147

TROISIEME CYCLE DE LA PHYSIQUE

EN SUISSE ROMANDE

NON-EQUILIBRIUM STATISTICAL MECHANICS

par

Joel L. LEBOWITZ, Professeur

Belfer Graduate School of Science

Yeshiva University, New York

New York 10033

Semestre d'été 1976

TABLE OF CONTENTS

I. INTRODUCTION

One of the most puzzling questions in macroscopic physics is the paradox : how can reversible dynamical laws describing molecular motions lead to the observed irreversible behavior of physical objects that are composed of these molecules ? There is a general feeling that the answer to the paradox involves two distinct features of statistical mechanics : the use of probability concepts, i.e. the macroscopic description of a physical system is given by an ensemble density (probability measure) on the phase space of the system, and the restricted character of the observations that it is possible to make on macroscopic bodies. A complete theory of irreversibility or what might be called the 'good thermodynamic behavior' of physical systems will presumably combine these two features with the laws governing the behavior of the elementary constituents of matter to derive a system of irreversible kinetic equations for macroscopic observables such as temperature, hydrodynamic velocity, etc. It would also include an estimate of the probability of observing a significant deviation from the behavior predicted by the kinetic equations. Unfortunately no such theory exists at present, and none seems likely to appear in the near future.

In the absence of a complete theory, it is desirable to investigate as much as possible the time evolution of non-equilibrium Gibbs ensembles which may approach equilibrium despite the reversibility of the dynamics. This can be done with the help of general results from ergodic theory. Ergodic theory arose out of the attempts by the founding fathers : Maxwell, Boltzmann, Gibbs and Einstein to justify the foundations of statistical mechanics. It directly provides a framework for the investigation of the non-equilibrium behavior of finite (classical) systems. It may be expected, however, that only in some appropriate thermodynamic limit is good thermodynamic behavior precisely achieved. Hence, if exact mathematical results are desired, infinite systems of particles should be directly investigated; their very large yet finite counterparts, which may for all practical purposes exhibit behavior of the type described by macroscopic laws, will nonetheless exhibit it only approximately, precluding the formulation and

proof of the appropriate theorems. (In the same way phase transitions, which are associated with non-analyticities in thermodynamic functions, do not occur for finite systems, though numerical computations on systems containing just a few hundred particles and experimental observations on macroscopic systems mimic this behavior very closely.)

An unresolved problem in non-equilibrium statistical mechanics is finding the limit appropriate to the task. I believe that the same thermodynamic limit as used in equilibrium statistical mechanics is appropriate; at least for part of the problem. (Different or additional limits may have to be used for obtaining more specific kinetic behavior, e.g. for the derivation of the Boltzmann equation.) The underlying triplet (X,T_t,μ) necessary for ergodic theory is, for infinite systems, the phase space of infinite (but locally finite) configurations of particles in R^ν x R^ν, (where $\nu = 3$ for realistic systems), the appropriate Hamiltonian time evolution (whose existence for realistic infinite systems has recently been proven by Lanford and others), and the infinite volume equilibrium measure μ.

II. ERGODIC THEORY

In these lectures I shall first describe some general concepts of ergodic theory, i.e., ergodicity, mixing, etc. I shall then discuss the ergodic properties of infinite systems in particular those of infinite harmonic crystals. Table 1 is essentially a summary of our present state of knowledge (or ignorance) in this area : as it relates to statistical mechanics. Not mentioned there is the concept of space-time ergodicity of an infinite system. This was developed by S. Goldstein to make distinctions between infinite systems having the same time ergodic properties. It avoids "some" of the difficulties I am about to describe.

Infinite systems : Ideal gas, Hard rod system, Perfect harmonic crystal	Bernouilli system	Equivalent to roulette wheel
Baker's transformation, Geodesic flow on space of negative curvature, Particle moving among fixed convex scatterers		
Infinite system : Lorentz gas	K-system	Essential randomness
Two or more hard spheres moving in two or higher dimensions		
Simple model system with collisions	Mixing system	Approach to equilibrium
One dimensional harmonic oscillator	Ergodic system	Use of microcanonical ensemble

Table 1 : Hierarchy of Systems

The middle column lists various ergodic properties with the strongest at the top. Every mixing system is ergodic, every K-system is mixing and every Bernouilli system is a K-system. At the left are examples of the system and at the right physical interpretations or implications.

