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Gibbs and Poincaré Statistical Equilibria in Systems with Slowly Varying Parameters

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1. STATISTICAL EQUILIBRIUM

The main object of study is an ideal gas as a collision-free solid medium in a vessel that has the shape of the right parallelepiped

$$\Pi_n = \{z_1, z_2, \ldots, z_n: 0 \le z_k \le l_k; 1 \le k \le n\}.$$

Of special interest is, of course, the case where $n = 3$. However, the theory developed in this paper does not depend on the dimension n. "Collision-free" means that the particles do not collide: they move uniformly and rectilinearly and are elastically reflected by the boundary of the vessel Π. We assume that the set of particles forms a continuum. More precisely, the gas particles are distributed in space according to velocities, and the density of such a distribution is a measurable summable function.

For the first time, this model problem was considered by Poincaré in [1]. *A propos*, for $n = 1$, the Poincaré model precisely corresponds to the common idea of a gas as a large number of small identical balls elastically colliding with each other. The point is that, under an elastic collision of identical balls moving along one straight line, a mere interchange of their rates occurs.

There is a different point of view, which goes back to Gibbs. Consider a simple dynamical system, namely, a particle in the parallelepiped Π which is elastically reflected by the boundary $\partial\Pi$. The initial position and velocity of the particle can be specified with an error distributed according to a certain law. In other words, the state of such a system is a random event. The corresponding probability distribution density evolves in time and satisfies the classical Liouville equation, which can be regarded as a continuity equation in the Poincaré model.

The fundamental observation of Poincaré is that, independently of the initial distribution, as $t \to \pm\infty$, a collision-free gas irreversibly tends to uniformly fill the entire volume of a rectangular box with mirror walls. A precise formulation of this remarkable result and its proof are given in [2] (see also [3]).

From a more general point of view, this observation of Poincaré fits into a general concept related to weak convergence of probability measures and statistical (thermal) equilibrium of Hamiltonian dynamical systems.

Let $z = (z_1, z_2, \ldots, z_n)$ be the position of a point moving at velocity $v = (v_1, v_2, \ldots, v_n)$. The set of states (z, v), where $z \in \Pi^n$ and $v \in \mathbb{R}^n$, is the phase space Γ. Next, let $\rho(z, v)$ be the density of the initial distribution of the gas. It can be assumed that $\rho \in L_1(\Gamma)$, although, in some cases, it is more convenient to assume that $\rho \in L_p(\Gamma)$, where $1 \le p < \infty$. The initial density of the distribution ρ is transferred by the phase flow and becomes a function of time t: $\rho_t(z, v)$. It satisfies the Liouville equation and is uniquely determined by the initial condition $\rho_0 = \rho$.

We say that ρ_t weakly converges to a function $\bar{\rho}$ if, as $t \to \infty$,

$$\int_\Gamma \rho_t \varphi \, d^n z \, d^n v \to \int_\Gamma \bar{\rho} \varphi \, d^n z \, d^n v \tag{1}$$

for any function $\varphi \in L_q(\Gamma)$, where $\frac{1}{p} + \frac{1}{q} = 1$. The case of $p = 1$ corresponds to $q = \infty$. Recall that the class L_∞ is formed by the measurable essentially bounded functions. The function $\bar{\rho}(z, v)$ belongs to $L_p(\Gamma)$, is a first integral of the system under consideration, is nonnegative, and satisfies (as well as ρ) the natural normalization condition

$$\int_\Gamma \bar{\rho} \, d^n z \, d^n v = 1.$$

It can be represented as the Birkhoff mean

$$\bar{\rho}(z_0, v_0) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \rho(z(t, z_0, v_0), v(t, z_0, v_0)) dt,$$

where z and v as functions of time are solutions to the equations of motion with the initial conditions z_0 and v_0. These results are also valid in the more general case,

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when the parallelepiped Π is replaced by an arbitrary domain in $\mathbb{R}^n$ with a piecewise-regular boundary (see [3, 4]).

It is natural to treat the function $\bar{\rho}$ as the distribution density in the state of statistical (thermal) equilibrium of the system. In the problem under consideration, $\bar{\rho}$ depends only on the squared velocities v_1^2, v_2^2, …, v_n^2. Such distributions generate an equation of state of the type of the Clapeyron–Mendeleev equation (see [2, 3, 5]).

