systems do tend to equilibrium as time goes on, this result is unacceptable. The usual way out of this difficulty is by means of the introduction of "coarse-grained averages".<sup>2,3)</sup> One argues that a macroscopic observer is not in a position to make sufficiently detailed "fine-grained" measurements to determine the complete density matrix  $U$ , and hence the entropy  $S$  of the system. The quantity  $S$  of equation (1.2) is called the "fine-grained entropy" and is in practice not measurable. Rather, macroscopic observers are restricted to "coarse-grained" measurements, i.e., measurements in which quantum states are lumped together into groups, and one determines which of these groups a given system of the ensemble falls into; no finer distinctions are made, and in particular the actual quantum state is not determined for any system on which measurements are carried out. One can allow for this coarse-graining process mathematically by introducing a mapping  $U \rightarrow \tilde{U}$  of the actual, fine-grained density matrix  $U$  onto a coarse-grained density matrix  $\tilde{U}$ . The coarse-grained entropy is then defined by

$$\tilde{S} = -k \operatorname{Tr}(\tilde{U} \ln \tilde{U}). \quad (1.5)$$

It is shown in reference 2 that, under very general assumptions concerning the nature of the coarse-graining process  $U \rightarrow \tilde{U}$ , the coarse-grained entropy  $\tilde{S}$  increases with time, thereby approaching the thermal equilibrium value which is the largest value it can reach.

This way out of the difficulty of equation (1.4) retains the Liouville equation (1.1) but modifies the definition of entropy, from (1.2) to (1.5), and at the same time gives up the idea of a unique equilibrium distribution  $U_e$ . We now say that equilibrium has been reached whenever the coarse-grained entropy  $\tilde{S}$  has attained its equilibrium value; this condition is much too weak to pick out a unique statistical matrix  $U_e$ , and; in fact, the Liouville equation is inconsistent with approach to any one unique limiting distribution  $U_e$ .

It should be noted that the coarse-graining approach depends crucially upon the assertion that "fine-grained" measurements are impracticable, and thus the fine-grained entropy is a meaningless concept. We shall show in section 2 of this paper that such measurements are not only possible in principle, but at least one such measurement has already been carried out by an actual macroscopic observer: The spin-echo experiment of Hahn.<sup>4)</sup> *It is therefore not permissible to base fundamental arguments in statistical mechanics on coarse-graining.* The failure of the fine-grained entropy, (1.2), to increase with time is not merely an unimportant

curiosity. Rather, it represents an important and measurable aspect of the physical situation. No theoretical approach which leads to constancy of  $S$  can constitute a satisfactory logical basis for statistical mechanics.

A different approach has already been considered in the literature.<sup>5),6),7),8)</sup> It consists in retaining the definition of entropy, but modifying the Liouville equation (1.1) through introducing the random influence of the thermal motion of the wall of the system. It has been shown that this approach leads to thermal equilibrium under very general conditions.

Nevertheless, this approach has not found general acceptance. There is a common feeling that it should not be necessary to introduce the wall of the system in so explicit a fashion. For example, a system contained inside a calorimeter approaches internal thermal equilibrium, at some temperature  $T$ , long before it reaches thermal equilibrium with the world outside the calorimeter, at room temperature. Furthermore, it is considered unacceptable philosophically, and somewhat "unsporting", to introduce an *explicit* source of randomness and stochastic behaviour directly into the basic equations. Statistical mechanics is felt to be a part of mechanics, and as such one should be able to start from purely causal behaviour.

Section 3 of the present paper is devoted to a discussion of these arguments. We arrive at the conclusion that the objections listed above are invalid, and that there exists a sound logical and philosophic basis for introducing stochastic concepts directly into the basic equations of statistical mechanics. The difficulty about the calorimeter is only apparent, and disappears when one distinguishes carefully between the relevant relaxation times.