I should point out that care must be exercised in drawing analogies between the ergodic properties of finite and infinite systems, as the dependence of these properties on the interactions between the particles, and thus also their physical interpretation, may be very different in the two cases. Thus while a finite ideal gas (classical system of non-interacting point particles) is not even ergodic, the infinite ideal gas has the strongest possible ergodic properties : it is a Bernouilli system. The same is true for the harmonic crystal.

The explanation of the good ergodic properties of the infinite ideal gas is simple : local disturbances 'fly off' unhindered to infinity where they are no longer observable. This means that the 'approach' or better the return to equilibrium of a large (infinite) system, which is perturbed locally away from equilibrium, may occur even in the absence of a local 'dissipative' mechanism such as is provided by collisions. It can happen simply, as it does in the ideal gas (or the perfect harmonic crystal) by the disturbance disappearing from sight by the free streaming motion of the particles (phonons). This kind of return to equilibrium is of course not described by a kinetic or hydrodynamic equation and is therefore not the kind of irreversibility which is of interest in real physical systems. It is therefore necessary to introduce additional structure, to that provided by ergodic theory alone, to distinguish between infinite systems of the ideal gas type and more realistic physical systems, such as the Lorentz gas, where there exists a local mechanism, e.g. collisions, for the approach to equilibrium. A start in this direction has been made, as mentioned, by S. Goldstein who considered the ergodic properties of an infinite system under the joint group consisting of the time evolution and space translations. He showed that these two different kinds of systems can indeed be clearly distinguished with this sharper tool.

My reason for not dealing with quantum systems here is that a finite quantum system can never exhibit any of the properties higher than simple ergodicity in our hierarchy (although, of course, a large quantum system may approximate closely the behaviour characterized by these concepts). This is because the spectrum of a finite quantum system in a box is necessarily discrete, whereas for a finite classical system the spectrum (of the Liouville operator) can be continuous. Infinite quantum systems can, and do, exhibit ergodic behaviour "similar" to classical systems. In particular they can be mixing which is the essential property required for decay of initial perturbation.

III. STATIONARY NON-EQUILIBRIUM ENSEMBLES

We have seen that while equilibrium systems are really well understood - at least in principle - the general non-equilibrium situation is very difficult even in principle and the right ingredients are not yet completely at hand. It seems therefore worthwhile to consider a situation which, in principle at least, ought to be more easy than the general non-equilibrium situation - namely the case where a system is in a stationary non-equilibrium state i.e. in which there are fluxes, such as energy flows going through the system. In order to be in a stationary state, a finite system must be in contact with outside reservoirs. We shall be particularly interested in the "steady state" energy flux in a system in contact with heat reservoirs at different temperatures T_α. Following the general principles of statistical mechanics, we identify the observable properties of such a system with averages over a "suitable" phase-space ensemble. To obtain such a Gibbs ensemble we use a formalism developed in earlier work, and look for the stationary solution of a generalized Liouville equation having the form

$$\frac{\partial \rho(x,t)}{\partial t} + (\rho, H) = \sum_\alpha \int \left[K_\alpha(x,x') \cdot \rho(x',t) - K_\alpha(x',x) \cdot \rho(x,t) \right] dx' \qquad (1)$$

Here $K_\alpha(x,x')dx\,dt$ is the conditional probability that when the system is at the point x' in its phase space it will, due to its interaction with the αth reservoir, make a transition to the volume element dx, about x, in the time interval dt. It is assumed here that the reservoirs are "stationary" so that the K_α's are independent of time.

