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A Boltzmann Map for Quantum Oscillators

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We define a map τ on the space of quasifree states of the CCR or CAR of more than one harmonic oscillator which increases entropy except at fixed points of τ. The map τ is the composition of a doubly stochastic map T^* and the quasifree reduction Q. Under mixing conditions on T, iterates of τ take any initial state to the Gibbs state, provided that the oscillator frequencies are mutually rational. We give an example of a system with three degrees of freedom with energies ω_1, ω_2, and ω_3 mutually irrational, but obeying a relation $n_1\omega_1 + n_2\omega_2 = n_3\omega_3$, $n_i \in \mathbb{Z}$. The iterated Boltzmann map converges from an initial state ρ to independent Gibbs states of the three oscillators at betas (inverse temperatures) β_1, β_2, β_3 obeying the equation $n_1\omega_1\beta_1 + n_2\omega_2\beta_2 = n_3\omega_3\beta_3$. The equilibrium state can be rewritten as a grand canonical state. We show that for two, three, or four fermions we can get the usual rate equations as a special case.

KEY WORDS: Boltzmann; entropy; quasifree projection.

1. INTRODUCTION

There are two main problems of nonequilibrium statistical mechanics. In the first, a system, not necessarily in a thermal state, is in thermal contact with a heat bath. This is an infinite system at a definite beta (our word for inverse temperature). The problem is to describe how the system warms up or cools down to the same beta as the heat bath. Heat is exchanged, being driven by the beta gradient, and the average energy of the system is not constant in time. To get the grand canonical ensemble, the system exchanges energy and particles with the heat bath, the particle flow being

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driven by the chemical potential. Such theories are described phenomenologically by a linear stochastic process[1] or more ambitiously by a limit of Hamiltonian systems.[2,3]

The second problem asks the question, how did the heat bath get its beta in the first place? The only successful type of theory is based on the Boltzmann equation[4] or its quantum version.[5] This is an ambitious program, attempting to work from a microscopic model of the interactions of particles to derive the laws of stochastic motion of a single particle in a dilute gas. One hopes to prove that the state of the particle converges to the Gibbs state at some beta. In this process the average energy is constant in time, reflecting the redistributions among the gas molecules, rather than the loss or gain of heat by the system as in the first problem. We are interested in the second type of problem, which we treat phenomenologically rather than from a particular microscopic model.

The present paper is a sequel to Ref. 6, where we studied a special class of population models with discrete time, which imitates the classical Boltzmann equation, and Ref. 7, where a quantum version was formulated. In either case a map τ, the "Boltzmann map," is defined, mapping states to states, the iterates of which, when applied to an initial state ρ, converge to a Gibbs state ρ_β. For finite systems, β is fixed by the requirement that ρ and ρ_β have the same average energy.

The map τ is the composition of a doubly stochastic map τ on the two-particle states of the form $\rho \otimes \rho$, representing a two-particle scattering conserving energy, and the conditional expectation P onto a state ρ' of the first particle. One then forms $\rho' \otimes \rho'$ and repeats; this step imitates Boltzmann's *Stosszahlansatz*, expressing the fact that before a collision the two participating particles are chosen at random, independently, from the total population. Thus, the models in Refs. 6 and 7 are, like Boltzmann's, descritions of the dynamics of dilute gases. But even in our quantum case[7] it is taken that the particles are distinguishable. It is therefore desirable to have a second-quantized version for Bose and Fermi statistics. This we construct here.

Let K be a complex Hilbert space with $\dim K = N < \infty$. The space K is called the "one-particle space" and a vector in K describes the state of a single particle. If the particle is a boson, then the (pure normal) state of a system of particles is described by a vector in $\Gamma_s(K)$, the symmetric Fock space over K:

$$\Gamma_s(K) = C \oplus K \oplus (K \otimes K)_s \oplus (K \otimes K \otimes K)_s \oplus \cdots$$

where $(K \otimes K)_s$ is the Hilbert space of symmetric second-rank tensors over

K, etc. If the particle is a fermion, then we use the antisymmetric Fock space:

$$\Gamma_A(K) = C \oplus K \oplus \Lambda^2 K \oplus \cdots \Lambda^N K$$

where $\Lambda^k(K)$ is the Hilbert space of totally antisymmetric tensors of rank k.

We take as the (bounded) observables the Hermitian elements of $\mathscr{A} = B(\Gamma_S(K))$ in the case of bosons. This is the c^*-algebra of all bounded operators on Fock space, and is generated by the creation and annihilation operators $a_j^\#$ (we denote a_j^* or a_j by $a_j^\#$, $j = 1, 2,..., N$): any bounded operator is a function of these.

For fermions, the creators and annihilators $b_j^\#$ also generate $B(\Gamma_A(K))$, the algebra of all operators, but we take as the observables the algebra $\mathscr{A} \subseteq B(\Gamma_A(K))$ generated by *gauge-invariant* functions of $b_j^\#$. Thus, an observable is a Hermitian element of $B(\Gamma_A(K))$, invariant under the automorphisms that on $b_j^\#$ reduce to gauge transformations of the first kind, namely, $b_j \to e^{i\theta} b_j$, $j = 1,..., N$, for $\theta \in \mathbb{R}$.

