

HAMILTONIAN FLOWS AND RIGOROUS RESULTS IN NONEQUILIBRIUM STATISTICAL MECHANICS

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I. INTRODUCTION

I will begin my talk by calling your attention to Art Wightman's lecture, *Statistical Mechanics and Ergodic Theory: An Expository Lecture*, given about two years ago not far from here at the symposium in honor of Professor George Uhlenbeck at Northwestern in 1969 [2]. Wightman's lecture has now been published [1], and I urge you strongly to read it. It describes in a physicist's language many of the ideas developed by mathematicians in the last 40, and more particularly in the last 20, years for the study of the qualitative features of the time evolution of isolated dynamical systems [3].

These concepts on the one hand are of central importance to the understanding of nonequilibrium phenomena in physical systems and on the other hand are almost entirely unknown in the statistical mechanics fraternity, a goodly many of whom are gathered here today. (At least they were unknown before you all heard the lectures by Professors Smale and Ornstein this morning.) Even the nomenclature of this work, such as mixing flow, K-system, are rarely or not at all to be found in any of the many books on statistical mechanics and kinetic theory written for physicists in recent years or, for that matter, in the physics journals. Even when time evolution, irreversibility, and approach to equilibrium are discussed in the standard books [4], all that is usually mentioned is something about ergodic systems and the Birkhoff theorem that a system is ergodic if and only if the Hamiltonian flow in phase space, restricted to a surface of constant energy, is metrically transitive. The latter means that the energy surface is not decomposable, in a "sensitive way," into separate parts which are left invariant by the flow.

Now I believe that almost all real physical systems are "essentially" ergodic. Indeed, this is necessary for understanding why equilibrium statistical mechanics, which includes a description

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of fluctuations in thermal equilibrium, works so well in the real world. I think, however, that just ergodicity alone is not sufficient for either the understanding of irreversible phenomena or-- and this is perhaps even more important to those of us who make a living working in this field-- for the existence of the integrals which we use in the computation of transport coefficients, such as the diffusion constant, viscosity, etc. [5]. What is necessary is something stronger which is more like Hopf's mixing flow or still stronger.

I want to devote my lecture to (1) defining these concepts in ways which are useful to statistical mechanics, (2) discussing the role of the thermodynamic limit, where systems become very large or infinite, in the study of irreversible phenomena, (3) relating these concepts to some simple model systems which have been worked out explicitly, or almost explicitly, by various authors, some of whom are in this audience, (4) raising some questions about the time evolution of quantum systems which do not fit in a simple way into the structure of ergodic theory, mixing flows, etc., the thermodynamic limit being essential for mixing in quantum systems, (5) questions about the existence of a heat conductivity in random harmonic crystals, and finally (6) to a few remarks about some recent work on the metastable state of systems with very long range interactions.

I would like to make it clear at this point that (1) this talk does not contain even all the rigorous results known to me in this field, much less all those known to others, and (2) nonrigorous does not mean incorrect any more than rigorous means relevant or interesting.

I have in particular left out all discussion of kinetic equations. These equations associated with the names of Boltzmann, Pauli, Kirkwood, Born and Green, Prigogine, van Hove, Bogolubov, and Uhlenbeck, to mention just a few, have played and continue to play a central role in our understanding, interpretation and prediction of nonequilibrium phenomena. (Boltzmann's great H-theorem will have its centenary next year.) Some of these equations, like the Boltzmann equation, may be exact at all times in special limiting situations [such as the Grad limit for hard spheres: particle density $n \rightarrow \infty$, particle diameter $a \rightarrow 0$, mean free path $\ell = (na^2)^{-1}$ remaining finite]. Other equations may be valid only asymptotically (in the Prigogine-van Hove type of equations these conditions are clearly stated), or may hold only approximately. In any case their physical validity is a question to be settled first by experiment and only later, if we ever get clever enough, by rigorous mathematics.

I could continue with other things I have left out--Green-Kubo formulas, master equations, Brownian motion, hydrodynamics, etc.,--but I think I had better start on the few things which I do want to discuss.

II. ERGODICITY, MIXING, AND DECAY OF CORRELATIONS

Since most of these concepts, and many more, are presented and defined in a clear and precise way in Wightman's lecture [1] and in the book by Arnold and Avez [3], I shall only sketch here the definitions which I need for this talk. I shall use the physicist's language, which sometimes sacrifices precision and generality for the sake of simplicity and familiarity.

Consider a conservative classical system of particles with canonical variables $q_i, p_i, i = 1, \dots, 3N$. The state of the system is represented in the N -dimensional phase space Γ by a point $x = \{q_i, p_i\}$. The time evolution of the system or its representative point in Γ, x_t [or $x(t)$], is governed by the canonical equations of motion coming from a time independent Hamiltonian $H(x)$,

$$H = \sum_{i=1}^N p_i^2/2m + V(q_1, \dots, q_{3N}); \quad V(q_1, \dots, q_{3N}) > -K, \quad K < \infty. \quad (2.1)$$

We assume in addition that the coordinates of the system are confined to a finite region of space Λ by rigid walls (or by some external potential which can be put into V), or that the system moves on some N -dimensional torus (periodic boundary conditions). (When the particles have hard cores, these can also be thought of as internal walls.) Under these conditions the motion of the system, i.e., the flow in Γ space, will be confined to a $(6N - 1)$ -dimensional energy S_E which is piecewise smooth and has finite "area," given by the equation

$$H(x) \equiv E = H(x_t), \quad -\infty \leq t \leq \infty. \quad (2.2)$$

The time evolution of any function $f(x)$ is given by

$$df(t)/dt = (f(t), H) = iLf, \quad (2.3)$$

$$f(t) \equiv f(x_t) = f(\exp[itL]x) \equiv \exp[itL]f(x) \equiv U_t f(x),$$

where L is the Liouville operator corresponding to the usual Poisson bracket. Thus if $\rho(x, 0)$ describes some Gibbsian ensemble density in Γ at $t = 0$, then the ensemble density at time t is given by the solution of the Liouville equation,

$$\frac{\partial \rho(x, t)}{\partial t} = (H, \rho) = -iL\rho \quad (2.4)$$

or

$$\rho(x, t) = \exp[-itL] \rho(x, 0) = U_{-t} \rho(x, 0) = \rho(x_{-t}, 0). \quad (2.5)$$

U_t is a unitary operator, and i is introduced so that L is self-adjoint.

Every $\rho(x, t)$ (which may be singular), which is nonnegative, defines a measure μ on Γ .

Thus if A is any set in Γ ,

$$\mu(A, t) = \int_A \rho(x, t) dx \equiv \int_A \rho(x_{-t}, 0) dx = \int_A \rho(x_{-t}, 0) dx_{-t} = \int_{A_{-t}} \rho(x, 0) dx = \mu(A_{-t}, 0). \quad (2.6)$$

The third equality following from the Liouville theorem that the volume element dx (Lebesgue measure) is invariant in time. We shall always assume that μ is normalized:

$$\mu(\Gamma, t) = \int \rho(x, t) dx = \int \rho(x, 0) dx = 1. \quad (2.7)$$

Of particular importance in statistical mechanics are time independent measures (or ensemble densities),

$$\rho(x, t) = \rho(x, 0) = \rho_0(x), \quad \mu(A, t) = \mu_0(A). \quad (2.8)$$

Particular examples of such time invariant ensembles are the micro-canonical and canonical ensembles. The first of these is

$$d\mu_o = \begin{cases} [\Omega(E)]^{-1} \frac{d\sigma}{|\text{grad } H(x)|}, & x \in S_E, \\ 0, & \text{otherwise} \end{cases} \quad (2.9a)$$

where $d\sigma$ is an element of the "surface area" of an element of the $(2N - 1)$ dimensional energy surface S_E and

$$\Omega(E) = \int_{S_E} \frac{d\sigma}{|\text{grad } H|}, \quad (2.9b)$$

which is finite by virtue of our assumption that the system is confined to a bounded region of physical space, Λ . The canonical ensemble measure is even more familiar:

$$d\mu_o = Z^{-1} \exp[-\beta H(x)] dx, \quad \beta > 0, \quad (2.10a)$$

where $\beta > 0$ is the reciprocal temperature and

$$Z = \int \exp[-\beta E] \Omega(E) dE = Z(\beta, N) \quad (2.10b)$$

is a normalizing constant. Another useful ensemble is the generalized microcanonical ensemble used by Griffith [6] in considering the thermodynamic limit problem in equilibrium statistical mechanics

$$d\mu_o = \begin{cases} \text{const. } dx, & \text{for } \{x; H(x) \leq E\}, \\ 0, & \text{otherwise} \end{cases} \quad (2.11)$$