Now, let us slowly change the size of the parallelepiped Π assuming that the edge lengths l_s are smooth functions of the "slow" time variable $\tau = \varepsilon t$, where ε is a small parameter. At $\varepsilon = 0$, the size of the vessel does not vary. In thermodynamics, it is assumed that an infinitely slow change of parameters leads to a reversible quasi-static process, when the state of the system can be considered virtually equilibrium at each moment of time. We shall try to rigorously substantiate this conjecture for the model system under consideration on the basis of the theory of adiabatic invariants. More precisely, we shall considered the following two problems:

(i) Can a collision-free gas attain a state close to a statistical equilibrium if the parameters vary slowly and time t is sufficiently large $\left(\sim\frac{1}{\varepsilon}\right)$?

(ii) Suppose that, at the initial moment of time $t = 0$, a collision-free gas is already in a state of statistical equilibrium and, at $t \geq 0$, the walls of the vessel start to move slowly and smoothly. Will the gas remain virtually in a state of statistical equilibrium at succeeding moments of time, and how long can such a process be considered quasi-static?

We start with a consideration of the second problem.

2. QUASI-STATIC STATES

Suppose that the side lengths $l_1, l_2, \ldots, l_n$ of the parallelepiped are smooth functions of εt and ρ is the initial probability distribution density. Then the density ρ_t at time t depends on ε (in addition to the phase variables z and v). We assume that the product $l_1, l_2, \ldots, l_n$ (the volume of Π) is bounded and nowhere vanishes.

Theorem 1. *If a density* $\rho \in L_p(\Gamma)$ *depends only on* $v_1^2, v_2^2, \ldots, v_n^2$, *then there exists a probability measure*

$$\nu_t(v_1^2, v_2^2, \ldots, v_n^2, \varepsilon)d^n z d^n v,$$

$$\nu_t \in L_p, \quad \nu_0 = \rho,$$

such that, for any $\varphi \in L_q(\Gamma)$ *and any* $t \in \left[0, \frac{c}{\varepsilon}\right]$ (*where c is a constant*),

$$\left|\int_\Gamma \rho_t \varphi d^n z d^n v - \int_\Gamma \nu_t \varphi d^n z d^n v\right| \to 0, \tag{2}$$

as $\varepsilon \to 0$.

According to the considerations of Section 1, the function ν_t can be treated as a stationary probability distribution density at time t: the mean values of the dynamical quantities are evaluated by the same rule as on the right-hand side of (1). For example, suppose that $p = 1$ and φ is the characteristic function of a measurable domain $\Phi \subset \Pi$. Then, according to (2), the integral

$$\int_\Gamma \rho_t \varphi d^n z d^n v \tag{3}$$

at small ε is arbitrarily close to the ratio $\frac{\text{mes}\Phi}{\text{mes}\Pi}$. The value of integral (3) coincides with the fraction of the particles from the Gibbs ensemble that are in the domain Φ at time t. Therefore, if ε is small, then the collision-free gas will remain virtually uniformly distributed over the volume of the vessel during a sufficiently long time interval $\left(\sim\frac{1}{\varepsilon}\right)$.

To prove Theorem 1, we set

$$\nu_t(v_1^2, v_2^2, \ldots, v_n^2, \varepsilon) = \rho\left(\frac{v_1^2 l_1^2}{l_1^2(0)}, \frac{v_2^2 l_2^2}{l_2^2(0)}, \ldots, \frac{v_n^2 l_n^2}{l_n^2(0)}\right). \tag{4}$$

Clearly, $\nu_t \in L_p$ (if $\rho \in L_p$), $\nu_0 = \rho$, and

$$\int_\Gamma \nu_t(v^2, \varepsilon)d^n z d^n v = 1$$

at all values of t. What does the solution ρ_t to the Liouville equation with Cauchy data ρ look like? To answer this question, we must invert the general solution

$$z = z(t, z_0, v_0), \quad v = v(t, z_0, v_0)$$

to the equations of a particle and substitute the resulting formula for $v_0 = v(0)$ into the expression for $\rho(v_1^2(0), v_2^2(0), \ldots, v_n^2(0))$. Thus, $\rho_t(z, v) = \rho(v_0^2)$. On the other hand, the products $v_k^2 l_k^2$ are adiabatic invariants [6], i.e.,

$$\left|v_k^2(t)l_k^2(\varepsilon t) - v_k^2(0)l_k^2(0)\right| \leq c\varepsilon$$

for $0 \leq t \leq \frac{1}{\varepsilon}$ ($c = \text{const} > 0$). Therefore, $v_k^2(0) = \frac{v_k^2 l_k^2}{l_k^2(0)} +$