A state of the system will mean a normal state on the c^*-algebra $\mathscr{A}$, that is, a positive linear map from $\mathscr{A}$ to C of the form $A \to \mathrm{Tr}(\rho A)$, $A \in \mathscr{A}$. Here, ρ is the density matrix of the state, i.e., a positive operator in $B(\Gamma)$ of trace 1. For fermions, it is natural to consider only even states.

It has been argued[3] that irreversibility in quantum mechanics should be introduced by replacing the one-parameter group of time-evolution by a one-parameter semigroup of completely positive stochastic maps. Complete positivity, as opposed to positivity, will play no role in this paper. A stochastic map is a linear map T from $\mathscr{A}$ to $\mathscr{A}$, taking positive operators to positive operators, and such that $T1 = 1$. Such a T is called a super-operator in the literature, because it acts on the space of operators. The space of Hilbert–Schmidt operators is a Hilbert space with scalar product $\langle A, B\rangle = \mathrm{Trace}(A^* B)$. Let T^* be the adjoint of T in this space, so that $\langle T^* A, B\rangle = \langle A, TB\rangle$. Then we shall be interested in bistochastic maps, i.e., T and T^* are both stochastic. Then T and T^* are both trace-preserving, and leave the identity operator of $\mathscr{A}$ fixed. The entropy of a density matrix is $s(\rho) = -\mathrm{Trace}(\rho \log \rho)$. The function $x \log x$ is convex; so, as explained in the nice book of Alberti and Uhlmann [Ref. 8, Theorem 2-2(f)], the entropy of a state is not decreased by a bistochastic map, i.e.,

$$s(T^*\rho) \geqslant s(\rho)$$

In a dilute gas, two particles scatter and leave each other's influence in a time short compared with the mean time between collisions. As an idealization, we describe the collision by a scattering matrix S computed as if there were an infinite time between collisions. This induces the scattering automorphism (Heisenberg picture)

$$T_S: \quad A \to SAS^*, \qquad A \in \mathscr{A}$$

on the algebra of observables, and its dual action (Schrödinger picture)

$$T_S^*: \quad \rho \to S^* \rho S$$

on the space of density matrices. This map is bistochastic. It is natural to replace this by a more general bistochastic map

$$A \to TA, \qquad \rho \to T^* \rho$$

This takes into account unknown features of the model that are not mentioned in our simplified description. For example, Spohn[5] has derived a linear master equation in quantum mechanics from a Hamiltonian model with random impurities.

In our model, we may imagine that the scattering automorphism $A \to SAS^*$ is obtained from an interaction V of short range, so that the total Hamiltonian $H + V$ is effective during the scattering, and $H = \sum \omega_k a_k^* a_k$ is the energy operator for the ingoing and outgoing particles. The scattering conserves energy, so that $[S, H] = 0$. If V is a random potential, i.e., V is an operator-valued function of a sample point $\omega \in \Omega$, where (Ω, μ) is a probability space, then the average effect of the scattering automorphism is the bistochastic map

$$T_\mu: \quad A \to \int_\Omega S(\omega)\, AS^*(\omega)\, d\mu(\omega)$$

Such maps, incidentally, are also completely positive. Since each $S(\omega)$ commutes with H, it commutes with the spectral resolutions of H; so if $H = \sum EP(E)$ is the spectral resolution of H, we see that

$$T_\mu P(E) = \int_\Omega S(\omega)\, P(E)\, S^*(\omega)\, d\mu(\omega) = \int P(E)\, d\mu(\omega) = P(E)$$

for all E. Similarly, $T_\mu^* P(E) = P(E)$. It is therefore natural to make this property the definition of an energy-conserving bistochastic map:

Definition. Let $\mathscr{H}$ be a Hilbert space and $H = \sum EP(E)$ a self-adjoint operator on $\mathscr{H}$. Let T be a bistochastic map, $B(\mathscr{H}) \to B(\mathscr{H})$. We say T is *H-conserving* if $TP(E) = P(E) = T^*P(E)$ for all E.

Let T be stochastic. Then the quantum analogue of a Markov chain is the sequence of states $\{T^{*n}\rho\}_{n=0,1\cdots} = \{\rho(n)\}$, where ρ is the initial state. This might be taken as the time evolution of a system. Perhaps a better model, with continuous time, would be to regard n as the number of collisions that have occurred by a random time, rather than as time itself. This would allow for the possibility that the time intervals between collisions are not all the same, but follow the law of a waiting time. We say that $\rho(n)$ is a linear process because it is linear as a function of ρ.