Equation (1) describes a stationary Markov process, and we may define the <u>stochastic</u> time evolution operator W^t, for $t > 0$, by

$$\rho(x,t) = W^t \rho(x,0) = \int W(x,t \,|\, x') \rho(x',0)\, dx \quad , \; t \geq 0. \qquad (2)$$

where $\rho(x,t)$ is the solution of equation (1) when the ensemble density at time zero is $\rho(x,0)$. The operators W^t form a semigroup

$$W^{t_1+t_2} = W^{t_1} \cdot W^{t_2} \quad , \; t_1, t_2 \geq 0$$

but are not unitary operators since the flow is not measure preserving. It is possible to show, under certain conditions on H and the K_α's,

generally satisfied by our systems, that as $t \to \infty$, $\rho(x,t)$ will approach (in some suitable sense) a stationary ensemble density $\rho_s(x)$ which is independent of the initial ensemble density $\rho(x,0)$,

$$\lim_{t\to\infty} W^t \rho(x,0) = \rho_s(x) \quad , \quad W^t \rho_s(x) = \rho_s(x) \tag{4}$$

When all the reservoirs have the same temperature this will be an equilibrium canonical ensemble, whereas for reservoirs at different temperatures this ensemble will represent a system in a steady non-equilibrium state through which heat is flowing. Define

$$W^t f(x) = \int f(y) W(y,t|x)\,dy \quad , \quad \langle f \rangle = \int f(y)\rho_s(y)\,dy$$
$$\langle f(t) g \rangle = \langle (W_t f) g \rangle = \int \left[\int dy f(y) W(y,t|x)\right] g(x)\rho_s(x)\,dx \tag{5}$$

When equation (4) holds and $W(y,t|x) \to \rho_s(y)$ as $t \to \infty$, we have

$$W^t f(x) \longrightarrow \langle f \rangle \quad , \quad \langle f(t) g \rangle \longrightarrow \langle f \rangle \cdot \langle g \rangle \text{ as } t \to \infty \tag{6}$$

To obtain the energy flow into the system from each reservoir we multiply equation (1) by H and integrate over x to obtain

$$\frac{\partial \langle H \rangle}{\partial t} = \sum_\alpha \int \left\{ \int K_\alpha(x,x') [H(x) - H(x')]\,dx \right\} \rho(x',t)\,dx' = \sum_\alpha J_\alpha \tag{7}$$

where J_α is the average energy flux from the αth reservoir. In the steady state we have, of course, $\Sigma J_\alpha = 0$. Thus if the geometry is set up in such a way that the system is in contact with only two reservoirs--"one on the left" at a temperature T_L and "one on the right" at a temperature T_R with $T_L > T_R$ --and if the system has a uniform "cross-section" S and "length" $\mathcal{L}$, then we expect that in the stationary state the heat flux $J = J_L = -J_R$ should, for macroscopic size systems, be related via Fourier's law to the average temperature gradient $(T_L - T_R)/\mathcal{L}$. More precisely, J shoud have the property that the quantity $\kappa(\mathcal{L}) \equiv (J/S)/[(T_L - T_R)/\mathcal{L}]$ should approach a well defined limit κ when $\mathcal{L} \to \infty$. This κ, if it exists, we would identify with the heat conductivity of the system at temperature T when $T_L \to T_R \to T$ (This limit should probably be taken prior to letting $\mathcal{L} \to \infty$).

This formalism has been applied to a harmonic crystal with some particular forms of interaction with the heat reservoirs. The stationary non-equilibrium ensemble density for such a harmonic system was found to be a generalized Gaussian. The covariance matrix of this Gaussian was obtained explicitly for a one-dimensional chain of equal masses with nearest neighbor interactions whose end atoms are in contact with heat reservoirs at temperature T_L and T_R. Identifying the number of particles in the chain with its length $\mathcal{L}$, it was found that in the stationary non-equilibrium state $\kappa(\mathcal{L}) \sim \mathcal{L}$; i.e., the heat flux achieves a constant value, for fixed $T_L - T_R$, independent of the length of the chain $\mathcal{L}$. A similar result obtains for any perfectly periodic harmonic crystal corresponding to an "infinite" heat conductivity, if one can speak of a heat conductivity in this case.

Searching for a model system in which Fourier's law could be shown to hold, Casher and Lebowitz, and A.J. O'Connor and J.L. Lebowitz, investigated what happens in the same situation to a crystal whose atoms are not all of the same mass, with the different masses distributed at "random". We were unable to obtain a definite result for the asymptotic behavior of $\kappa(\mathcal{L})$ but could show rigorously only that the heat flux J will not vanish as $\mathcal{L} \to \infty$ if the spectral measure of the infinite chain has an absolutely continuous part. Indeed, this is the reason why the heat flux in a periodic chain becomes independent of $\mathcal{L}$ as $\mathcal{L} \to \infty$.