## § 2. Arguments against coarse-graining

On general, philosophical grounds, the coarse-graining procedure is somewhat disconcerting, in that it makes an actual physical process (the approach of the system to equilibrium) dependent on the accidental shortcomings of the observer who makes measurements on the system.\* Close interaction between observer and observed system is of course a commonplace in quantum mechanics. But the ergodic problem already occurs in classical statistical mechanics, and (with the possible exception of von Neumann<sup>9)</sup>) there is general agreement that the transition from classical mechanics to quantum mechanics makes no essential difference to this problem. If we take a purely classical view, then there is no objection in principle to a fine-grained observation of each system of our ensemble of systems. Coarse-graining is not intrinsic to the problem under study, and it is dragged in artificially, so to speak, in order to save the principle of increasing entropy. The same is true in quantum mechanics, the only difference being that we mean

---

\* A different interpretation of the meaning of the coarse-graining procedure is possible, and will be discussed at the end of section 3.

something different by a “measurement”, namely the determination of the quantum state  $\psi$  rather than the determination of  $3N$  coordinates and  $3N$  momenta.

We shall now go on to demonstrate by means of a Gedanken-experiment that coarse-graining can be misleading, and we then show that an actual experiment closely analogous to this Gedanken-experiment has already been carried out.

Consider an ideal gas of particles constrained to move in the  $x$ -direction only, confined by walls at  $x=a$  and  $x=-a$ . Initially, at time  $t=0$ , all  $N$  particles are located at the centre, at  $x=0$ , and they have a Maxwellian distribution of velocities. Thus the combined probability distribution in  $x$  and  $v$  at time  $t=0$  is

$$U(x, v) = P_0 \delta(x) \exp(-\frac{1}{2}mv^2/kT) \quad \text{at } t=0 \quad (2.1)$$

where  $P_0$  is a normalization constant.

As time goes on, the particles are reflected back and forth between the two walls. Under the usual assumption that the walls are perfectly reflecting mirrors, the speed of any one particle does not change. However, their initial non-uniform distribution in space is smeared out rather quickly. The characteristic time for this process is the time which the “average” particle takes to traverse the distance  $2a$ , i.e.,

$$T_0 = 2a/v_0, \quad (2.2)$$

where  $v_0$  is some average speed, for instance the root-mean-square velocity. After, say,  $10T_0$ , the distribution of the particles in space will be sensibly uniform. Their distribution in momentum space is Maxwellian to start out with, and stays that way. Hence, any “coarse-grained” experiment to determine the combined distribution function  $U(x, v)$  is bound to lead to the equilibrium result,

$$U(x, v) = \frac{P_0}{2a} \exp(-\frac{1}{2}mv^2/kT). \quad \text{Equilibrium} \quad (2.3)$$

This is the way in which coarse-graining leads to the thermal equilibrium distribution.

Actually, however, the true distribution function is not at all equal to (2.3). Rather, there are complicated correlations between the positions and momenta of all the particles. To see that this is true, consider the following Gedanken-experiment: At time  $t=T$ , reverse the velocities of all particles of the gas. It follows immediately that at time  $t=2T$ , the initial state (all particles at  $x=0$ ) reoccurs. We shall call this the *reversal experiment*.

This kind of recurrence of the initial configuration has nothing to do with the Poincaré recurrence cycle. The time for the latter is unimaginably long. Thus, if we carry out the reversal experiment on a system whose distribution function is truly (2.3), we shall indeed reach any unusual distribution (including the one with all particles at  $x=0$ ) eventually, but the time involved is so long that it is of no practical importance. Conversely, if the reversal experiment, carried out on

an unknown system, leads to all particles congregating at  $x=0$  some finite, small time  $T$  later, then we are perfectly safe in concluding that the unknown system was not really in equilibrium, i.e., did not really have the distribution function (2.3) in the fine-grained sense.

To distinguish between the true equilibrium distribution (2.3) and the distribution obtained in our Gedanken-experiment at time  $T$ , we shall use the term "quasi-equilibrium" for the latter. To an observer constrained to make coarse-grained measurements only, there is no difference between quasi-equilibrium and true equilibrium. If we accept the restriction that macroscopic observers can make only coarse-grained measurements, our reversal experiment is not a possible experiment for a macroscopic observer, and there is no difficulty. No macroscopic observer can distinguish between quasi-equilibrium and true equilibrium, and thus this distinction is simply sophistry of no consequence to physics.

However, macroscopic observers *can* carry out reversal experiments in principle. It is not necessary to *measure* a velocity in order to *reverse* it. Thus, the process of *reversing* all velocities does not imply *measurement* of all velocities (which latter would indeed be impossible for a macroscopic observer). Hence there is no difficulty *in principle* with our reversal experiment.