Glauber[1] has used a (classical) linear stochastic process to describe the approach to equilibrium of the Ising model in a heat bath at beta β. The stochastic map represents the intrinsic dynamics of the system. It is easy to see that a linear process cannot in general describe the approach to equilibrium of an autonomous system. For, let T, a stochastic map, be such that $T^{*n}\rho_1 \to \rho_{\beta_1}$ and $T^{*n}\rho_2 \to \rho_{\beta_2}$ as $n \to \infty$, where ρ_β is the canonical state

$$\rho_\beta = e^{-\beta H}/\text{Tr}\, e^{-\beta H}$$

and $\beta_1 \neq \beta_2$.

Let $w_1, w_2 \geqslant 0$, $w_1 + w_2 = 1$, and let $\rho = w_1\rho_1 + w_2\rho_2$ be a mixture of ρ_1 and ρ_2. Then $T^{*n}\rho$ converges to a mixture of ρ_{β_1} and ρ_{β_2}, $w_1\rho_{\beta_1} + w_2\rho_{\beta_2}$, which is not a canonical state except in trivial cases. The linear model describes a system which ends up at β_1 with probability w_1 and at β_2 with probability w_2, rather than the physical mixture, which we hoped for.

A linear bistochastic process can describe the approach to the microcanonical state. For, suppose that the vectors of a Hilbert space $\mathscr{H}$, with $\dim \mathscr{H} = k < \infty$, describe the states of the system, each state having the same energy E. Let T be a bistochastic map on the Hilbert space of Hilbert–Schmidt such that 1 is a simple eigenvalue of TT^*. Then for any initial density matrix ρ, one can prove that $T^{*n}\rho \to (1/k)\, 1_k$.[7] This limit is the uniformly distributed state at energy E, also known as the microcanonical state.

Suppose now we have a system described by a Hamiltonian $H = \sum EP(E)$ with eigenvalues $E_0, E_1, \ldots$, each of finite multiplicity $k_0, k_1, \ldots$. Let T be an H-conserving bistochastic map. Then T^* conserves the mean energy of any state ρ with $\rho(H) < \infty$; for

$$T^*\rho(H) = \text{Tr}(T^*\rho H) = \text{Tr}(\rho TH) = \text{Tr}\left[\rho \sum ETP(E)\right]$$

$$= \text{Tr}\left[\rho \sum EP(E)\right] = \rho(H)$$

Regarded as a density matrix, $P(E_\alpha)/k_\alpha$ is the microcanonical state of energy E_α. The property $T^*P(E)=P(E)$ then means that the microcanonical states are fixed points of T^*, and so is any mixture $\sum_\alpha w_\alpha P(E_\alpha)$. Such states constitute the positive functions of H of unit trace, that is, they are the *ergodically mixed states.* Let us say that an H-conserving bistochastic map T is *ergodic* if the only fixed points of TT^* are erodically mixed. This is as much mixing as can be expected from an energy-conserving map. Since T^* cannot redistribute the probability among the energy shells, further stochasticity is needed, if any initial state is to converge to a canonical state.

In Boltzmann's work, further stochasticity is postulated, namely, the *Stosszahlansatz.* This requires that after two particles have been scattered, they reenter the population as independent particles. For a second-quantized model, we suggest that this is well-described by applying the quasifree projection Q after the map T^*. The projection Q is described as follows.[9] Let ρ be a density matrix for the CCR or CAR with finite second moments: $\rho(a_j^\# a_k^\#)$ is finite (this is automatic for the CAR). Then $Q\rho$ is the quasifree state with the same first and second moments as ρ. As shown in Ref. 9, Q is entropy-increasing, i.e., $s(Q\rho)\geqslant s(\rho)$.

The quasifree projection Q conserves the average of every quadratic function of the $a^\#$, and in particular a Hamiltonian of the form $H=\sum_k \omega_k a_k^* a_k$. We interpret Q as the extra stochasticity caused by elastic scattering, during the time between the collisions of the quanta themselves, from large random impurities, random walls, stray radiation, and degrees of freedom omitted from our description. The usual argument of Boltzmann, that the particle just scattering is unlikely (in three-dimensional space) to meet the same particle it has just met, and is more likely to meet a fresh, uncorrelated sample particle, loses some of its force in a theory with indistinguishable particles; on the other hand, the cluster properties of the scattering, as well as full rescattering corrections, are supposed to be described by T, so we avoid one of the criticisms.

We define the Boltzmann map by $\tau=QT^*$ and examine conditions under which $\tau^n\rho$ converges to a canonical state ρ_β as $n\to\infty$. For this, T must have some mixing properties; for example, $T=1$ is energy-conserving, but then $\tau^n=Q^n=Q$ does not work. It is easy to construct examples of ergodic T: let TT^* reduce the density matrix $[\rho]_{ij}$ in the energy basis to a diagonal matrix, where, on the subspace $\Gamma(E)$ of energy E, $TT^*\rho$ is $\mathrm{Tr}[P(E)\,\rho P(E)]/\dim\Gamma(E)$ times the identity on $\Gamma(E)$.