We also showed, by using a theorem of Matsuda and Ishii, that for a random chain $J \to 0$ as $\mathcal{L} \to \infty$ with probability one with $\langle J \rangle > 0(\mathcal{L}^{-3/2})$, where $\langle J \rangle$ is the heat flow averaged over the random mass distribution. This may suggest that the eigenfrequencies of a disordered infinite chain are all isolated; but this is not so, as we show that the spectrum of an infinite chain in which the masses can have only two different values contains a non-denumerable infinity of points and is thus, in particular, not exhausted by a set of discrete eigenvalues having a denumerable number of accumulation points. This result is based on a proof that the cumulative frequency distribution of such a chain is continuous.

These results raise the possibility that the spectrum of a disordered chain may be of the singular continuous type; i.e., its continuous spectrum may have its support in a kind of Cantor set. They also raise the question of whether in other systems, too--e.g., hard spheres--the existence of transport coefficients in the infinite system may not require the absence of an absolutely continuous spectrum, i.e., the kind of spectrum Sinai proved exists for a finite system. On the other hand, as we already seen, the irreversible decay of local disturbances requires the absence of localized bound states (corresponding to a point spectrum).

An alternative way of investigating heat flow in a crystal (or for that matter in a more general system) is to consider an isolated system whose "left side" and "right side" act as reservoirs at different temperatures, T_L and T_R. To make this a bit more precise, we might imagine separating the system into three parts, left, middle and right, and consider an initial distribution which is a direct product of equilibrium distributions μ_L , μ_R in the right and left part and an "arbitrary distribution in the middle : $\mu_0 = \mu_L \otimes \mu_M \otimes \mu_R$. We might hope than that if the right and left sides are very large compared to the middle part then, for "large" times, when the transients have died out, the middle part should behave as if it was in a quasi-stationary state with heat flowing through it. I say quasi-stationary since for a finite system the ensemble average of the heat flux would vanish, as $t \to \infty$, if the system is mixing and might oscillate indefinitely otherwise. It would therefore again seem reasonable to consider the case in which the left and right sides became infinitely large while the middle remained fixed. In such a situation the initial state would be singular with respect to any stationary measure and ergodic theory would have nothing to say about the asymptotic, $t \to \infty$, behaviour of the heat flux. We might still expect however (on the basis of the solution of the heat equation) that for "real" systems the middle part of the system would eventually come to equilibrium at some temperature intermediate between T_L and T_R and the heat flux would therefore still vanish as $t \to \infty$. To extract a "stationary" state from this type of system, it would be therefore necessary that we somehow find a way to

express the measure of the middle part of the system at time t, $\mu_M(t)$, (obtained as a projection of the total measure) as a sum of an equilibrium part and of a stationary non-equilibrium part proportional to the "temperature gradient", ΔT; $\mu_M(t) \sim \mu_M(\infty) + \Delta T(t)\, \Psi_s + o(\Delta T)$. (We may expect that $\Delta T(t) \sim t^{-1/2}$). It is Ψ_s which ought to describe the behaviour of stationary non-equilibrium states, i.e. we expect, for systems having good thermodynamic behavior, that Ψ_s would have a limit as a linear functional on the phase space of the system which is independent of the initial μ_M.

The situation is, of course, quite different for the perfect harmonic crystal where we can have a heat flux even in the absence of a temperature gradient. For a harmonic chain containing $2(M' + N) + 1$ particles we might consider the first M-particles, indexed by j, $-(M' + N) \leq j < -N$ as constituting the left side of the system at temperature T_L, etc. Letting now $M' \to \infty$, we have a model of a system, consisting of N-oscillators, in contact with heat reservoirs. Working with H. Spohn, we have recently shown that, as $t \to \infty$, $\mu(t) \to \mu_s$ a stationary heat conducting state independent of initial conditions in the middle part. Indeed we show for this system that the stationary (infinite crystal) state μ_s has as good ergodic properties as the equilibrium state. Unlike the equilibrium state however it is not "stable" against perturbations in the Hamiltonian of the system.

