Boltzmann's Statistical Mechanics

Saig Summer School : The Nature of Entropy I - From Thermodynamics to Black Holes

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Can “Irreversible macroscopic laws” be deduced from or “reduced to” “Reversible microscopic laws”?

(definitions later)

Brief answer (goal of this talk) :

Yes, but in a certain sense, to be made precise.

The basic idea goes back to Boltzmann, but there are also many pseudo-solutions, confused answers etc.

Very little is on firm mathematical grounds

Consider classical mechanics.
Given $\mathbf{x}(t) = (\mathbf{q}(t), \mathbf{p}(t))$
for a (closed) mechanical system,
q = the positions of the particles
p = the momenta of the particles,
then "everything" follows.
In particular, macroscopic quantities, like the density or the energy density, are functions of **x**.

Simple example of macroscopic equation : diffusion

$$\frac{d}{dt}u = \Delta u$$

$u = u(x,t), x \in \mathbb{R}^3$.

Let u = density (or energy density).

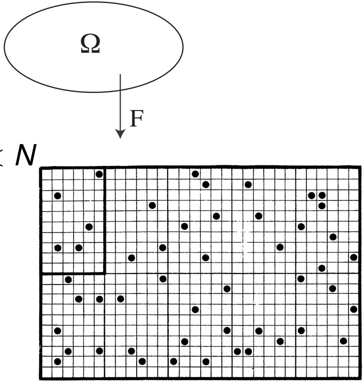
u = example of ‘macroscopic’ variable.

Same idea with Navier-Stokes, Boltzmann...

$u(x,t) \to$ constant as $t \to \infty$

Ω = “BiG” PHASE SPACE $\subset \mathbb{R}^{6N}$
$N \sim$ AVOGADRO

$n << N$
Ex :



n CELLS

$F(\mathbf{x})$ = $(F_1(\mathbf{x}), ...; F_n(\mathbf{x})) \in \mathbb{R}^n =$ fraction of particles in each cell
$U(x)$ in diffusion equation is a continuous approximation to F.

Simple example
Coin tossing

$\mathbf{x} \rightarrow (H, T, T, H...)$
2^N possible values

$F(\mathbf{x})$ = Number of heads or tails
= $N + 1$ possible values
$N + 1 << 2^N$.

$$\begin{array}{lcl} \mathbf{x}(0) \to \mathbf{x}(t) = T^t\mathbf{x}(0) & & \text{Hamilton} \\ \downarrow \qquad\quad \downarrow & & \\ F_0 \;\; \to \;\; F_t & & \end{array}$$

Is the evolution of F

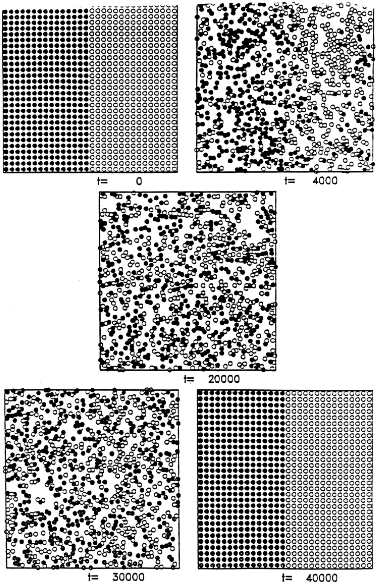
AUTONOMOUS, i.e. independent of the $\mathbf{x}$ mapped onto F ?

$\mathbf{x}(0) \to \mathbf{x}(t)$
Reversible : $\mathrm{I}T^t\,\mathrm{I}\,\mathbf{x}(t) = \mathbf{x}(0)$
$\mathrm{I}(\mathbf{q},\mathbf{p}) = (\mathbf{q},-\mathbf{p})$

But $F_0 \to F_t$ often irreversible, as in the example of diffusion.

$F_t \to$ UNIFORM DISTRIBUTION (in $\mathbb{R}^3$!) There is no I operation that leaves the diffusion equation invariant.

Besides, the evolution of F is NOT autonomous !