The proof of convergence is similar to that of Refs. 6 and 7. We use the increasing entropy to show that any convergent subsequence of $\tau^n\rho$ converges to a simultaneous eigenoperator of Q and TT^*, while preserving the mean energy. It turns out that in the case where the oscillator frequencies $\{\omega_k\}$ are mutually rational, then there is only one quasifree, ergodically mixed state of given energy, namely a canonical state ρ_β with β fixed by $\rho_\beta(H)=\rho(H)$. Hence all converging subsequences have the same limit, so the sequence itself converges, to ρ_β. The condition that the ratios ω_j/ω_k are rational is exactly the condition for instability or chaotic motion of a classical system of oscillators.[11] The chaotic motion is caused by the resonances among the oscillators when $m\omega_1 = n\omega_2$. The same mechanism is at work in the quantum case. If, however, all ratios are irrational, and no relation exists among the ω_k with integer coefficients, then the spectrum of H is simple, and no energy-conserving maps exist that mix the oscillators together. Thus, for example, the tensor product of Gibbs states σ_{β_1} and σ_{β_2} of two oscillators is quasifree and ergodically mixed, but is not a canonical state of the combined system if $\beta_1 \neq \beta_2$.

The reader might be puzzled about how a system of oscillators with a finite number of degrees of freedom, and a discrete energy with finite multiplicity, could possibly converge to thermodynamic equilibrium. The answer is that randomness is *put in by hand* in the choice of T and the application of Q, to describe the effects of the myriad of unknown degrees of freedom and their interactions. We do this because we sincerely believe in the use of probability in physics. Irreversibility is no more surprising than the damping of a classical oscillator obeying the equation

$$\ddot{x} + \gamma\dot{x} + \omega^2 x = 0$$

As an intermediate example between the rational and irrational cases, we give an example of three oscillators with mutually irrational energies obeying $\omega_1 + \omega_2 = 2\omega_3$; $T^n\rho$ converges to a product of independent Gibbs states of betas $\beta_1, \beta_2, \beta_3$, related by $\omega_1\beta_1 + \omega_2\beta_2 = 2\omega_3\beta_3$. We also work out an example of two fermions of the same frequency, and show that two particles with densities n_1 and n_2 approach equilibrium at an exponentially decreasing rate via a linear Markov chain. When we include two-particle scattering, a nonlinear model results.

The limitation of the theory to discrete time does not seem to be essential. It would be interesting to formulate these questions in a second-quantized version of Ref. 12.

2. PROOF OF CONVERGENCE

Let Γ be the Fock space (either boson or fermion) of the N oscillators with energies $\omega_1,..., \omega_N$, and let $H = \sum_{k=1}^{N} \omega_k a_k^* a_k$ be the Hamiltonian.

A quasifree state ρ of the CCR or CAR is determined by the complex parameters $\rho(a_j^\# a_K^\#)$ (see, e.g., Ref. 9). A state has average energy $\mathscr{E}$ if

$\rho(\sum_k \omega_k a_k^* a_k) = \mathscr{E}$; in such states the parameters run over a bounded set. This is because $\omega_k > 0$, so the positivity of ρ implies

$$\rho(a_k^* a_k) \leqslant \mathscr{E}/\min_k \omega_k$$

The Schwarz inequality then gives a similar bound on $\rho(a_j^* a_k^*)$.

Let $\tau = QT^*$, where Q is the quasifree map and T is bistochastic and conserves energy, as in Section 1. Then, for any initial state ρ of energy $\mathscr{E}$ the sequence $\{\tau^n \rho\}_{n=0,1,\ldots}$ lies in the ω^*-compact set of states, and also the parameters of the two-point functions lie in a compact set. Therefore, it has a W^* convergent subsequence whose two-point functions converge. To show that $\{\tau^n \rho\}$ itself converges, it is enough to show that every convergent subsequence has the same limit.

Lemma 1. Let T be bistochastic. Then $s(T^*\rho) > s(\rho)$ unless ρ is a fixed point of TT^*.

Proof. We proved (Ref. 7, Lemma 2.1) that

$$s(T^*\rho) - s(\rho) \geqslant \tfrac{1}{2}\langle \rho, (1 - TT^*)\, \rho \rangle_2$$

where $\langle A, B\rangle_2 = \mathrm{Tr}(A^* B)$. Also, $1 - TT^*$ is a positive superoperator, and so can be written as $x^* x$, say. Then, let $\rho = \rho_0 \oplus \rho^\perp$; ρ_0 is the component of ρ in the subspace of operators invariant under TT^*. Then

$$\begin{aligned} s(T^*\rho) - s(\rho) &\geqslant \tfrac{1}{2}\langle \rho_0 \oplus \rho^\perp, (1 - TT^*)(\rho_0 \oplus \rho^\perp)\rangle \\ &= \tfrac{1}{2}\langle \rho^\perp, (1 - TT^*)\, \rho^\perp \rangle \\ &= \tfrac{1}{2}\langle \rho^\perp, x^* x \rho^\perp \rangle = \tfrac{1}{2}\|x\rho^\perp\|^2 \end{aligned}$$

If this is zero, then $x\rho^\perp = 0$, so $x^* x \rho^\perp = 0$, so $(1 - TT^*)\, \rho^\perp = 0$, i.e., $\rho^\perp$ is invariant under TT^*, and so is zero. Hence $s(T^*\rho) > s(\rho)$ unless ρ is a fixed point of TT^*.