Even more striking is the fact that just such a reversal experiment *has actually been carried out* already. This is the "spin-echo" experiment of Hahn.<sup>4</sup> In this experiment, spins are aligned by a strong pulse at time  $t=0$ . As a result of small inhomogeneities in the "constant" magnetic field  $H_0$  applied to the specimen, different nuclear spins undergo Larmor precession at slightly different rates. Hence the spins get out of alignment rather quickly, in a time  $T_2$  determined principally by the inhomogeneities in  $H_0$ . At some later time,  $t=T \gg T_2$ , quasi-equilibrium has been reached for the spin distribution. At this time, Hahn puts on another strong pulse, whose main effect is to reverse the direction of precession of every spin.\* At time  $t=2T$  all the spins are aligned once more, and this fact shows itself through the observation of a coherent magnetization at that time, known as the "spin-echo".

Since an experiment essentially equivalent to our hypothetical reversal experiment has actually been carried out by a macroscopic observer, we conclude that *macroscopic observers are not restricted to coarse-grained experiments. It is therefore not permissible to base fundamental arguments in statistical mechanics on coarse-graining.*

---

\* Our description of this experiment is deliberately simplified. Actually, the pulse at  $t=T$  does not reverse the directions of precession, but rather reverses the direction in which each spin points at this moment. In terms of our previous ideal-gas analogy, this amounts to leaving all velocities unaltered, but moving each particle  $i$  of the gas instantaneously from position  $x_i$  to position  $-x_i$ . In view of the symmetry around  $x=0$ , the ultimate result at time  $t=2T$  is the same as in the velocity reversal experiment.

Some additional comments are desirable here:

(1) One may exclude the spin-echo experiment from consideration by saying that it is not a "thermodynamic measurement", and statistical mechanics is meant to apply only to results of thermodynamic measurements. We consider this attitude unacceptable, both philosophically and practically: From the practical point of view, one would need a clear-cut and easily applicable definition of just what constitutes a thermodynamic measurement, as opposed to non-thermodynamic measurements. We are not aware of such a definition, nor do we believe it would be easy to construct one. From the philosophical point of view, we feel that statistical mechanics should aim to describe as big a part of nature as possible; limiting the range of applicability of statistical mechanics to certain types of measurements requires its own philosophical justification; we see no valid philosophical justification for limiting statistical mechanics to the results of "thermodynamic measurements", whatever may be meant by this term. In the next section we shall discuss another limitation on the applicability of statistical mechanics, a limitation for which we feel there is adequate philosophical justification.

(2) In the discussion of the spin-echo experiment, we have ignored the influence of spin-spin interactions. The spin-spin interactions do decrease the size of the echo pulse, but this is from our present point of view accidental. The reversal pulse of Hahn produces, not a complete reflection of all spin directions, but rather a rotation of 180 degrees around the  $x$ -axis. As long as all spins remain in the  $x$ - $y$  plane, this is equivalent to a reversal of all spin orientations; i. e., the spin making an angle  $\theta$  with the  $x$ -axis initially, finally makes an angle  $-\theta$  with the  $x$ -axis. Thus, if one could constrain all spins to remain in the  $x$ - $y$  plane, then the spin-spin interactions would not alter the size of the echo pulse at all. In fact, however, the spin-spin interactions force individual spins out of the  $x$ - $y$  plane, and for those spins the reversal pulse of Hahn does not produce a complete reversal in our sense. This is the origin of the decrease in size of the echo pulse due to spin-spin interactions, and it is of no fundamental interest in our present discussion.

### § 3. The origin of randomness in statistical mechanics

Having realized that the fine-grained entropy  $S$  contains meaningful and measurable information about the ensemble of systems under study, we now investigate what must be done to allow  $S$  to increase with time. The constancy of  $S$  in the usual theory, equation (1.4), follows directly from the fact that the time development of the density matrix  $U$  is given by a similarity transformation, and this latter fact follows directly from the Liouville equation (1.1). *As long as the ensemble can be described validly by a Hamiltonian formalism, the fine-grained entropy fails to increase with time.* Since the spin-echo experiment forces us to retain the fine-grained definition of entropy, we must necessarily give up the completely causal, Hamiltonian description of the time-development of the ensemble, in order to obtain an increasing entropy.