The grand canonical ensemble has as its domain the disjoint union of the phase spaces Γ_N of systems in Λ having different numbers of particles N , $N = 0, 1, \dots, \infty$, $x_N \in \Gamma_N$, $x_N = (q_1, \dots, q_N, p_1, \dots, p_N)$. The lower bound on the potential energy $-K$ in equation (2.1) has now to be written as $K = BN$, $B < \infty$ independent of N . Its invariant measure is

$$d\mu_o = \Xi^{-1} (N!)^{-1} \exp[-\beta [H(x_N) - \mu N]] dx_N, \quad (2.12a)$$

with

$$\Xi = \sum_{N=0}^{\infty} (N!)^{-1} \exp[\beta \mu N] Z(\beta, N). \quad (2.12b)$$

We shall now restrict our attention to the microcanonical measure, given in equations (2.9), for some particular S_E .

Definition A. Ergodic System (Birkhoff). A system is said to be ergodic on an energy surface S_E if and only if

$$f(x) \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(x_t) dt = \int f(x) d\mu \equiv \langle f \rangle \quad (2.13)$$

for all $f(x)$ in L_1 ,

$$\int |f(x)| d\mu_o < \infty, \quad (2.14)$$

and for almost all x . The latter means that the set A consisting of all points x for which equation (2.13) fails has zero measure, $\mu_o(A) = 0$.

Definition B. Mixing Flow (Hopf). The Hamiltonian flow on S is called mixing if and only if

$$\lim_{t \rightarrow \infty} \mu_0(A_t \cap B) = \mu_0(A) \mu_0(B), \quad \mu_0(S_E) = 1 \quad (2.15)$$

for all sets $A \subset S_E$ and $B \subset S_E$ of positive measure $\mu_0(A) > 0$. $A_t = U_t A$ is the set of points into which A is carried in a time t by the action of the time evolution operator U_t ; i.e., $A_t = \{x: x_{-t} \in A\}$.

The significance of mixing is thus that the fraction of systems of the ensemble originally in the set A that are located in some set B at time t approaches, as $t \rightarrow \infty$, the ratio of the volume of B to the volume of S_E .

$$\frac{\mu_0(A_t \cap B)}{\mu_0(A)} \xrightarrow{t \rightarrow \infty} \mu_0(B); \quad \mu_0(S_E) = 1. \quad (2.16)$$

This property of mixing is stronger than and implies ergodicity [3]. It represents the kind of irreversibility which one always hoped that "coarse graining" in some way or another would bring about. The most remarkable thing though is that Sinai [7] was actually able to prove that a system consisting of a finite number N ($N \geq 2$) hard spheres (or hard disks in two dimensions) confined to a box is a mixing system.

To make the meaning and significance of mixing even clearer and more directly connected with the formalism commonly used in statistical mechanics, we define, as usual, the correlation functions

$$\langle f(t) \rangle \equiv \int f(x_t) g(x) d\mu_0, \quad \langle fg \rangle \equiv \langle f(0)g \rangle. \quad (2.17)$$

It can then be shown, ([3]: Theorem 9.8) that

B'. A system is mixing if and only if

$$\langle f(t)g \rangle \xrightarrow{t \rightarrow \infty} \langle f \rangle \langle g \rangle \quad (2.18)$$

for all square integrable functions f and g ; i.e.,

$$\int |f|^2 d\mu_0 < \infty, \quad \int |g|^2 d\mu_0 < \infty. \quad (2.19)$$

It follows therefore in particular from Sinai's work that for a finite system of two or more hard spheres in a box, in two or three dimensions, the velocity autocorrelation of any particle, say particle one, approaches zero as $t \rightarrow \infty$,

$$\langle v_1(t)v_1 \rangle \xrightarrow{t \rightarrow \infty} \langle v_1 \rangle \langle v_1 \rangle = 0. \quad (2.20)$$

This is indeed a remarkable result and contrary to some folklore which holds that it is necessary to go to an infinite size system in order to obtain a decay of the correlation functions. Here, on the other hand, this is shown to be true for a system consisting of N ($N \geq 2$) particles, as long as N is finite. (It is presumably true also for an infinite system, but this is far from proven.) The usual folklore reason for the belief in the necessity of going to an infinite system is that for a finite system one always has a finite Poincaré recurrence time. Note, however, that the mixing definition is meaningful only for sets of positive measure and that the equivalent decay of correlation functions (B') applies only to square integrable functions (with respect to $d\mu_0$). What mixing therefore implies is that the times when different systems which were initially together in the same set A [which can be as small as desired as long as $\mu_0(A) > 0$] return to the "neighborhood

of A'' are so different from each other that eventually the set A_t spreads out uniformly over all S_E . This is the important property of mixing flows which does not follow at all from ergodicity alone, and is in striking contrast to what occurs in assemblies of oscillators such as harmonic crystals where all the phase points have essentially the same time dependence. We shall discuss these later.

Having debunked one piece of folklore, we shall now show that another piece of folklore does survive and becomes a rigorous result for mixing systems. To this end consider a function $f(x)$, which is equal to $(F(x), H(x))$, the Poisson bracket of $F(x)$ with the Hamiltonian $H(x)$, with f and F square integrable as in inequalities (2.19). (We are always dealing here with a finite system.) Let $\varphi(x)$ also be a square integrable function. Then

$$\int_0^T \langle f(t)\varphi \rangle dt = \int_0^T \left\langle \frac{d}{dt} F(x_t) \varphi(x) \right\rangle dt = \langle F(T)\varphi \rangle - \langle F\varphi \rangle. \quad (2.21)$$

In a similar way if $g(x) = (G(x), H(x))$, with g and G square integrable, then

$$\int_0^T \langle f(t)g \rangle dt = \int_0^T \left\langle \varphi(t+t') \frac{dG(t')}{dt'} \right\rangle dt = -[\langle \varphi(T)G \rangle - \langle \varphi G \rangle], \quad (2.22)$$

where we have used the time invariance of μ_0 ,

$$\langle \psi(t+t') \chi(t') \rangle = \langle \psi(t) \chi \rangle. \quad (2.23)$$

Finally if $f = (F, H)$ and $g = (G, H)$, then we can also write

$$\int_0^T \langle f(t)g \rangle dt = \int_0^T \frac{d}{dt} F(t+t') \frac{d}{dt'} G(t') dt = -\frac{d}{dT} \langle F(T)G \rangle + \langle (F, H)G \rangle. \quad (2.24)$$

If we now set $f = g$, $F = G$, then since $\langle (F, H)F \rangle = \frac{1}{2} \langle dF^2/dt \rangle = 0$, we find, for the time integral of the autocorrelation function,

$$\int_0^T \langle f(t)f \rangle dt = -\frac{d}{dT} \langle F(T)F \rangle = -\langle f(T)F \rangle. \quad (2.25)$$

Now if our system is mixing, we can use condition (2.18) to take the limit $T \rightarrow \infty$ in the above equations and obtain the following theorem.