$O(\varepsilon)$ and

$$\rho_t = \rho\left(\frac{v_1^2 l_1^2}{l_1^2(0)} + O(\varepsilon), \frac{v_2^2 l_2^2}{l_2^2(0)} + O(\varepsilon), \dots, \frac{v_n^2 l_n^2}{l_n^2(0)} + O(\varepsilon)\right). \quad (5)$$

Comparing (4) and (5), we can derive the required relation (2).

As is well known [1], the Gibbs entropy is always constant:

$$S_t = -\int_\Gamma \rho_t \ln\rho_t d^n z d^n v = \text{const}. \quad (6)$$

Interestingly, the entropy of quasi-static states

$$\bar{S}_t = -\int_\Gamma \nu_t \ln\nu_t d^n z d^n v \quad (7)$$

does not change with time either. Thus, the quasi-static process under consideration is adiabatic. It is interesting to compare this observation with the result that, under an irreversible extension of a collision-free gas, the entropy increases: we replace the density ρ_t in expression (6) by its weak limit $\bar{\rho}$, then, as a rule, the entropy will increase [2].

As opposed to entropy, the internal energy e of an ideal gas (which is proportional to the absolute temperature τ) may change under adiabatic processes. We set

$$e(t) = \int_\Gamma \frac{v^2}{2}\rho_t d^n z d^n v \quad (8)$$

(assuming that this integral converges). Consider the case where $n = 3$ and $l_1 = l_2 = l_3 = l$ (the vessel has the shape of a cube). By Theorem 1, when the walls of the vessel slowly move, integral (8) differs little from the integral

$$\bar{e}(t) = \int_\Gamma \frac{v^2}{2}\nu_t d^n z d^n v = \frac{w_0^{2/3}}{w^{2/3}}\bar{e}_0, \quad \bar{e}_0 = \bar{e}(0), \quad (9)$$

where w is the volume of the vessel Π. Formula (8) is easily derived with the use of (4). Since $e = c\tau$ (c = const), (9) implies the well-known equation of an adiabatic curve for an ideal one-atom gas:

$$\tau w^{2/3} = \text{const}. \quad (10)$$

3. APPROACHING OF A STATISTICAL EQUILIBRIUM

Now, let us discuss the first problem concerning the "zeroth" law of thermodynamics under slowly varying boundary conditions. Suppose that $\rho \in L_p(\Gamma)$ and $\varphi \in L_q(\Gamma)$ is a test function. More precisely, we assume that φ is a function of $\frac{z_1}{l_1}, \frac{z_2}{l_2}, \dots, \frac{z_n}{l_n}, l_1 v_1, l_1 v_2, \dots, l_n v_n$, which belongs to L_q at each value of t. We set

$$K(t) = \int_\Gamma \rho_t \varphi d^n z d^n v.$$

Theorem 2. *If l_s are smooth functions of εt, then there exists a function $\bar{\rho}(l_1^2 v_1^2, l_2^2 v_2^2, \dots, l_n^2 v_n^2)$ such that*

$$\lim_{\varepsilon \to 0} K\left(\frac{c}{\varepsilon}\right) = \int_\Gamma \bar{\rho}\varphi d^n z d^n v, \quad c = \text{const} \neq 0. \quad (11)$$

For example, suppose that $p = 1$ and φ is the characteristic function of a measurable domain $\Phi_t \subset \Pi$. This domain slowly varies, similarly to a deformation of the ambient parallelepiped Π. Theorem 2 asserts that, for small values of ε (independently of the initial distribution), the fraction of collision-free gas located in the domain Φ_t will become virtually equal to the fraction of this domain in the parallelepiped Π at a sufficiently large time $\left(\sim\frac{1}{\varepsilon}\right)$ [see (11)]. For example, if Π is divided into two equal parts by a wall, then, in time $\sim\frac{1}{\varepsilon}$, the gas will become distributed virtually equally between these domains.