Let us return to the spin-echo experiment. The size of the spin-echo pulse is in fact less than the size of initial pulse, the more so the longer the time  $T$  in the experiment. The spins fail to return to a fully aligned configuration. Under the conditions which we have outlined in section 2,\* the relaxation time characteristic for this failure to re-align is the relaxation time for interchange of energy between the system of spins and the lattice vibrations. If the time  $T$  of the

---

\* In the actual spin-echo experiment, spin-spin interactions also produce failure to align. However, for reasons given at the end of section 2, we consider this effect accidental, whereas the effect of the spin-lattice interaction is basic.

experiment is much longer than this “spin-lattice” relaxation time, the spin system has reached full thermal equilibrium, and no spin-echo pulse can be observed; the spin system has “forgotten” its initial state. Thus, *the approach to true equilibrium is governed by interactions between the system and the outside world, not by interactions within the system itself.* The latter interactions lead only to pseudo-equilibrium, not to true equilibrium.

A particularly striking case is obtained by imagining a system initially in a pure quantum state,  $\phi_0$ . That is, the density matrix  $U_0$  at time  $t=0$  is a projection operator onto  $\phi_0$ , and the entropy  $S=0$ . If there are no interactions with outside world, the wave function  $\phi_0$  develops in time into a wave function  $\psi(t)$ , and the density matrix at time  $t$  is the projection operator onto  $\psi(t)$ . Since this is still one pure state, the entropy is still zero. There is simply no mechanism in this picture by which the system can go from an initial pure state to a final statistical distribution of states.

The failure of  $S$  to increase with time is due to the fact that we have overidealized an “isolated” system. Every system in statistical mechanics must be thought of as enclosed within walls of some kind. Every wall has an outside as well as an inside, and the outside surface of the wall is subject to collisions with molecules outside the system proper. We now proceed to point out that there is an important philosophical distinction between molecules inside the system and molecules outside the walls. Molecules inside the system are in principle accounted for by equations of motion plus initial conditions, i.e., they can be described causally. Molecules outside the system are *in principle* not amenable to a causal description, and *must of necessity* be described in stochastic terms. The momentum and energy transferred between outside molecules and the system proper then acts as a source of true randomness influencing the dynamical behaviour of the system inside the walls. We maintain that this is the origin of randomness and increasing entropy in statistical mechanics.

To see that the outside molecules *must* be treated statistically, let us imagine the opposite for a moment. In order to make a causal description of the motion of the outside molecules, we would have to include them in the Hamiltonian and specify their initial coordinates and momenta. That is, we would have to count these molecules formally as part of a larger system under study. This larger system, however, also has a wall, and there are outside molecules beyond *that* wall. Hence, we have arrived at the following dilemma :

*Either we make a causal, Hamiltonian description of the whole Universe, or else we must allow for an essential element of randomness in the description of the motion of the limited system under study.*

The random element here is not due to accidental shortcomings of the observer, but rather to the fact that the observer restricts his observations to a finite part of the Universe. Whereas human observers are not in fact restricted to coarse-grained experiments they are surely incapable of observing the whole Universe at

once. The whole measurement process depends on a dichotomy between observer and system observed. A man trying to observe the whole Universe simultaneously would be completely confounded by logical as well as by practical difficulties. He could not use any measuring apparatus (since that is part of the Universe), and he would have to observe, among other things, the workings of his own brain. Thus, there is a sound philosophical basis for the assertion that we are *in principle* limited to observing finite parts of the Universe, and are therefore forced to introduce a random element (due to the remainder of the Universe interacting with our limited system) into the basic equations of motion of the system. Conversely, a Laplace demon who observes the whole Universe at once would describe the world in terms quite different from statistical mechanics; he would not need to introduce any random element into his description.

Once this point of view is accepted, the conventional discussions of the ergodic problem become irrelevant, since they start from the assumption of perfectly reflecting, stationary walls, and Hamiltonian equations of motion. These assumptions lead inevitably to constant fine-grained entropy  $S$ , and hence to quasi-equilibrium rather than true equilibrium. The ergodic problem has been discussed from the present point of view by Lebowitz and co-workers.<sup>5),6),7),8)</sup> The present work provides a philosophical foundation for the model adopted in these papers.