Theorem. Let f, g, φ, F, G be square integrable with $f = (F, H)$, $g = (G, H)$. For a mixing system

$$\lim_{T \rightarrow \infty} \int_0^T \langle f(t)\varphi \rangle dt = \langle F \rangle \langle \varphi \rangle - \langle F\varphi \rangle, \quad (2.26)$$

$$\lim_{T \rightarrow \infty} \int_0^T \langle \varphi(t)g \rangle dt = \langle \varphi G \rangle - \langle \varphi \rangle \langle G \rangle, \quad (2.27)$$

$$\lim_{T \rightarrow \infty} \int_0^T \langle f(t)g \rangle dt = \langle (F, H)G \rangle, \quad (2.28)$$

$$\lim_{T \rightarrow \infty} \int_0^T \langle f(t)f \rangle dt = 0. \quad (2.29)$$

Example: For a finite mixing system confined by a wall,

$$\lim_{T \rightarrow \infty} \int_0^T \langle v_1(t)v_1 \rangle dt = \lim_{T \rightarrow \infty} \langle q_1(T)v_1 \rangle = 0. \quad (2.30)$$

Proof: $v_1 = (q_1, H)$ and $\int v_1^2 d\mu_0 < \infty$, $\int q_1^2 d\mu_0 < \infty$.

Note that when q_1 is an angle variable, e.g., in the case of periodic boundary conditions, then $v_1 \neq (q_1, H)$ and equation (2.30) need not hold. We would still have, however, $\langle v_1(t)v_1 \rangle \rightarrow 0$ if the system is mixing.

When the system is not mixing, the limit $T \rightarrow \infty$ in the above integrals need not exist. We see, however, from equation (2.25) that for any finite system in a box

$$\lim_{T \rightarrow \infty} \int_0^T \langle f(t)f \rangle dt = 0, \text{ if it exists.} \quad (2.31)$$

This is so since

$$\langle F(T)F \rangle \leq \langle F(T)F(T) \rangle^{\frac{1}{2}} \langle F^2 \rangle^{\frac{1}{2}}, \quad (2.32)$$

so that when F is square integrable, $\langle F(T)F \rangle$ can either oscillate or approach zero.

The significance of these results for nonequilibrium statistical mechanics comes from the fact that the Kubo formulae [5] for transport coefficients all involve integrals over time, from $t = 0$ to $t = \infty$, of correlation functions of "fluxes" which can be written as Poisson brackets. These integrals will therefore, if they exist at all, be equal to zero in any finite system. (The important point of our theorem is that they do exist for mixing systems, which possibly include all real systems.) These formulae can therefore possibly yield transport coefficients only in the thermodynamic limit. In the thermodynamic limit, functions like q_1 need no longer be square integrable. Hence, even when $\langle f(t)f \rangle \rightarrow \langle f \rangle^2$ in such systems for square integrable functions f like v_1 , $\langle v_1(t)v_1 \rangle \rightarrow 0$ we can still define $\int_0^T \langle v_1(t)v_1 \rangle dt = \langle q_1(T)v_1 \rangle$, there is no reason to expect that $\langle q_1(t)v_1 \rangle$ will also vanish (or even exist) as $t \rightarrow \infty$. (This will become clear in the examples given in the next section.)

One of the most important problems in statistical mechanics (if you care about rigorous results), at the present time, is therefore to investigate and hopefully to establish the existence in the thermodynamic limit of the time integrals used in the Kubo formulae. Unfortunately it seems impossible even to tackle this problem before one proves the existence of a time evolution in the thermodynamic limit. This has been established so far, for a general class of systems, only in one dimension, Lanford [8]. I shall come back to this later.

I shall conclude this section by defining still another class of systems; those with homogeneous Lebesgue spectrum. This will enable us to clarify somewhat the relation between the mixing properties of the flow and the properties of the Liouville operator L .

Definition C. Homogeneous Lebesgue Spectrum (Koopman). A system has a homogeneous Lebesgue spectrum if, when one diagonalizes L , every real number λ lies in the spectrum and has the same multiplicity and the spectral weight is just $d\lambda$. (This definition is copied from Wightman [1].) The space on which L acts here is the Hilbert space of complex-valued square integrable functions $f(x)$, $x \in S_E$.

Conditions A, B, and C are members of a hierarchy of increasingly stronger conditions on the flow (or the Hamiltonian H which generates it). It has been shown (see [3] for references) that

$$\text{Homogeneous Lebesgue spectrum} \longrightarrow \text{Mixing} \longrightarrow \text{Ergodicity}, \quad (2.33)$$

but not the converse. Mixing does, however, imply that L has no discrete eigenvalues other than zero. Such a property of L implies in turn that the system is at least weakly mixing, which implies ergodicity. A weakly mixing system is one in which [3]

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T |\mu_0(A_t \cap B) - \mu_0(A) \mu_0(B)| dt = 0. \quad (2.34)$$

An eigenfunction corresponding to the eigenvalue zero is of course any constant of S_E . It follows already from ergodicity that the eigenvalue zero is simple; i. e., constants are the only eigenfunctions of L with eigenvalue zero. The converse is also true; i. e., if zero is a simple eigenvalue of L , then the flow is ergodic. This is indeed another way of stating the Birkhoff theorem, alluded to earlier, about the equivalence between ergodicity and the nondecomposability of S_E .

III. MODEL SYSTEMS

1. Two Particles in a One-Dimensional Box

It is not easy to find nontrivial yet simple examples of an ergodic Hamiltonian system. To give you something to do with your idle time here, consider a one-dimensional system consisting of two hard particles of masses m_1 and m_2 in a box of length L having rigid walls. The energy surface S_E is three-dimensional $0 \leq q_1 \leq q_2 \leq L$; $p_1^2/2m_1 + p_2^2/2m_2 = E$. I came here

believing that this system is ergodic if $\theta = \cos^{-1} \left[1 - 2 \frac{(m_1 - m_2)^2}{(m_1 + m_2)^2} \right]$ is not a rational multiple of π . After talking with some people, I am now very doubtful. I also wonder what happens for more than two particles with different masses.

2. One-Dimensional Harmonic Oscillator

A trivial example of an ergodic system is a one-dimensional harmonic oscillator

$$H = \frac{1}{2} m^2 p^2 + \frac{1}{2} m \omega^2 q^2. \quad (3.1)$$

The energy surface is a one-dimensional ellipse and certainly nondecomposable. The eigenfunctions of L are $(p \pm i m \omega q)^l$, where l is an integer, with eigenvalues $\lambda_l = l\omega$. In terms of the action variables, (J, θ) , the Hamiltonian is simply $H = \omega J$ and the flow is described by

$$\theta_t = \theta + \omega t \pmod{2\pi}; J_t = J. \quad (3.2)$$

3. General Harmonic System

For a general harmonic system with N degrees of freedom (e.g., a harmonic crystal in one, two or three dimensions), we can always write the Hamiltonian in action-angle variables (J_i, θ_i) , $i = 1, \dots, N$,

$$H = \sum_{i=1}^N \omega_i J_i, \quad iL = \sum_{i=1}^N \omega_i \frac{\partial}{\partial \theta_i}, \quad (3.3)$$

where

$$J_i(t) = J_i, \quad \theta_i(t) = \theta_i + \omega_i t \pmod{2\pi}. \quad (3.4)$$

All the J_i are constants of the motion, and therefore the system will not be ergodic on the $(2N - 1)$ -dimensional energy surface S_E for $N > 1$. This system may, however, still be ergodic on some M -dimensional subspaces of S_E , $M < N$. Such a subspace is a torus $\Pi(\{\theta\}_M)$ whose coordinates are the angle variables $(\theta_{i_1}, \dots, \theta_{i_M}) = \{\theta\}$ for which the corresponding frequencies ω_{i_ℓ} are not resonant [3]

$$\sum_{\ell=1}^N n_{i_\ell} \omega_{i_\ell} \neq 0, \text{ for } n_{i_\ell} \text{ integers not all zero.} \quad (3.5)$$

What we mean here by ergodicity is that the flow induced on $\Pi(\{\theta\}_M)$ by the projection onto $\{\theta\}_m$ on the flow on S_E (really on $\{\theta\}_N$ since the J_i stay constant) is ergodic. (The measure $d\mu_0$ on $\Pi(\{\theta\}_M)$ is the usual Cartesian M -dimensional volume properly normalized.) In other words, any function $f(x)$ which depends only on the variables $\{\theta\}_M$ is ergodic with respect to the microcanonical measure $d\mu_0$ on S_E ,

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(\{\theta_t\}_M) dt = \int_{S_E} f(\{\theta_M\}) d\mu_0 = \langle f \rangle. \quad (3.6)$$

The fact that some functions $f(x)$ are ergodic even though the system is not ergodic may be true also in other than harmonic systems. A similar situation may happen also with regard to mixing and suggests the following definition.