The heat flow in this model, in the case where the masses in the middle part are random while the ends have unit masses was first investigated by Rubin and Greer. It can be shown that the stationary heat flux in this system is proportional to $\int_0^2 |t_N(\omega)|^2 d\omega$ where $|t_N(\omega)|$ is the "transmission coefficient" for a sound wave of frequency ω through the middle part of the system. The integration is over the spectrum of the infinite harmonic chain of unit masses (with nearest neighbor unit coupling). Fürstenberg's theorem implies that for fixed ω, $|t_N(\omega)|$ decays exponentially in N. The only contribution to the heat flux which does not vanish exponentially in N can therefore come only from values of ω which are $O(N)$. It was recently shown by G. Papanicolos that the flux goes $N^{-1/2}$ for this system.

REFERENCES

GENERAL REFERENCES ON ERGODIC THEORY

V.I. ARNOLD, A. AVEZ, "Ergodic Problems of Statistical Mechanics", Benjamin, New York, (1968).

A.S. WIGHTMAN, in "Statistical Mechanics at the Turn of the Decade", (E.G.D. Cohen, ed.), M. Dekker, New York, (1971).

J.L. LEBOWITZ, "Hamiltonian Flows and Rigorous Results in Non-equilibrium Statistical Mechanics", in Statistical Mechanics, New Concepts, New Problems, New Applications (S.A. Rice, K.F. Freed, J.C. Light eds.) U. of Chicago Press, (1972).

I.E. FARQUHAR, in "Irreversibility in the Many-Body Problem", (J. Biel and J. Rae, eds.), Plenum, New York, (1972).

J.L. LEBOWITZ and O. PENROSE, "Modern Ergodic Theory", Phys. Today, Febr. 1973, p. 23.

O.E. LANFORD III, "Ergodic Theory and Approach to Equilibrium for Finite and Infinite Systems", contribution in Boltzmann Equations (Theory & Applications), Proceeding, Symposium, Vienna (Sept. 1972), Springer Verlag, (1973).

Ya.G. SINAI, "Ergodic Theory", ibid.

S.G. BRUSH, "Transport Theory and Stat. Phys.", (1971), for history of ergodic hypothesis.

O. PENROSE, "Foundations of Statistical Mechanics", Pergamon, Oxford, (1970).

G. GALLAVOTTI, "Problèmes ergodiques de la mécanique classique", C.I.C.P., Lausanne, (1976).

"Dynamical Systems, Theory and Applications", Lecture notes in physics 38 (Ed. J. Moser), Berlin - Heidelberg - New York, Springer, (1975).

J.L. LEBOWITZ, "Ergodic Theory and Statistical Mechanics", Transport Phenomena, Sitges International School of Statistical Mechanics, June (1974); edited by G. Kirczenow and J. Marro.

E. HOPF, J. Math. and Phys. 13, 51 (1934); "Ergoden Theorie", Springer, Berlin (1937).

M. SMORODINSKI, "Ergodic Theory, Entropy", Springer Lecture Notes, 214 (1970).

K.L. VOLKOVYSSKII and Ya.G. SINAI, "Ergodic Properties of an Ideal Gas with an Infinite Number of Degrees of Freedom", Funct. Anal. Appl. 5, 185 (1971).

Ya.G. SINAI, "Ergodic Properties of a Gas of One-dimensional Hard Rods with an Infinite Number of Degrees of Freedom, Funct. Anal. Appl. 6, 35 (1972).

S. GOLDSTEIN and J.L. LEBOWITZ, "Ergodic Properties of an Infinite System of Particles Moving Independently in a Periodic Field", Comm. Math. Phys. 37, 1 (1974).

O. DE PAZZIS, "Ergodic Properties of a Semi-infinite Hard Rods System", Commun. Math. Phys. 22, 121 (1971).

S. GOLDSTEIN, "Space-time Ergodic Properties of a System of Infinitely Many Independent Particles", Commun. Math. Phys. 39, 303 (1975).

REFERENCES ON HARMONIC CRYSTALS

O.E. LANFORD and J.L. LEBOWITZ, "Time Evolution and Ergodic Properties of Harmonic Systems", Springer Lecture Notes in Physics 38, 144 (1975).

U.M. TITULAER

a) "Ergodic Features of Harmonic-oscillator Systems I";

b) "Ergodic Features of Harmonic-oscillator Systems II : Asymptotic Ergodicity";

c) "Ergodicity Features of Harmonic-oscillator Systems III : Asymptotic Dynamics of Large Systems";

Physica 70, Nr. 3, a) p. 257, b) p. 276, c) p. 456 (1973).