It is a corollary of this point of view that the number of particles of which the system is composed need not be large. In principle, one single molecule inside the box is enough. As a result of the random impacts of outside molecules on the walls of the box, the motion of the one inside molecule is not determined causally by a Hamiltonian equation of motion, but contains a random, statistical element which changes an initial pure state into a statistical distribution of states, and eventually into the equilibrium, Maxwell-Boltzmann distribution. The large number of molecules in actual systems is a great help in carrying out calculations in statistical mechanics, but it is not an essential aspect of statistical mechanics. *Statistical mechanics is not the mechanics of large, complicated systems; rather it is the mechanics of limited, not completely isolated systems.*

We believe that the above arguments dispose of the usual objections against introducing an explicit source of randomness directly into the basic equations of statistical mechanics. A mechanics of limited systems cannot be entirely causal, even if the mechanics of the whole Universe is causal (which latter of course we do not know). It remains to deal with the objection that the system inside a calorimeter reaches internal thermal equilibrium, at its own temperature, long before it reaches thermal equilibrium with the world outside the calorimeter. To discuss this objection, let us return to the Gedanken-experiment of section 2.

Let us make a crude estimate of the time required for the system of our Gedanken-experiment to approach true equilibrium. We introduce the variable  $x'$  as follows: With perfect mirror walls, for a particle with initial velocity  $v$ , we define



$$x' = vt. \tag{3.1}$$

The relation between  $x'$  and the actual position  $x$  is then as follows :

$$\begin{aligned} \text{For } -a < x' < a, & \quad x = x'. \\ \text{For } a < x' < 3a, & \quad x = 2a - x'. \\ \text{For } 3a < x' < 5a, & \quad x = x' - 4a. \\ \text{For } 5a < x' < 7a, & \quad x = 6a - x'. \\ & \dots\dots\dots \end{aligned} \tag{3.2}$$

It should be noted that the mapping  $x' \rightarrow x$  is a many-to-one mapping.

Now let us allow for the thermal motion of the two walls by assuming that each wall has a mass  $M$  and a randomly varying velocity  $V$ ; an elastic impact between a gas particle of mass  $m$  and initial velocity  $v$  results in reflection of the particle with an altered speed. The change in speed (ignoring the change in direction) is given by

$$\delta v = \frac{2MV + 2mv}{M + m}. \tag{3.3}$$

If  $M \gg m$ , and  $\frac{1}{2}MV^2 \sim \frac{1}{2}mv^2 \sim \frac{1}{2}kT$ , (3.3) can be approximated by

$$\delta v \cong 2V. \tag{3.4}$$

Since  $V$  is a random variable, so is the speed change  $\delta v$ . Let us denote the speed change at the first impact (at  $x' = a$ ) by  $\delta v_1$ , at the second impact ( $x' = 3a$ ) by  $\delta v_2$ , etc. Then the variable  $x'$ , from which  $x$  can be deduced according to (3.2), is given by an equation more complicated than (3.1), namely :

$$\begin{aligned} x' = vt + \delta v_1 \left( t - \frac{a}{v} \right) + \delta v_2 \left( t - \frac{a}{v} - \frac{2a}{v + \delta v_1} \right) \\ + \delta v_3 \left( t - \frac{a}{v} - \frac{2a}{v + \delta v_1} - \frac{2a}{v + \delta v_1 + \delta v_2} \right) \\ + \dots\dots\dots \end{aligned} \tag{3.5}$$

The series in (3.5) breaks off after  $k$  terms, where  $k$  is the number of wall impacts the particle has suffered before time  $t$ .

Since we need only a crude estimate of the relaxation time, we replace this complicated expression by a much simpler one :

$$x' \cong vt + \delta v_1 \left( t - \frac{a}{v} \right) + \delta v_2 \left( t - \frac{3a}{v} \right) + \delta v_3 \left( t - \frac{5a}{v} \right) + \dots\dots \tag{3.6}$$

This is a reasonable first approximation based on the idea that the quantities  $\delta v_1$ ,  $\delta v_2$ , etc. in the denominators of (3.5) all have zero average values, and thus, on the average,  $v + \delta v_1 + \delta v_2$ , for example, can be replaced by  $v$ .