Time evolution of a system of 900 particles all interacting via the same potential. Half of the particles are colored white, the other half black. All velocities are reversed at $t = 20,000$. The system then retraces its path and the initial state is fully recovered. But at $t = 20,000$, the density is uniform both for the configuration obtained at that time and for the one with the reversed velocities.

ANOTHER PROBLEM : POINCARÉ'S RECURRENCES
Let $A \subset \Omega \subset \mathbb{R}^{6N}$ be a set of positive Lebesgue measure (for example, an open set, but as small as you wish).
Then, for almost all $\mathbf{x}(0) \in A$,
there exists a sequence of times $t_i \to \infty$, such that
$\mathbf{x}(t_i) = T^{t_i}\mathbf{x}(0) \in A$.
INFINITE RETURN.
SO, MATHEMATICALLY SPEAKING, NO CONVERGENCE TO EQUILIBRIUM.

The evolution of the macroscopic variable CANNOT be autonomous. PARADOX ?

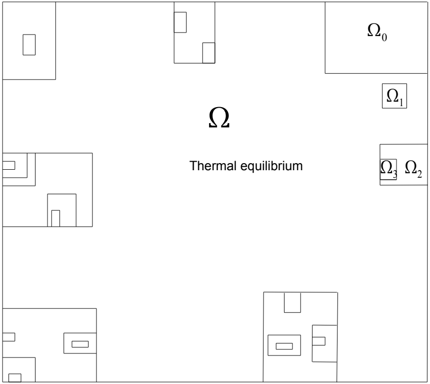
Basis of the **Solution**

The map F is many to one in a way that depends on value taken by F.

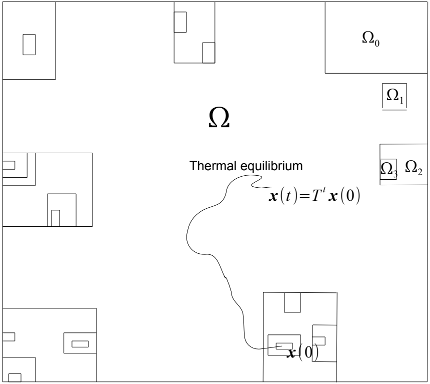
Think of coin tossing

$F = N \rightarrow$ one 'configuration'

$F = \frac{N}{2} \rightarrow \simeq \frac{2^N}{\sqrt{N}}$ 'configurations'



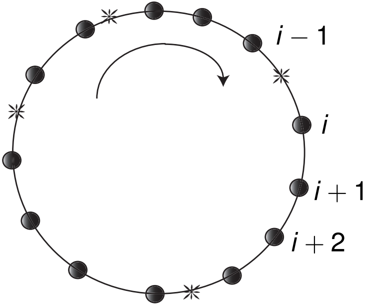
A partition of the phase space Ω (represented by the entire square) into regions $\Omega_0, \Omega_1, \Omega_2, \ldots$ corresponding to microstates that are macroscopically indistinguishable from one another, i.e. that give rise to the same value of F (e.g. $F(\Omega_0) = F_0$, $F(\Omega_1) = F_1$ etc.). The region labelled "thermal equilibrium" corresponds to the value of F corresponding to the overwhelming majority of microstates.



The curve $\mathbf{x}(t) = T^t\mathbf{x}(0)$ describes a possible evolution of a microstate, which tends to enter regions of larger volume until it enters the region of thermal equilibrium.

CONSIDER A CONCRETE EXAMPLE

THE KAC RING MODEL



N points

1 particle at each point

"SIGN"

$\eta_i(t) = +1$

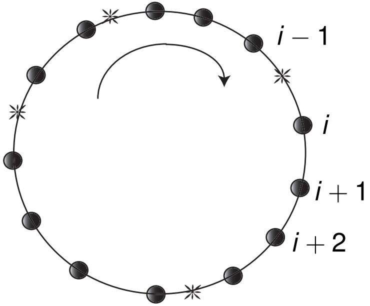
$\eta_i(t) = -1$

M CROSSES

= "scatterers"

$\varepsilon_{i-1} = -1$

$\varepsilon_i = +1$



Dynamics – TURN
– CHANGE SIGN
when particle goes through a cross.