J.L. Van HEMMEN, "Dynamics and Ergodicity of the Infinite Harmonic Crystal, Thesis, (1976), University of Groningen, Groningen, Holland.

REFERENCES ON "OPEN SYSTEMS"

P.G. BERGMANN and J.L. LEBOWITZ, "New Approach to Non-equilibrium Processes", 99, 578 (1955).

J.L. LEBOWITZ and P.G. BERGMANN, "Irreversible Gibbsian Ensembles", Ann. Phys. 1, 1 (1957).

J.L. LEBOWITZ and H.L. FRISCH, "Model of Non-equilibrium Ensemble : Knudsen Gas", Phys. Rev. 107, 917 (1957).

J.L. LEBOWITZ, "Stationary Non-equilibrium Gibbsian Ensembles", Phys. Rev. 114, 1192 (1959).

J.L. LEBOWITZ and A. SHIMONY, "Statistical Mechanics of Open Systems", Phys. Rev. 128, 1945 (1962).

Z. RIEDER, J.L. LEBOWITZ and E. LIEB, "Properties of a Harmonic Crystal in a Stationary Non-equilibrium State", J. Math. Phys. 8, 1073 (1967).

R. BROUT and I. PRIGOGINE, "General Theory of Weakly Coupled Systems", Physica 22, 621 (1956).

H. NAKAZAWA, "Energy Flow in Harmonic Linear Chain", Prog. Theor. Phys. 39, 236 (1968).

M. BOLSTERLI, M. RICH and W.M. VISSCHER, "Simulation of Non-harmonic Interactions in a Crystal by Self-Consistent Reservoirs", Phys. Rev. A1, 1086 (1970).

A. CASHER and J.L. LEBOWITZ, "Heat Flow in Regular and Disordered Harmonic Chains", J. Math. Phys. 12, 1701 (1971).

H. MATSUDA and K. ISHII, "Localization of Normal Modes and Energy Transport in the Disordered Harmonic Chain", Suppl. Prog. Theor. Phys. 45, 56 (1970); see also H. MATSUDA, T. MIYATA and K. ISHII, "Localization of Eigenfunctions in Disordered Systems", Suppl. to J. Phys. Soc. Japan 26, 40 (1969).

R.H.G. HELLEMAN, "Heat Transport in Harmonic and Anharmonic Lattices, thesis, Yeshiva University, (1971).

H. NAKAZAWA, "On the Lattice Thermal Conduction", Suppl. Prog. Theor. Phys. 45, 231 (1970).

R.J. RUBIN and W.L. GREER, "Abnormal Lattice Thermal Conductivity of a One Dimensional, Harmonic, Isotopically Disordered Crystal", J. Math. Phys. 12, 1686 (1971).

E.W. FORD, M. KAC and P. MAZUR, "Statistical Mechanics of Assemblies of Coupled Oscillators", J. Math. Phys. 6, 504 (1965).

R.J. RUBIN

a) "Transmission Properties of an Isotopically Disordered One-dimensional Harmonic Crystal I", J. Math. Phys. 9, 2252 (1968);

b) "Transmission Properties of an Isotopically Disordered One-dimensional Harmonic Crystal II : Solution of a Functional Equation", J. Math. Phys. 11, 1857 (1970).

P.L. SULEM and H. FRISCH, "Total Reflection of a Phase Wave by a Semi-Infinite Random Medium", J. Plasma Phys. 8, 217 (1972).

U. FRISCH, C. FROESCHLE, J.P. SCHEIDECKER and P.L. SULEM, "Stochastic Resonance in One-dimensional Random Media", Phys. Rev. A8, 1416 (1973).

W.M. VISSCHER, "Localization of Normal Modes and Energy Transport in the Disordered Harmonic Chain", Prog. Theor. Phys. 46, 729 (1971).

ACKNOWLEDGEMENT

The work reported here was supported by AFOSR Grant #73-2430B and NSF Grant #MPS 75-20638.

Swiss students enjoyed your lectures and it was an invaluable pleasure for me to be your assistant.

Mireille Auberson

Neuchâtel, juillet 1976