The mean value of  $x'$  from equation (3.6) is given by (3.1). We are interested in the fluctuation of  $x'$  around this mean value. From (3.6) we get

$$\overline{(x' - vt)^2} \cong \overline{(\delta v_1)^2} \left(t - \frac{a}{v}\right)^2 + \overline{(\delta v_2)^2} \left(t - \frac{3a}{v}\right)^2 + \overline{(\delta v_3)^2} \left(t - \frac{5a}{v}\right)^2 + \dots \quad (3.7)$$

The cross terms vanish on averaging since the speed changes at different wall impacts are statistically independent. We now use  $\overline{(\delta v_i)^2} = 4\overline{V^2}$  and approximate the series by an integral to get

$$\overline{(x' - vt)^2} \cong \frac{2vt^3}{3a} \overline{V^2}. \quad (3.8)$$

This quantity must be compared with  $(2a)^2$ , for once the uncertainty in  $x'$  exceeds  $2a$  appreciably, the memory of the initial distribution-in- $x$  has been effectively lost, without hope of recovery even by a reversal experiment. Introducing the mean number of wall impacts by:

$$r = vt/2a \quad (3.9)$$

the condition for the attainment of equilibrium becomes:

$$\frac{\overline{(x' - vt)^2}}{4a^2} \cong \frac{vt^3}{6a^3} \overline{V^2} = \frac{4r^3}{3} \frac{\overline{V^2}}{v^2} \gg 1. \quad (3.10)$$

Solving for the mean number of impacts required, we get, upon replacing  $v^2$  by its thermal average value,

$$r \gg \sqrt[3]{M/m} \cdot \text{Number of wall impacts for loss of memory.} \quad (3.11)$$

The corresponding relaxation time is  $rT_0$ , where  $T_0$  is given by (2.2). That is,  $r$  is the ratio of the relaxation time for true loss of memory of the initial distribution, to the relaxation time for the apparent loss of memory associated with pseudo-equilibrium. It should be noted that the mass of the wall,  $M$ , enters into (3.11). Thus the estimate depends on properties of the wall, and cannot be made without considering the wall itself as an essential element.

Let us now consider another relaxation time: If the average kinetic energy of the wall,

$$\frac{1}{2} M \overline{V^2} = \frac{1}{2} k T_w \quad (3.12)$$

differs somewhat from the average kinetic energy of the gas particles,

$$\frac{1}{2} m \overline{v^2} = \frac{1}{2} k T_g \quad (3.13)$$

then the wall impacts lead not only to loss of memory of the initial distribution, i.e., attainment of the distribution function (2.3) with  $T = T_g$ , but eventually the temperature of the gas must approach the temperature of the wall (the latter is maintained constant by collisions with outside molecules). The change in energy of a gas particle in a wall collision is given by

$$\frac{1}{2} m (v')^2 - \frac{1}{2} m v^2 = 4mM / (M + m)^2 \cdot [\frac{1}{2} M V^2 - \frac{1}{2} m v^2 - \frac{1}{2} (M - m) v V].$$

Averaging over the random velocities  $V$  of the wall, the last term on the right drops out. With the usual approximation  $M \gg m$ , we get

$$\overline{\frac{1}{2} m (v')^2 - \frac{1}{2} m v^2} \cong (4m/M) (\frac{1}{2} k T_w - \frac{1}{2} m v^2). \tag{3.14}$$

It follows from this that the fractional change in the effective temperature of the gas, produced by each wall collision, is of order  $m/M$ . Thus the number of wall collisions required to bring the gas temperature close to the temperature of the wall is of order :

$$r' \gg M/m \cdot \text{Number of wall impacts for effective energy transfer between gas and wall.} \tag{3.15}$$

The difference between (3.11) and (3.15) becomes significant if the mass ratio  $M/m$  is large. For example, consider a box of dimensions  $a \sim 1$  cm, with gas particles of mean speed of order  $10^5$  cm/sec, so that the "coarse-grained relaxation time"  $T_0$  is of the order of  $10^{-5}$  sec. Assuming for the sake of illustration that  $M/m \sim 10^9$ , then the relaxation time for loss of memory of the initial distribution is of order  $rT_0 \sim 10^{-2}$  sec, whereas the relaxation time for full temperature equilibrium between wall and gas is of order  $r'T_0 \sim 10^4$  sec, i.e., several hours. In other words, *the wall collisions produce loss of memory of the initial distribution much more quickly than they produce full thermal equilibrium with the wall.*