Lemma 2. Suppose T, T^* map each $P(E)$ to itself. Let ρ have average energy $\mathscr{E}$. Then the limit of any convergent subsequence of $\{\tau^n \rho\}_{n=0,1,\ldots}$ is a quasifree fixed point of TT^*.

Proof. All states $\tau^n \rho$ have energy $\mathscr{E}$, and so the limit has energy $\mathscr{E}$. Also, $s(T^*\rho) \geqslant s(\rho)$,[8] and $s(QT^*\rho) \geqslant S(T^*\rho)$.[9] Hence, the entropy of $\tau^n \rho$ is an increasing sequence, and being bounded (by the entropy of the canonical state ρ_β), converges as $n \to \infty$. Entropy is a continuous function on quasifree states of energy $\mathscr{E}$, since $\rho \log \rho$ is a continuous function of the (finitely many) parameters $\rho(a_j^{\#} a_k^{\#})$. Hence, if $\{\tau^{n_j}\rho\}_{j=1,2,\dots}$ is the convergent subsequence, we have

$$S(\rho_\infty) = S \lim_{j \to \infty} (\tau^{n_j}\rho) = \lim_{j \to \infty} S(\tau^{n_j}\rho) = \lim_{j \to \infty} S(\tau^n \rho) = S_\infty$$

say. Hence the limit of any convergent subsequence has the same entropy. Also, τ is a continuous function of the state parameters, so

$$S(\tau\rho_\infty) = S(\lim_{j \to \infty} \tau(\tau^{n_j}\rho)) = S_\infty$$

Now, $S(Q\rho) > S(\rho)$ unless ρ is quasifree.[9] Hence $T^*\rho_\infty$ is quasifree; and $S(\rho_\infty) = S(QT^*\rho_\infty) = S(T^*\rho_\infty)$. Hence, by Lemma 1, ρ_∞ is a fixed point of TT^*. It is quasifree, being the limit (in the sense of two-point functions) of quasifree states; this proves Lemma 2.

Lemma 3. Suppose the frequencies $\omega_1, \dots, \omega_N$ are such that the only quasifree, ergodically mixed states are canonical, i.e., of the form $\rho_\beta = e^{-\beta H}/\mathrm{Tr}\, e^{-\beta H}$ for some β. Suppose T conserves energy and is ergodic; then, for any state ρ of finite energy $\mathscr{E}$, $\tau^n \rho \to \rho\beta$, where β is determined from $\rho_\beta(H) = \mathscr{E}$.

Proof. By Lemma 2, any convergent subsequence of $\tau^n\rho$ converges to a quasifree, ergodically mixed state. By assumption, this will be a canonical state ρ_β. Since the sense of the convergence is in the topology given by the parameters of the two-point functions (as well as W^*), the energy of the limit state is $\mathscr{E}$, and so β is determined. Thus, all convergent subsequences have the same limit. Therefore $\tau^n \rho \to \rho_\beta$.

Theorem 1. Let $\omega_1, \dots, \omega_N > 0$ be mutually rational, and consider a bosonic system with Hamiltonian $\sum_{j=1}^N \omega_j a_j^* a_j$. Let T be ergodic and ρ a state of energy $\mathscr{E}$. Then $\tau^n \rho$ converges to the canonical state ρ_β of energy $\mathscr{E}$.

Proof. Let ρ_∞ be a limit point of $\tau^n \rho$. By Lemma 2, ρ_∞ is a quasifree fixed point of TT^*, with $\rho_\infty(H) = \mathscr{E}$, and since T is ergodic, ρ_∞, in the particle basis, is diagonal and is a multiple of the identity on each energy eigenspace. Thus $\rho_\infty(a_j^{\#} a_k^{\#}) = 0$ if $j \neq k$, so the oscillators are uncorrelated and, being quasifree, are independent. The restriction σ_k of ρ_∞ to the jth oscillator is stationary, so $\sigma_k(a_k a_k) = 0 = \sigma_k(a_k^* a_k^*)$. It is quasifree and so is determined by $\sigma_k(a_k^* a_k) = n_k$, say. It is therefore a canonical state, at β_k, say, for the Hamiltonian $H_k = \omega_k a_k^* a_k$, with β_k determined by

$$\mathrm{Tr}(a_k^* a_k e^{-\beta H_k})/\mathrm{Tr}(e^{-\beta H_k}) = n_k$$

Hence, $\rho_\infty = \sigma_{\beta_1} \otimes \cdots \otimes \sigma_{\beta_N}$.