4. Definition

The set of ergodic and mixing functions \mathcal{E} and \mathcal{M} , respectively, is defined as follows:

$$f \in \mathcal{E} \text{ iff } \int |f|^2 d\mu_0 < \infty \text{ and}$$

$$\overline{f}(x) \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(x_t) dt = \int f d\mu_0 = \langle f \rangle; \quad (3.7)$$

$$f \in \mathcal{M} \text{ iff } \int |f|^2 d\mu_0 < \infty \text{ and } \lim_{t \rightarrow \infty} \langle f(t)f \rangle = \langle f \rangle^2. \quad (3.8)$$

The set \mathcal{E} is clearly a linear subspace of L_2 . By Khinchin's ergodic theorem, $\mathcal{M} \subset \mathcal{E}$.

5. Harmonic Crystals

We may summarize now a few of the known results about harmonic crystals in one, two, and three dimensions.

Beginning with Schrodinger, various authors [9] have studied, among other things, the velocity autocorrelation function of a specified particle in a harmonic crystal of N particles (using the canonical ensemble as the invariant measure). Since the velocity of the j th particle v_j depends, when expressed as a function of the action-angle variables $(\{J_i\}, \{\theta_i\})$, $i=1, \dots, Nd$ (d = dimensionality of space), not only on the θ_i but also on the J_i , it is not an ergodic function: $v_j \notin \mathcal{E}$ for fixed N . It is, however, possible to show that in the thermodynamic limit v_j is a mixing function. Mazur and Montroll [9] found that in this limit the velocity autocorrelation function decays as $t^{-d/2}$,

$$\langle v_j(t)v_j \rangle = \lim_{N \rightarrow \infty} \langle v_j(t)v_j \rangle_N \sim (\sin t)/t^{d/2}. \quad (3.9)$$

It is seen from equation (3.9) that $|\langle v_j(t)v_j \rangle|$ is integrable in three dimensions but not in two or one dimension. This appears related (cf. discussion after equation [2.24]) to the Peierls result [10] that the mean square displacement $\langle q_i^2 \rangle$ of a particle at a fixed lattice site behaves (when the size of the crystal increases so that the boundaries of the crystals, where the particles are tied down to fixed positions, recede in all directions) like

$$\langle q_i^2 \rangle \sim \begin{cases} D_N & , \text{ one dimension,} \\ \ln D_N & , \text{ two dimensions,} \\ \text{constant,} & \text{three dimensions.} \end{cases} \quad (3.10)$$

Here D_N is the distance of the boundary from the j th site and approaches infinity. [Since in three dimensions each particle remains localized about its equilibrium position when $N \rightarrow \infty$, I expect that $\int_0^T \langle v_j(t)v_j \rangle dt$ will go to zero as $t \rightarrow \infty$. This is what happens when particle one has a mass much larger than that of the other particles.]

While Mazur and Montroll established their results explicitly only for cubic lattices with nearest neighbor interactions, the essential feature of the system responsible for the decay of the velocity autocorrelations in the thermodynamic limit appears to be the absence of localized modes as $N \rightarrow \infty$. This "corresponds" to the Liouville operator L not having any discrete eigenvalues in this limit. (If L had this property for a finite system, then, as already mentioned at the end of Section II, the system would be at least weakly mixing which implies ergodicity.) We may therefore conjecture that whenever the spectrum of the infinite crystal is entirely continuous, all "local" functions are mixing and cross-mixing. We define a local function F as one which depends on the coordinates q_i and momenta p_i of a fixed finite number of particles $i = 1, \dots, \ell$ and is square integrable,

$$\int |F(x_1, \dots, x_\ell)|^2 d\mu_0 \leq K, \quad x_i = (q_i, p_i), \quad (3.11)$$

where $K < \infty$, as a constant independent of the size of the crystal characterized by N . If our conjecture is right, then, in the absence of localized modes for the infinite crystal,

$$\lim_{t \rightarrow \infty} \left\{ \lim_{N \rightarrow \infty} \langle F_\ell(t) G_j \rangle_N \right\} = \lim_{N \rightarrow \infty} \left[\langle F_\ell \rangle_N \langle G_j \rangle_N \right], \quad (3.12)$$

where F_ℓ and G_j are localized functions depending on ℓ and j coordinates and momenta, respectively.

The importance of isolated modes in determining the ergodic properties of local functions was exhibited very clearly by Cukier and Mazur [11], who investigated the ergodicity of the kinetic energy of a single "impurity," i.e., of a particle of mass M placed at position j in a harmonic chain of particles of mass m . They found that the function $p_j^2(t)$ will be ergodic as $N \rightarrow \infty$ if $M > m$ and is not ergodic if $M < m$. This difference is brought about by the existence of a localized mode when $M < m$ and its absence when $M > m$.

6. XY Model Spin System and General Quantum Systems

The inhibiting effect of an isolated eigenvalue (of the time evolution operator) on the relaxation of a local disturbance can also be seen explicitly in the work of Abraham et. al. [12] on the time evolution of a quantum spin system. They consider a one-dimensional system of spins with nearest-neighbor XY interactions without or with an external magnetic field h in the z -direction acting on the j th spin. The Hamiltonian of the system in these two cases is then

$$H_0 = \frac{1}{2} \sum_{i=-N}^N \left[(1+\gamma) \sigma_i^x \sigma_{i+1}^x + (1-\gamma) \sigma_i^y \sigma_{i+1}^y \right], \quad (3.13)$$

$$H' = H_0 + h \sigma_j^z. \quad (3.14)$$

Their results may then be extrapolated and interpreted [13] as showing that all "local" functions F and G which depend only on a finite set of spins $F(\sigma_{i_1}, \dots, \sigma_{i_\ell})$, $G(\sigma_{j_1}, \dots, \sigma_{j_k})$ will be mixing when $N \rightarrow \infty$:

$$\langle F(t)G \rangle - \langle F \rangle \langle G \rangle \rightarrow 0, \quad \text{as } t \rightarrow \infty \quad (3.15)$$

$$\langle GF(t)G \rangle - \langle F \rangle \langle G^2 \rangle \rightarrow 0,$$

if $H = H_0$ but not (generally) if $H = H'$. The approach to zero for a single spin correlation in the first case is as t^{-1} . The different behavior under the action of H_0 and H' is due [13] to the presence of an isolated eigenvalue in the spectrum of H' .

This fits in with the general C^* algebra formulation of the time evolution of infinite quantum systems [13]. It appears indeed that because of the discrete nature of the spectrum for all finite quantum systems confined to a bounded domain Λ there will be no mixing (decay of correlations) in such a system. The remarkable thing about Sinai's result is that it shows that finite classical systems can and do have purely continuous spectra. (Note that when Planck's constant $h \rightarrow 0$ the

number of energy levels between some fixed E and $E + \Delta E$ becomes infinite.)