If the function $\bar{\rho}$ is taken for the initial distribution density, then, during a large time interval $\left(\sim\frac{1}{\varepsilon}\right)$, the collision-free gas virtually remains in a state of static equilibrium (Theorem 1).

Theorem 2 is proved with the use of regularization (passage to a 2^n-fold covering of Π by an n-torus), the methods of [2], and the theory of adiabatic invariants.

4. SCATTERING BILLIARDS

A statistical equilibrium of a collision-free gas takes place inside an arbitrary closed vessel with piecewise-regular surface. Any initial distribution with density $\rho \in L_p$ generates a solution ρ_t to the Liouville equation, and this solution weakly converges to some function $\bar{\rho} \in L_p$. This function is the Birkhoff mean of ρ, is invariant with respect to the phase flow of the dynamical system with collisions under consideration, and has the meaning of a stationary probability distribution density (see [3, 4]).

This result suggests a generalization of problems 1 and 2 from Section 1 to domains of arbitrary shapes. Suppose that the boundary of a vessel is changed very slowly and smoothly. Will a collision-free gas manifest quasi-static behavior? Analyzing this situation in the general case requires developing the theory of adiabatic invariants. This theory was created for two extreme cases: when completely integrable systems are perturbed and when the nonperturbed system is ergodic on almost all level surfaces of the energy integral (see [6]). The former case occurs precisely when Theorems 1 and 2 apply. The second case is covered by a well-known theorem of Kasuga [7].

Now, suppose that the vessel $\Pi \subset \mathbb{R}^n$ is bounded by a piecewise-smooth surface strictly convex inside Π. A particle moving by inertia inside Π and elastically reflected by the boundary generates a dynamical system, which is called a scattering billiard (or a Sinai billiard). This system is certainly ergodic at the positive values of the particle energy h [8, 9]. The weak limit of the solution to the Liouville equation with Cauchy data $\rho \in L_p$ is a function $\bar{\rho} \in L_p$ depending only on the energy h.

Now, suppose that the shape of the vessel depends on a parameter, which, in its turn, smoothly depends on the slow time variable εt, where ε is a small parameter. In particular, the volume w of the vessel Π also smoothly depends on εt.

Theorem 3. *If the initial density* ρ *depends only on the energy* $h = \dfrac{(v_1^2 + v_2^2 + \ldots + v_n^2)}{2}$, *then the probability measure*

$$\nu_t d^n z d^n v = \rho\left(h\frac{w^\alpha}{w_0^\alpha}\right) d^n x d^n v, \quad \alpha = \frac{2}{n}, \quad w_0 = w(0),$$

determines a quasi-static invertible process, i.e.,

(i) (2) *holds*;

(ii) *entropy* (7) *is constant*;

(iii) *equation* (10) *of an adiabatic curve is valid* (*for* $n = 3$).

The proof of Theorem 3 is similar to that of Theorem 1. An important role is played by the Kasuga theorem that an adiabatic invariant is the volume of the phase space enclosed inside an isoenergy hypersurface [7] (the results of [7] should be somewhat modified, because they refer to smooth, Hamiltonian systems). It is easy to understand that this volume is proportional to the product $h^{n/2}w$.

The Kasuga theorem (after an appropriate modification) makes it possible to give a positive answer to problems 1 and 2 as applied to a "real" Boltzmann–Gibbs gas contained in a rectangular box with mirror walls. This gas is a large set of small identical balls which elastically collide with each other and with the walls of the box. If the box's size does not vary with time, then, independently of the initial distribution of these balls with respect to the spatial coordinates and velocities, the Boltzmann–Gibbs gas irreversibly tends to a state of statistical (thermal) equilibrium. According to [8], the billiard system under consideration is ergodic on the energy surfaces. In particular, in a state of statistical equilibrium, all possible positions of balls in a rectangular vessel are equiprobable (the limit density $\bar{\rho}$ depends only on the energy of the system).

Now, let us move one of the box walls slowly and smoothly. If the Boltzmann–Gibbs gas was in a state of statistical equilibrium, then the state of the gas will differ little from the corresponding equilibrium state in a sufficiently large time interval. If the state of the gas was not a statistical equilibrium, then the gas will attain a state close to a state of statistical equilibrium in a sufficiently large (but finite) time.

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