Let integers n_1, n_2 be such that $n_1\omega_1 = n_2\omega_2$. Then the states with n_1 quanta ω_1 and n_2 quanta ω_2 (and no other quanta) have the same energy. The projectors onto these states therefore have the same weight in the density matrix of any ergodically mixed state. In ρ_β, these weights are

$$e^{-n_1\omega_1\beta_1} e^{-0\beta_2} \cdots e^{-0\beta_N} / Z_1 \cdots Z_N$$

and

$$e^{-0\beta_1} e^{-N_2\omega_2\beta_2} \cdots e^{-0\beta_N} / Z_1 \cdots Z_N$$

respectively (where Z_k is the partition function for one degree of freedom at beta β_k). Hence

$$-n_1\omega_1\beta_1 = -n_2\omega_2\beta_2, \qquad \text{i.e.,} \qquad \beta_1 = \beta_2$$

Similarly, $\beta_1 = \cdots = \beta_N = \beta_1$ and any quasifree, ergodically mixed state is ρ_β. Convergence follows from Lemma 3. This proves Theorem 1.

4. FURTHER EXAMPLES

An interesting possibility is where ω_j/ω_k is not rational, but where an integer relation $n_1\omega_1 + n_2\omega_2 + \cdots = n_3\omega_3 + \cdots$ holds with at least three terms. Then a quasifree stationary state must as usual be the product $\sigma_{\beta_1} \otimes \cdots \otimes \sigma_{\beta_3} \otimes \cdots$. However, now the Fock states $|n_1, n_2, 0,\ldots\rangle$ and $|0, 0, n_3 n\ldots\rangle$ have the same energy, and in any ergodically mixed state, must come in with the same weight. Hence

$$e^{-n_1\omega_1\beta_1} e^{-n_2\omega_2\beta_2} \cdots = e^{-n_3\omega_3\beta_3} \cdots$$

giving the equations

$$n_1\omega_1\beta_1 + n_2\omega_2\beta_2 + \cdots n_3\omega_3\beta_3 + \cdots$$

for each such relation among the ω's. The classical theory of systems[11] usually treats only the two cases where either all ω's are mutually rational (the chaotic case) or no rational relationship between any number of them holds (the stable case). It would be interesting to ask if the intermediate case, where ω_j/ω_k is irrational, but a relationship with integer coefficients holds among three or more ω's, has any significance for the stability theory of classical systems, such as the theory of gears with a real number of teeth.

We now consider the example with three degrees of freedom, with $\omega_1 = \pi - 3$, $\omega_2 = 4 - \pi$, $\omega_3 = \frac{1}{2}$; these obey $\omega_1 + \omega_2 = 2\omega_3$. Scattering maps T that conserve energy must convert quanta ω_1 and ω_2 into two quanta

ω_3, and so must conserve $N = N_1 + N_2 + N_3$, the total number operator. Let T be ergodic, mapping the spectral resolutions of N to themselves. Let $\tau = QT^*$. Then, for any ρ, each state $\tau^n \rho$ has the same energy and mean particle number. Any subsequence $\tau^{n_j} \rho$ converges to a quasifree, ergodically mixed state ρ_∞. Clearly, ρ_∞ has the same energy and particle number as ρ. To show that $\tau^n \rho$ converges, it is enough to show that there is only one such limit. In fact, ρ_∞ is stationary and quasifree, and so must be $\sigma_{\beta_1} \otimes \sigma_{\beta_2} \otimes \sigma_{\beta_3}$, with β_1, β_2 obeying

$$\omega_1 \beta_1 + \omega_2 \beta_2 = 2\omega_3 \beta_3$$

as ρ_∞ is ergodically mixed. This equation, together with the known values $\rho_\infty(H)$ and $\rho_\infty(N)$ determine β_1, β_2, and β_3. To see this, note that $H = H_1 + H_2 + H_3 = \omega_1 N_1 + \omega_2 N_2 + \omega_3 N_3$, so for any β, μ we have

$$\beta(H - \mu N) = (\beta - \beta\mu/\omega_1)\, H_1 + (\beta - \beta\mu/\omega_2)\, H_2 + (\beta - \beta\mu/\omega_3)\, H_3.$$

So, three β's obeying $\omega_1 \beta_1 + \omega_2 \beta_2 = 2\omega_3 \beta_3$ define β, μ by

$$\beta_k = \beta - \beta\mu/\omega_k$$

and then $\sigma_{\beta_1} \otimes \sigma_{\beta_2} \otimes \sigma_{\beta_3}$ is the grand canonical state $e^{-\beta(H - HN)}/\mathrm{Tr}\, e^{-\beta(H - HN)}$. This is well known to be determined by $\langle H \rangle$ and $\langle N \rangle$. In this model, $N_1 - N_2$ is concerved, too: the first and second quanta appear or disappear together. This is not an independent conservation law, but follows that of N and H.