A "coarse-grained" measurement of the distribution function  $U(x, v)$  at a time  $t \sim 10^{-4}$  sec, say, would give no hint of the retention of memory; thus, from the coarse-grained point of view, internal equilibrium has been attained at such time. In fact, however, only quasi-equilibrium has been attained, as can be demonstrated directly by carrying out a reversal experiment.

On the other hand, at time  $t \sim 1$  sec, say, the memory of the initial distribution has been completely lost, and no experiment, no matter how fine-grained, can distinguish this system from one which started out from full equilibrium (distribution function (2.3)) right at  $t=0$ . This loss of memory is *not* connected with observation of the system during the intervening time interval. The loss of memory is an objective, physical phenomenon which takes place irrespective of the presence of observers.

In spite of this complete loss of memory of the initial distribution, the *energy* transfer between gas and wall can be ignored, and the gas is effectively in an adiabatic enclosure. This, then, answers the objections concerning the calorimeter: the relaxation time for loss of memory is very much less than the relaxation time for effective interchange of energy, and thus the effect of the outside molecules in producing loss of memory must be allowed for in discussions of the ergodic problem, even though the effect of the wall in producing thermal equilibrium with the outside world can be ignored completely. The general feeling that the outside molecules cannot be of fundamental importance is due simply to a confusion of

these two quite different relaxation times.

It should be noted, in closing, that in very many practical cases the relaxation time for complete loss of the initial distribution is longer than the observed relaxation time for the approach to "equilibrium": after all, usually one does not do a spin-echo experiment, and hence usually no distinction is made between equilibrium and quasi-equilibrium. Since the relaxation time for attainment of quasi-equilibrium is shorter than the relaxation time for attainment of true equilibrium, the former is measured by most experiments. This, however, is of no concern to us here in this discussion of the basic principles, important as it may be from a more practical point of view.

Although it may perhaps be possible to replace, formally, the actual effect of the wall by a specially adjusted, ad hoc coarse-graining procedure,<sup>10)</sup> this procedure must necessarily depend on the detailed properties of the wall, and must differ essentially from the "ordinary" coarse-graining—for example, in leading to a much longer relaxation time. We feel that such a re-interpretation of the meaning of coarse-graining would be artificial and unsatisfactory. Once it is admitted that the thermal motion of the wall is essential for the attainment of true equilibrium, then this motion should be taken into account as such, not disguised as a coarse-grained measuring process.

It is a pleasure to acknowledge helpful and informative discussions on these matters with Professors S. T. Butler, H. S. Green, R. Kubo, T. Matsubara, H. Matsuda, J. E. Mayer, L. Onsager, M. R. Schafroth, G. Slichter and M. Toda. The author is very grateful to Professor H. Yukawa and the Yukawa Foundation for making possible his visit to Japan, during which these ideas were conceived.

#### References

- 1) M. R. Schafroth, unpublished manuscript and private communication.
- 2) R. C. Tolman, "*The Principles of Statistical Mechanics*", Oxford (1938).
- 3) D. ter Haar, "*Elements of Statistical Mechanics*", New York (1954).
- 4) Hahn, *Phys. Rev.* **80** (1950), 580; *Physics Today* **6** (1953), 4.
- 5) P. G. Bergmann and J. L. Lebowitz, *Phys. Rev.* **99** (1955), 578.
- 6) J. L. Lebowitz and P. G. Bergmann, *Annals of Physics* **1** (1959), 1.
- 7) J. L. Lebowitz and H. L. Frisch, *Phys. Rev.* **107** (1957), 917.
- 8) E. P. Gross and J. L. Lebowitz, *Phys. Rev.* **104** (1956), 1528.
- 9) J. von Neumann, "*Mathematical Foundations of Quantum Mechanics*", Dover Publications, New York (1943), Chapter V.
- 10) M. Fierz, *Helv. Phys. Acta* **28** (1955), 705; see the abstract. The paper itself is concerned with coarse-graining in its usual sense.