7. One-dimensional System of Hard Rods

An interesting model system which exhibits some "real fluid" -like properties is a one-dimensional system of hard rods with "diameter", a , and equal masses $m = 1$. The dynamics of this system consists entirely of an interchange of the velocities of pairs of neighboring particles upon collision and free motion between collisions. It is clear that when the diameter is zero, $a = 0$, then all functions $f(x)$ which are symmetric in the coordinates and velocities (q_i, v_i) of all the particles, e.g.,

$$f(x) = \sum_{i=1}^N \varphi_1(q_i, v_i)$$

will have the same time evolution as the corresponding function in an ideal gas where the particles simply pass through each other. (For an ideal gas the q_i and v_i behave, except possibly for boundary conditions on the q_i , in exactly the same way as do the action-angle variables J_i and θ_i in a harmonic system [14].)

Hence the only "interesting" functions in a system of rods of zero diameter are those which depend on the coordinates and momenta of a specified set of particles, which we may consider to be "labeled," e.g., $\varphi_1(q_1, v_1)$, $\varphi_2(q_1, v_1, v_2)$, etc. Different aspects of the time evolution of such labeled one-particle functions, say $\varphi_1(q_1, v_1)$, were investigated in detail by Jespen [15], Lebowitz and Percus [16], and Spitzer [17], while the time evolution of some symmetric one-particle functions (such as van Hove's coherent neutron scattering function) in a system of hard rods with finite diameters was investigated by Lebowitz, Percus, and Sykes [18]. I shall only mention here a few of those results (and some conjectures of mine) which are related to the problems we have been discussing here.

Let the particles be labeled with index i , $i = -n, \dots, n$, $2n+1 = N$, and confined to a box (or circle) of length \mathcal{L} . Then in the thermodynamic limit $N \rightarrow \infty$, $\mathcal{L} \rightarrow \infty$, $N/\mathcal{L} \rightarrow \rho$, the properly behaved functions [square integrable functions $\varphi_1(q_1, v_1)$, $\psi_1(q_1, v_1)$, $\langle \varphi_1^2 \rangle \leq K$, $\langle \psi_1^2 \rangle < K$, independent of N , ?] are mixing,

$$\langle \varphi_1(t) \psi_1 \rangle \equiv \lim_{N \rightarrow \infty} \langle \varphi_1(t) \psi_1 \rangle_N \rightarrow \langle \varphi_1 \rangle \langle \psi_1 \rangle, \quad t \rightarrow \infty. \quad (3.16)$$

In particular,

$$\langle v_1(t) v_1 \rangle \rightarrow 0, \quad t \rightarrow \infty, \quad (3.17)$$

$$\int_0^\infty \langle v_1(t) v_1 \rangle dt = (2\rho)^{-1} \langle |v_1| \rangle = D, \quad (3.18)$$

with D the self-diffusion constant. The mixing property in expression (3.17) is true only when $N \rightarrow \infty$, for it is possible to show explicitly in some cases that in a finite system the velocity autocorrelation function $\langle v_1(t) v_1 \rangle_N$ does not approach zero [19]. When the rods have a finite

parameter a , ρ in expression (3.18) is replaced by $\rho/(1 - \rho a)$. The same is true for other correlations of the form (3.16).

The form of the asymptotic approach to zero of $\langle v_1(t)v_1 \rangle$ depends on the invariant measure μ_0 used. Since, as already mentioned, the entire dynamics of this system consists of an interchange of velocities during a collision, any ensemble density of the form

$$\rho_0(q_{-n}, v_{-n}, \dots, q_n, v_n) = \mathcal{L}^{-N} \prod_{i=-n}^n h_0(v_i) - \mathcal{L}/2 \leq q_i \leq \mathcal{L}/2, \quad (3.19)$$

$$h_0(v) \geq 0, h_0(v_i) = h_0(-v_i), \int_{-\infty}^{\infty} h_0(v) dv = 1, \quad (3.20)$$

is invariant in time. It is furthermore required that the diffusion constant be finite, $\int |v| h_0(v) dv < \infty$, for the thermodynamic limit of the "process" to exist [17].

Several forms of $h_0(v)$ have been studied explicitly with the results that when $h_0(v)$ is the Maxwellian distribution [15]

$$h_0(v) = (\beta/2\pi)^{1/2} \exp[-v^2/2], \quad (3.21)$$

or [16]

$$h_0(v) = \frac{1}{2} c^2 (c^2 + v^2)^{-3/2}, \quad (3.22)$$

then

$$\langle v(t)v_1 \rangle \sim t^{-3} \quad t \rightarrow \infty. \quad (3.23)$$

where $h_0(v)$ is discrete,

$$h_0(v) = \frac{1}{2} [\delta(v - c) + \delta(v + c)], \quad c < 0, \quad (3.24)$$

then [16]

$$\langle v_1(t)v_1 \rangle = c^2 \exp[-2\rho ct]. \quad (3.25)$$

Note that for the velocity distribution (3.22) v_1 is not square integrable. The time integral of $\langle v_1(t)v_1 \rangle$ in equation (3.18) still exists, however, since $\langle v_1(t)v_1 \rangle \sim |\ln t|$ as $t \rightarrow 0$.

Another result of interest is that the spatial density of a labeled particle which was specified initially (at $t = 0$) to be at a fixed position r' (i.e., the van Hove self-function of neutron scattering theory),

$$\rho G_s(r, t/r') = \lim_{N \rightarrow \infty} \langle \delta[q_s(t) - r] \delta(q_1 - r') \rangle_N = \rho G_s(r - r', t), \quad (3.26)$$

has the asymptotic form appropriate to a Brownian diffusion process

$$G_s(r, t) \sim (4\pi Dt)^{-1/2} \exp[-r^2/4Dt] \quad (3.27)$$

as $|r| \rightarrow \infty$, $t \rightarrow \infty$, $r/t^{1/2}$ finite. More precisely, if $q(t) = q_1(t) - q_1$ is the displacement of the j th particle, then in the thermodynamic limit, $A^{-1/2} q(At) \rightarrow z(t)$ as $A \rightarrow \infty$ with $z(t)$ a standard Brownian diffusion process with D given in equation (3.18) [17].

Let me conjecture that in this system as in the harmonic crystal all square integrable local functions are mixing in the thermodynamic limit. (This seems to follow indeed from the work O. de Pazzes reported at this conference; Abstract, II.25. Similar results were also proven recently by Sinai [private communication].)

IV. THE LANFORD THEOREM

As you have heard from Griffith in his lecture, the rigorous study of the thermodynamic limit of equilibrium statistical mechanics has already achieved notable results. The comparable investigation of the infinite volume limit of nonequilibrium systems is much more difficult and has begun only recently.

Let $\{q, p\}$ represent the positions and momenta of a set (not necessarily finite) of particles of unit mass each. Then Newton's equations of motion have the explicit form

$$\dot{q}_i(t) = p_i(t), \quad \dot{p}_i(t) = \sum_{j \neq i} F[q_j(t) - q_i(t)], \quad (4.1)$$

where F is the interparticle force. If we have a finite number of particles, then there is clearly a unique solution to this set of differential equations for all sets of initial conditions $\{q_i(0), p_i(0)\}$ (when F is suitably bounded). The existence of a meaningful solution to Newton's equations, i.e., the existence of a time evolution of the system, becomes, however, far from trivial when we consider a system consisting (from the beginning or in some limit) of an infinite number of particles. In such a system it is quite possible to begin with a perfectly reasonable set of initial values $\{q_i(0), p_i(0)\}$ and find after some finite time t that there are an infinite number of particles in a finite region of space and that the right side of equation (4.1) is infinite. We illustrate this with a simple example given by Lanford. Consider a system in which there are no forces, i.e., an ideal gas, and assume that at time zero $p_i = -q_i$ for each i ; then at time $t = 1$ all the particles will be situated at the origin.