In general, suppose we have a system of oscillators with energies $\omega_1, \ldots, \omega_N$, between which a certain number of integer relations hold. Then there are always enough conserved number-operators for suitable energy-conserving maps T so that the quasifree stationary states $\sigma_{\beta_1} \otimes \cdots \otimes \sigma_{\beta_N}$ can be identified with a grand canonical state

$$e^{-\beta(H - \mu_1 N_1 - \mu_2 N_2 - \cdots)}/Z$$

for which $\langle H \rangle$, $\langle N_1 \rangle$, $\langle N_2 \rangle, \ldots$, are determined by the initial state. In this way we prove the convergence of the Boltzmann map in the general case.

This difference between the rational and irrational cases, the first going to the canonical state and the second to the grand canonical state, arises because we have insisted on the *exact* conservation of energy. If ω_j/ω_k is irrational, and we allow a small violation of the law of energy conservation, then we can arrange mixing, but $\langle H \rangle$ is no longer exactly constant with time.

If $\omega_1, \ldots, \omega_N$ are mutually rational, but their ratios are rationals that in lowest terms involve large integers, then the mixing only takes place in states of high particle number. Thus, the state $\sigma_{\beta_1} \otimes \cdots \otimes \sigma_{\beta_N}$, while not ergodically mixed, is nearly so and is nearly a fixed point of τ even if $\beta_1 \neq \beta_2$, etc. Thus, there is not much physical difference between irrational ratios and rational ratios with large integers.

For fermions, the method of Theorem 1 no longer works, since one cannot have n fermions in the same state, $n > 1$. But if $n = m = 1$, the proof goes through, *mutatis mutandis*, if all ω_k are equal. Thus we have proved the following result.

Theorem 2. Let $\omega = \omega_1 = \cdots = \omega_N$ be the frequencies of N fermion oscillators. Let T be ergodic with respect to the Hamiltonian $H = \sum_k^N \omega a_k^* a_k$. Then $\tau^n \rho \to \rho_\beta$ for any ρ as $n \to \infty$.

Let us illustrate Theorem 2 with an example. Take $N = 2$, and use the basis in $\Lambda C^2 = C^4$ given by $|0\rangle$, $|1\rangle$, $|2\rangle$, and $|12\rangle$, where $|1\rangle = a_1^* |0\rangle$, etc. Then

$$H = \begin{pmatrix} 0 & & & \\ & 1 & & \\ & & 1 & \\ & & & 2 \end{pmatrix}$$

Let $T\rho$ be diagonal, of the form

$$T \begin{bmatrix} p_0 & & & \bullet \\ & p_1 & & \\ \bullet & & p_2 & \\ & & & p_3 \end{bmatrix} = \begin{bmatrix} p_0 & & & \bigcirc \\ & (1-\lambda) p_1 + \lambda p_2 & & \\ & \bigcirc & (1-\lambda) p_2 + \lambda p_1 & \\ & & & p_3 \end{bmatrix}$$
$$= \operatorname{diag}(p_0', p_1', p_2', p_3'), \qquad 0 < \lambda < 1$$

Then T is ergodic relative to H. The special form of T eliminates the correlations between the oscillators, since $T\rho$ has no terms like $|j\rangle\langle k|$ with $j \neq k$. If the initial state ρ is $\rho_{\beta_1} \otimes \rho_{\beta_2}$, then $\tau\varphi$ is $\rho_{\beta_1'} \otimes \rho_{\beta_2'}$, i.e., we can follow the motion of the system entirely in terms of the changes in the betas, which are related in a quasifree state to p_0, p_1, p_2, p_3 by $Z_j = (1 + e^{-\beta_j})$ and

$$p_0 = Z_1^{-1} Z_2^{-2}, \qquad p_1 = e^{-\beta_1} Z_1^{-1} Z_2^{-1}$$
$$p_2 = e^{-\beta_2} Z_1^{-1} Z_2^{-1}, \qquad p_3 = e^{-\beta_1 - \beta_2} Z_1^{-1} Z_2^{-1}$$

Note that $T^* \rho$ is not quasifree, since $p_1' p_2' \neq p_3' p_0'$ in general, which is needed for a diagonal matrix to be quasifree. Since the correlations in $T^* \rho$

are zero, $\rho'' = QT^*\rho$ is determined by $n_1' = \rho'(a_1^* a_1) = p_1' + p_3'$ and $n_2' = \rho'(a_2^* a_2) = p_2' + p_3'$. This gives the new betas

$$(1 + \beta_1'')^{-1} = p_1' + p_3', \qquad (1 + \beta_2'')^{-1} = p_2' + p_3'$$

which is consistent with (but not independent of) $p_0' + p_1' = Z_2''^{-1}$, $p_0' + p_2' = Z_1''^{-1}$, the marginal distributions. One easily derives the relations between the densities n_1, n_2 of a quasifree state and the p_k:

$$p_0 = (1 - n_1)(1 - n_2), \qquad p_1 = n_1(1 - n_2)$$
$$p_2 = n_2(1 - n_1), \qquad p_3 = n_1 n_2$$