When the particles have hard cores, then it is possible (Ginibre) in two or three dimensions to construct "reasonable" initial configurations in which, through a cascade of collisions, some particle will have an infinite velocity after a finite time.

Thus, we need to find a class of initial conditions for which such catastrophes do not happen. In fact, since we are interested also in the equilibrium state of our systems, we would like to show that those classes of initial conditions which have nonzero probability of occurring in equilibrium do not give rise to such catastrophes. An even stronger desired result is to show that the time evolution of a part of the system contained in a fixed region of space Λ will, at any time t , be determined entirely by the state of the system at time $t = 0$ in the neighborhood of Λ (how large this neighborhood is will of course depend on t). This was indeed proven by Lanford [8] for one-dimensional systems. Assuming that F has a finite range, $F(q) = 0$ for $q > D$, and that F is bounded, $|F(q)| < K$, D and K some positive constants, Lanford proved the existence for all times of a "regular" solution of Newton's equations of motion for a "regular" initial configuration. A regular configuration is, roughly speaking, one in which the number of particles in a unit interval and the magnitude of the momentum of any particle in that interval have a bound of the form $\delta \log R$, where R denotes the distance of the interval from the origin. It was further proven by Lanford that, when the interparticle potential is positive or the activity is small, the set of nonregular configurations has probability zero in the equilibrium grand canonical ensemble.

Lanford's results have been extended recently to one-dimensional systems with hard cores [20]. (This is a "marriage" of Lanford's systems and the hard rod system discussed earlier.)

A question left open by these results is whether a state which at time $t = 0$ is described by a set of correlation functions can still be described by a set of correlation functions when $t \neq 0$. This was investigated by Gallavotti, Lanford, and Lebowitz [21], who proved that, for certain classes of initial states, the time-evolving state is described by correlation functions and that these correlation functions satisfy the BBGKY hierarchy in the sense of distributions.

The initial states we consider can be described as follows: Suppose that the system is in equilibrium at temperature β^{-1} and activity z under the influence of a pair potential and an external potential h which is localized in a finite region I_h . At time $t = 0$ we switch off the external field, and the system begins to evolve. We prove that if the correlation functions exist for the equilibrium state at $t = 0$ and if the Lanford theorem holds, then the system can always be described by a set of correlation functions which vary in time according to the BBGKY hierarchy. We are, however, unable to prove the convergence of the fugacity (or density) expansion for these functions at any $t > 0$ [22]. We are also unable to prove even that the time averaged correlation functions evolve toward the correlation functions which correspond to the equilibrium state at temperature β^{-1} and activity z (in the absence of an external field) as would be expected. We are, however, able to prove that the time-averaged correlation functions converge to a limit satisfying the stationary BBGKY hierarchy.

Note that when there are no interactions between the particles, i.e., for an ideal gas, the correlation functions we have been discussing here have (as indicated in section III) all the desirable mixing properties. This is due to the disappearance, through the unimpeded motion of the particles, of any local disturbance. The "approach to equilibrium" thus exhibited by an ideal gas is, however, different in an essential way from the irreversible behavior of real systems. The approach to equilibrium in real systems can be described by hydrodynamics and/or kinetic equations whereas the ideal gas does not obey Fourier's law of heat conduction or Fick's law of diffusion. (The model systems discussed in the last section are similar to the ideal gas in this respect.)

The origin of these differences presumably lies in the existence of a mechanism (collisions) in real systems which acts locally to bring the system to a state of local equilibrium and the absence of such a mechanism in the ideal gas and in the model systems we have discussed. This difference is also exhibited when we consider systems in which the departure from the equilibrium state is "global." Consider, for example, a system whose state at $t = 0$ is specified by correlation functions whose spatial part is that obtained from a grand canonical (or canonical) ensemble at temperature T and fugacity z but whose velocity part is not Maxwellian (the mean kinetic energy is, however, specified by T). I would expect that in a real system, but clearly not in an ideal gas, these correlations would approach their true equilibrium values; e.g., the velocity distribution would become Maxwellian.

V. OPEN SYSTEMS

We shall now extend our analysis to systems whose time evolution is not given by a Hamiltonian flow in phase space. These are systems which are 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 [4], 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 [23], [24], and look for the stationary solution of a generalized Liouville equation having the form

$$\frac{\partial \rho(x, t)}{\partial t} + (\rho, H) = \sum_\alpha \int [K_\alpha(x, x') \rho(x', t) - K_\alpha(x', x) \rho(x, t)] dx'. \quad (5.1)$$

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 α th 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 (5.1) describes a stationary Markov process, and we may define the stochastic time evolution operator W^t , for $t > 0$, by

$$\rho(x, t) = W^t \rho(x, 0) = \int W(x, t | x') \rho(x', 0) dx', \quad t \geq 0, \quad (5.2)$$

where $\rho(x, t)$ is the solution of equation (5.1) when the ensemble density at time zero is $\rho(x, 0)$.

The operators W^t form a semigroup

$$W^{t_1+t_2} = W^{t_1} W^{t_2}, \quad t_1, t_2 \geq 0, \quad (5.3)$$

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 [23], [24], generally satisfied by our systems, that as $t \rightarrow \infty$, $\rho(x, t)$ will approach (in some suitable sense) a stationary ensemble density $\rho_s(x)$ which is independent of the initial ensemble density $\rho(x, 0)$,

$$\lim_{t \rightarrow \infty} W^t \rho(x, 0) = \rho_s(x), \quad W^t \rho_s(x) = \rho_s(x). \quad (5.4)$$

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 nonequilibrium state through which heat is flowing. Define

$$W_t f = \int f(y) W(y, t | x) dy, \quad \langle f \rangle = \int f(y) \rho_s(y) dy, \quad (5.5)$$

$$\langle f(t)g \rangle = \langle (W_t f)g \rangle = \int \left[\int dy f(y) W(y, t | x) \right] g(x) \rho_s(x) dx.$$

When equation (5.4) holds and $W(y, t | x) \rightarrow \rho_s(y)$ as $t \rightarrow \infty$, we have

$$W_t f \rightarrow \langle f \rangle, \quad \langle f(t)g \rangle \rightarrow \langle f \rangle \langle g \rangle \text{ as } t \rightarrow \infty. \quad (5.6)$$

To obtain the energy flow into the system from each reservoir we multiply equation (5.1) by H and integrate over x to obtain

$$\frac{\partial \langle H \rangle}{\partial t} = \sum_{\alpha} \int \left\{ \int K_{\alpha}(x, x') [H(x) - H(x')] dx' \right\} \rho(x', t) dx' \equiv \sum_{\alpha} J_{\alpha} \quad (5.7)$$

where J_{α} is the average energy flux from the α th reservoir. In the steady state we have, of course, $\sum J_{\alpha} = 0$. 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 should 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 $\mathcal{L} \rightarrow \infty$. This κ , if it exists, we would identify with the heat conductivity of the system at temperature T when $T_L \rightarrow T_R \rightarrow T$.

This formalism has been applied [24] to a harmonic crystal with some particular forms of interaction with the heat reservoirs. The stationary nonequilibrium ensemble density for such a harmonic system was found to be a generalized Gaussian. The covariance matrix of this Gaussian was obtained there 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 there that in the stationary nonequilibrium 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 [25], [26].

Searching for a model system in which Fourier's law could be shown to hold, Casher and Lebowitz [27] 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" [28]. 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 $\mathcal{L} \rightarrow \infty$ 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 $\mathcal{L} \rightarrow \infty$.

We also showed, by using a theorem of Matsuda and Ishii [29], that for a random chain $J \rightarrow 0$ as $\mathcal{L} \rightarrow \infty$ 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 nondenumerable 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 have already seen, the irreversible decay of local disturbances requires the absence of localized bound states (corresponding to a point spectrum).

(Visscher has suggested that J may depend on the boundary conditions placed on the end atoms of the chain. This appears to agree with the finding of Rubin and Greer in a paper which will appear in J. Math. Phys.)

VI. METASTABLE STATES IN THE VAN DER WAALS-MAXWELL THEORY

Until now I have been talking about (a) time-dependent phenomena in isolated dynamical systems and (b) stationary nonequilibrium phenomena which are maintained in open systems by externally imposed gradients. I shall now speak briefly about a third kind of nonequilibrium situation: the metastable state of an isolated system [30].

We may characterize metastable thermodynamic states by the following properties:

- (a) Only one thermodynamic phase is present.
- (b) A system that starts in this state is likely to take a long time to get out. (6.1)
- (c) Once the system gets out, it is unlikely to return.

In order to discuss the static and dynamic properties of metastable states in a rigorous fashion it is necessary to make precise the notion, inherent in all physical theories of metastability [31], of imposing a restriction on the system which keeps its density roughly uniform. In general, such a restriction may be represented by confining the configuration of the system to a suitable region R in configuration space. In order for this region to correspond to a metastable state, the restrictions defining it should correspond to the imposition of a roughly uniform density, in accordance with the criterion (6.1a), and it should also have properties corresponding to the conditions (6.1b) and (6.1c) mentioned earlier: if the dynamical state is initially in R , it is unlikely to escape quickly; and once it has escaped it is unlikely to return.

With this in mind we investigated the existence of such a region R for a system whose liquid vapor phase transition can be proven to be of the van der Waals type and is clearly understood [32]. The main feature of this system is that its interparticle potential $v(r)$ can be cleanly divided into "short-range repulsive" and "long-range attractive" parts:

$$v(r) = q(r) + \gamma^\nu \varphi(\gamma r) \quad (0 \leq r < \infty), \quad (6.2)$$

where ν is the number of space dimensions and γ^ν is the range of the "Kac potential" $\gamma^\nu \varphi(\gamma r)$. We take here $\varphi(r) \leq 0$ and set

$$\gamma^\nu \int \varphi(\gamma r) d^\nu r = \int \varphi(y) d^\nu y \equiv \alpha. \quad (6.3)$$

Under suitable conditions on q and φ , the thermodynamic limit of the Helmholtz free energy density (f.e.d.) at a given particle density ρ (the dependence on temperature is not displayed) is given in the limit $\gamma \rightarrow 0$ by [32]

$$f(\rho, 0^+) = \lim_{\gamma \rightarrow 0} f(\rho, \gamma) = \text{CE}[f_0(\rho) + \frac{1}{2} \alpha \rho^2] . \quad (6.4)$$

Here $f_0(\rho)$ denotes the free energy of the reference system--that is, the system whose interaction potential function is q instead of v --and the symbol CE indicates the convex envelope of the expression following it, i.e., the value of the maximal convex function whose value nowhere exceeds $f_0(\rho) + \frac{1}{2} \alpha \rho^2$. Since $\alpha \leq 0$, the function $f_0(\rho) + \frac{1}{2} \alpha \rho^2$ need not be convex even though $f_0(\rho)$ must be (see Fig. 1).

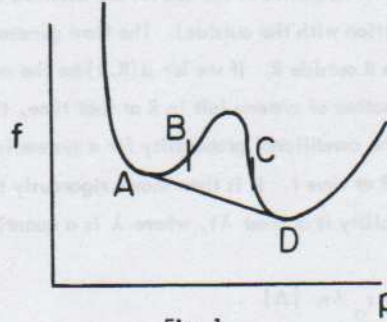


Fig. 1

The smooth curve in the figure is the graph of $f_0(\rho) + \frac{1}{2} \alpha \rho^2$, whose convex envelope is obtained by replacing the arc ABCD by the corresponding double tangent AD.

The parts of the curve which Maxwell associated with metastable states are the arcs AB, CD; these may be specified by the conditions

$$f_0(\rho) + \frac{1}{2} \alpha \rho^2 > f(\rho, 0^+) \quad (6.5a)$$

and

$$f_0''(\rho) + \alpha > 0 , \quad (6.5b)$$

where f_0'' denotes the second derivative of f_0 .

To define our phase-space region R we start with a finite system in a domain Λ , of volume $|\Lambda|$, and divide Λ into cubical cells $\omega_1, \omega_2, \dots, \omega_M$, each of volume $|\omega|$, $M|\omega| = |\Lambda|$. We define the dynamical variable n_i ($i = 1, \dots, M$) to be the number of particles in ω_i , and we choose two numbers ρ^- and ρ^+ such that $\rho^- < \rho^+$ and the condition

$$f_0''(x) + 2\alpha > \text{const.} > 0 \quad (6.6)$$

holds for all $x \in [\rho^-, \rho^+]$. Since α is negative, this is more restrictive than condition (6.5b), but the precise values of ρ^- and ρ^+ chosen are unimportant. In particular, they may be arbitrarily close. In accordance with the condition (6.1a) that the metastable state should correspond to a single thermodynamic phase, we now define R to be the set of all configurations compatible with M constraints:

$$\rho^- |\omega| < n_i < \rho^+ |\omega| \quad (i = 1, 2, \dots, M) . \quad (6.7)$$

We now assume that at time $t = 0$ our system is in a state represented by a restricted grand canonical ensemble that is one constructed by selecting from a grand canonical ensemble those systems whose configuration is in R . The chemical potential of this grand ensemble is $f_0(\rho) + \alpha \rho$

with ρ satisfying condition (6.5a) and $\rho^- < \rho < \rho^+$. These conditions assure that the equilibrium state of this system has an average density which is not in (ρ^-, ρ^+) and hence the equilibrium probability of finding the system in R will be small (zero in the thermodynamic limit).

The choice of the grand canonical ensemble (rather than the canonical or microcanonical ensembles which are believed to be essentially equivalent to it) is a matter of convenience. It is used only for setting up the restricted ensemble at time 0; it does not imply that the system is open for times greater than 0. The dynamics of the system are assumed to be determined entirely by its own Hamiltonian (no interaction with the outside). The flow generated by this Hamiltonian will carry some systems initially in R outside R . If we let $\mu(R, t)$ be the measure of R at time t as in equation (2.6), i.e., the fraction of systems left in R at that time, then $\mu(R, 0) = 1$. We have that $p(R, t) = 1 - \mu(R, t)$ is the conditional probability for a system initially in R (i.e., in the metastable state) not to be in R at time t . It is then shown rigorously that for periodic boundary conditions, this conditional probability is at most λt , where λ is a quantity that goes to 0 in the limit

$$|\Lambda| \gg \gamma^{-\nu} \gg |\omega| \gg r_0 \ln |\Lambda|. \quad (6.8)$$

Here r_0 is a length characterizing the potential q , and $x \gg y$ means $x/y \rightarrow +\infty$. For rigid walls the same result is proved under somewhat more restrictive conditions. It is argued that a system started in the metastable state will behave (over times $\ll \lambda^{-1}$) like a uniform thermodynamic phase with f.e.d. $f_0(\rho) + \frac{1}{2}\alpha\rho^2$, but that having once left this metastable state the system is unlikely to return.

The form of our upper bound on λ , is roughly $|\Lambda| \exp(-\Delta/kT)$ with Δ a positive "activation energy" proportional to $|\omega|$. Similar formulae for escape rates occur in other theories [32]. The main difference between these formulae and ours is that they are intended to be approximations to the true escape rate, whereas ours is a rigorous upper bound, but not necessarily a good approximation.