The action of T is therefore

$$p_0' = (1 - n_1)(1 - n_2)$$
$$p_1' = n_1(1 - n_2)(1 - \lambda) + \lambda n_2(1 - n_1)$$
$$p_2' = n_2(1 - n_1)(1 - \lambda) + \lambda n_1(1 - n_2)$$
$$p_3' = p_3 = n_1 n_2$$

The new densities in terms of the old are therefore

$$n_1' = n_2(1 - n_1)(1 - \lambda) + \lambda n_2(1 - n_1) + n_1 n_2 = (1 - \lambda)\, n_1 + \lambda n_2$$
$$n_2' = n_2(1 - n_1)(1 - \lambda) + \lambda n_1(1 - n_2) + n_1 n_2 = \lambda n_1 + (1 - \lambda)\, n_2$$

This is a linear Markov chain, converging exponentially to the equilibrium point, $n_1 = n_2$, with $n_1 + n_2$ the conserved quality. The linearity arises because all the action is on the one-particle space.

Consider now the example of three fermions of the same frequency. In the particle basis, the states are $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$, $|12\rangle$, $|13\rangle$, $|23\rangle$, and $|123\rangle$. Suppose T causes exchange scattering $|12\rangle \leftrightarrow |13\rangle$, $|13\rangle \to |23\rangle$, etc., according to

$$p_{12}' = p_{12} + \lambda p_{13} + \lambda p_{23} - 2\lambda p_{12}$$
$$p_{13}' = p_{13} + \lambda p_{23} + \lambda p_{12} - 2\lambda p_{13}$$
$$p_{23}' = p_{23} + \lambda p_{12} + \lambda p_{13} - 2\lambda p_{23}$$

This is ergodic on the space of two particles. Suppose, again, that T reduces ρ to the diagonal in this basis. T is not ergodic, since TT^* leaves invariant any diagonal matrix in the space of one-particle states. Nevertheless, the only quasifree fixed point of TT^* is a Gibbs state, so by Lemma 2, $\tau^n \rho$ converges, since there is only one Gibbs state of that energy.

By a method similar to that in the previous example, we find for the number density $n_k = \rho(a_k^* a_k)$, $n'_k = \tau\rho(a_k^* a_k)$ the relations

$$n'_1 = n_1 - \lambda n_1 n_2 - \lambda n_1 n_3 + 2\lambda n_2 n_3$$

$$n'_2 = n_3 - \lambda n_2 n_3 - \lambda n_2 n_1 + 2\lambda n_2 n_3$$

$$n'_3 = n_3 - \lambda n_1 n_3 - \lambda n_2 n_3 + 2\lambda n_1 n_2$$

which converges, on iterating, to the unique limit (for fixed $n_1 + n_2 + n_3$), namely $n_1 = n_2 = n_3$.

For four fermions we obtain a simplified version of the usual fermionic Boltzmann equation, cubic in n, which we can guarantee converges to equilibrium. In the form derived by Hugenholtz, T is the Born approximation to the unitary scattering amplitude; it remains an unsolved problem to prove convergence to equilibrium in Hugenholtz's form. If we assume no intrinsic three-body scattering and a transition matrix T on the space of two particles of the form $T_{aa} = (1 - 5\lambda)$ for $a = |12\rangle, |13\rangle, \ldots, |34\rangle$ and $T_{ab} = \lambda$, $a \neq b$, we get for the densities the equation

$$n'_1 = n_1 - 3\lambda(n_1 n_2 + n_1 n_3 + n_1 n_4 - n_2 n_3 - n_2 n_4 - n_3 n_4$$
$$- n_1 n_2 n_3 - n_1 n_2 n_4 - n_1 n_3 n_4 + 3 n_2 n_3 n_4)$$

which converges to equilibrium. This is because T is ergodic on the two-particle subspace (of projections onto ($|12\rangle$, $|13\rangle$, etc.) and the only quasifree states that are constant on this space are canonical. We can understand this equation: $-\lambda$ is the rate of scattering out of occupied states.

Finally, if we have four fermions of energies $\omega_1, \omega_2, \omega_3, \omega_4$, which exchange scatter by the process $1 + 2 \leftrightarrow 3 + 4$ with rate λ, then we obtain the usual rate equation[13] by the same method:

$$\frac{dn_j}{dt}(t) = \lambda[n_1 n_2(1 - n_3)(1 - n_4) - (1 - n_1)(1 - n_2) n_3 n_4], \qquad j = 3, 4$$

Please note that whereas the *Stosszahlansatz* (= hypothesis of molecular chaos) is often regarded as a further approximation, we see it here as a *necessary* ingredient if the system is to converge to equilibrium.

To get the usual rate equation if bosons are present, we must take note of the fact that a realistic scattering matrix must satisfy clustering; so, together with a process like fermion (1) → fermion (2) + boson at a certain rate, we must include any number of spectator bosons, as in the process fermion (1) + n bosons → fermion (2) + (n + 1) bosons with the same rate for each "Feynman" diagram. If T fails to satisfy clustering, then we will not get the usual boson rate equation as given in Ref. 13.

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