This upper bound was made possible by the fact that, in the limit we are considering, the range γ^{-1} of the Kac potential becomes very large compared with the other physical lengths, r_0 and $\rho^{-1/\nu}$. This permits a clean separation of the effects of the Kac potential from those of the short-range potential q . This separation is accomplished by introducing an artificial new length $|\omega|^{1/\nu}$ satisfying the two conditions (both coming from inequality [6.8])

$$\begin{aligned} |\omega|^{1/\nu} &\gg \rho^{-1/\nu} \ln |\Lambda| \\ |\omega|^{1/\nu} &\ll \gamma^{-1} \end{aligned} \quad (6.9)$$

and defining R through constraints (eq. [6.7]) on density variations over the length scale $|\omega|^{1/\nu}$.

In the canonical ensemble for a system of $N = \rho |\Lambda|$ particles the first condition in (6.9) ensures that there are enough particles in each cell to make a fluctuation from the average occupation number assumed in the metastable state which violates the "constraints," an unlikely event in the restricted equilibrium ensemble, and hence enables us to prove that the escape rate is small.

The second condition ensures that any phase transition due to the Kac potential is completely

suppressed by the constraints, and hence makes the state defined by these constraints a very unlikely one in the full equilibrium ensemble, if this ensemble predicts such a phase transition. This also ensures that this state is spatially uniform.

Since both parts of (6.9) are crucial to our treatment of metastability, the result that λ can be made as small as we please does not apply to real physical systems, for which there is no $\gamma \rightarrow 0$ limit. For a realistic potential, it may well be impossible to find regions R which have both arbitrarily small escape rates and arbitrarily small equilibrium probabilities--particularly in view of the apparent impossibility of analytically continuing the equilibrium free energies and correlation functions for such potentials into the domain of metastability [32], [33].

I would like to thank J. Percus, B. Simon, J. Sykes, and particularly R. Resibois for many valuable and clarifying discussions during the preparation of this talk.

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DISCUSSION

A. Siebert: Is there any indication in Sinai's proof that the limit is, for practical purposes, reached in a reasonable time, and not, for instance, in a time comparable with a Poincaré cycle?

B. Simon: The time it takes to reach the limit will depend on the particular observable that one is interested in. The autocorrelation function for a given observable differs from its final value in general by the Fourier transform of an L_1 function and therefore goes to zero. The approach may, however, be arbitrarily slow. Sinai's theorem involves showing that certain quantities approach zero exponentially fast, so it may be possible to prove that autocorrelation functions of interesting observables approach their asymptotic value exponentially; but obviously such an attempt must await the publication of Sinai's proof.

A. Scotti: Since it is reasonable to expect that Sinai's theorem for hard spheres will be generalized to physically more realistic potentials, and the considerations you have made on the limiting values of $\langle v(t)v(0) \rangle$ and $\int_0^T \langle v(t)v(0) \rangle dt$ depend only on the system being mixed, would you care to comment a little bit more on your philosophy regarding results that are valid only for a finite number of particles?

J. Lebowitz: I expect that for any fixed t , $\langle v(t)v(0) \rangle_N \xrightarrow{N \rightarrow \infty} \langle v(t)v(0) \rangle_\infty$, where the subscript indicates the size of the system.

B. Robertson: Dr. Lebowitz pointed out, equivalently, that the Fourier, Laplace transform of the Green-Kubo velocity autocorrelation function vanishes if the $\omega \rightarrow 0$ limit is carried out before the $k \rightarrow 0$ limit. This singular behavior does not occur in autocorrelation functions that include a suitable projection operator as given, for example, in J. Math. Phys. 11, 2482 (1970).

G. Emch: The kind of classical ergodic theory Professor Lebowitz just talked about has been (partly) extended to quantum situations, by Charles Radin and myself. As a particular application of that general theory, one can show exactly that certain infinite systems provide a thermal bath for all of their finite parts; specifically, local thermal deviations do decay to equilibrium. This result thus provides a proof of a specialized form of the second principle of thermodynamics. The XY model belongs to the class for which the above assertions (as well as some other such statements concerning local perturbations) hold.

[At that point a question was asked by M. Green on necessity versus sufficiency. The answer to that question was: What we have are certain conditions on the time evolution, which are sufficient to ensure the above behavior. What we say is that these conditions are in particular satisfied by the Hamiltonian of the XY model.]

H. Matsuda: Concerning the thermal conductivity of the isotopically disordered harmonic chain, Allen and Ford discussed it applying the Kubo formula. Although their formal expression for the thermal conductivity κ is right, they obtained a finite κ in the limit $N \rightarrow \infty$ which is found not correct. By making a correction to their results, Ishii and I obtained a κ which is proportional to \sqrt{N} . Apart from the question of the validity of the Kubo formula in this model, I believe that the above N -dependence of the Kubo thermal conductivity is the right answer.

W. Visscher: The thermal conductivity of a disordered harmonic chain does, in fact, depend strongly on the boundary conditions one assumes. For example, if the (0) th and $(N+1)$ th atoms are clamped, with the first and (N) th atoms weakly coupled to heat reservoirs at different temperatures, then, as Professor Matsuda says, the effective thermal conductivity goes as $N^{-\frac{1}{2}}$. On the other hand, if the ends of the chain are free, the effective thermal conductivity for large N goes as $N^{\frac{1}{2}}$. The reason for this is that in a disordered chain only the very low frequency normal modes contribute to the heat current because all the other modes are localized, and the coupling of the low frequency, long wavelength modes to the reservoirs is suppressed if the ends of the chain are clamped. If weak anharmonicities are introduced, exchange of energy between normal modes becomes possible, and the behavior of the thermal conductivity becomes more reasonable, namely, independent of N for long chains.

H. Wergeland: The peculiar nature of the energy transport in harmonic lattices to which Dr. Lebowitz alludes has of course given rise to a great many studies. Perhaps it is most strikingly brought out in the example chosen by Hemmer: When two contiguous parts of an infinite linear chain start with unequal temperatures, the temperature gradient at the junction will indeed gradually decrease to zero but the flow of heat across this point will increase to a constant value.

In this sense, therefore, one may say that the heat conductivity is infinite. Now, one can make more complicated harmonic models by distributing impurities (randomly or otherwise) in the

lattice. And one can in this way obtain an averaged leveling of energy gradients which is different from simple elastic signals. Yet the transport of heat does not become freely diffusive. One cannot derive a purely parabolic Fourier equation along such lines because the dispersion function--however complicated one makes it--will always remain a causal one.

J. Harrison: The behavior of the linear chain of harmonic oscillators can be understood in terms of the electrical network analogy described in my contributed paper at this conference. By the described theorem of Haus and Adler, valid for linear circuits and hence for harmonic oscillators, the temperature "looking" toward one end of the chain will be invariant along the chain and will be the temperature of the far end. Thus the temperature source at one end looks into a sink characterized by the temperature at the other end. The heat transfer will therefore be proportional to the temperature difference, with the proportionality constant solely dependent upon the impedance "match" between the impedance of the temperature source and that of the sink as transformed along the chain. For long uniform chains this impedance factor will have a characteristic value averaged over a small frequency interval, which is independent of the length of the chain. For the chain with random masses, the average value of impedance of the sink as transformed over the length of the chain will tend to grow proportionally to the square root of length, modifying the heat transfer accordingly. A uniform thermal gradient varying inversely as the length can be recovered for both the uniform chain and the statistically homogeneous random chain by the introduction of a small amount of dissipative attenuation in the chain in a manner equivalent to the use of self-consistent heat reservoirs by Bolsterli, Rich, and Visscher.

G. Wannier: There is a development in experimental physics running parallel to the difficulties in the theory discussed here. Measurement of a coefficient of heat conduction is becoming increasingly difficult as crystals become more perfect and data more precise. The range in which the coefficient is determined by crystal imperfections is increasing. If the concept can be saved for perfect crystals, it will probably need more careful definition. Such a definition must take into account that part of the heat always travels with the velocity of sound.