So, e.g.

$$\eta_i(t+1) = -\eta_{i-1}(t)$$

$$\eta_{i+1}(t+2) = \eta_i(t+1)$$

$$\eta_i(t) = \eta_{i-1}(t-1)\varepsilon_{i-1}$$

= NEWTON'S EQUATION

– DETERMINISTIC

– ISOLATED

– REVERSIBLE : IF, AFTER TIME t, PARTICLES START TO MOVE BACKWARD, THEY GO BACK TO THE INITIAL STATE IN TIME t.

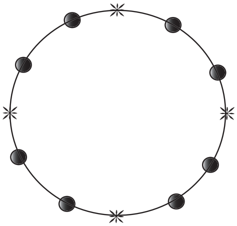
– EVERY CONFIGURATION IS PERIODIC OF PERIOD $2N << 2^N = \#$ STATES
(THIS IS MUCH STRONGER THAN POINCARE'S RECURRENCES).

CONVERGENCE TO EQUILIBRIUM ?

$N_+ = N - N_-$ <u>MACROSCOPIC VARIABLES</u>

$$N_+ = N_- = \frac{N}{2} \text{ = EQUILIBRIUM}$$

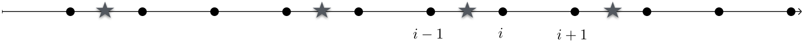
START WITH $N_+(0) = N$



CONFIGURATION OF PERIOD 4

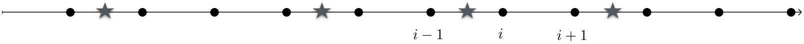
NO CONVERGENCE TO EQUILIBRIUM
$\longrightarrow$ Convergence to equilibrium CANNOT hold for all initial conditions, i.e. for all distributions of crosses.

We can have the same model but on the line $\mathbb{Z}$: at each site $i \in \mathbb{Z}$ there is a particle with a sign $\eta_i(t) = \pm 1$ and a scatterer $\varepsilon_i = \pm 1$.
The values of the scatterers are fixed once and for all and are "random" (e.g. with a Bernoulli distribution).



So, here $\varepsilon_{i-1} = -1$, $\varepsilon_i = +1$.

Dynamics : EACH PARTICLE MOVES TO THE RIGHT AND CHANGES SIGN WHEN THE PARTICLE GOES THROUGH A CROSS.



Since

$\varepsilon_{i-1} = -1$, $\varepsilon_i = +1$, we have :

$$\eta_i(t+1) \quad = -\eta_{i-1}(t)$$

$$\eta_{i+1}(t+2) = \eta_i(t+1)$$

The time evolution is as before :

$$\eta_i(t) = \eta_{i-1}(t-1)\varepsilon_{i-1}.$$

The natural macroscopic variable is :

$$M(t) \equiv \frac{1}{2N+1}\sum_{i=-N}^{N}\eta_i(t).$$

DOES THAT CONVERGE TO A GIVEN TIME EVOLUTION AS $N \to \infty$ INDEPENDENTLY OF THE INITIAL CONFIGURATION $\{\eta_i(0)\}_{i\in\mathbb{Z}}$?

CONSIDER THE RING MODEL FIRST :

1. BOLTZMANN's EQUATION

$$N_+(t+1) = N_+(t) - N_+(S,t) + N_-(S,t)$$
$$N_-(t+1) = N_-(t) - N_-(S,t) + N_+(S,t)$$

WHERE $N_+(S,t)$ DENOTES THE NUMBER OF $+$ SIGNS THAT HAVE A CROSS (OR SCATTERER) AHEAD OF THEM (AND, THUS WILL CHANGE SIGN AT THE NEXT TIME STEP). $N_-(S,t)$ IS SIMILAR.

ASSUME

$$N_+(S,t) = \frac{M}{N} N_+(t)$$
$$N_-(S,t) = \frac{M}{N} N_-(t)$$

$\longleftrightarrow$ HYPOTHESIS OF MOLECULAR CHAOS : " SIGN UNCORRELATED WITH CROSSES "

$$\Rightarrow \Big(N_+(t+1) - N_-(t+1)\Big)$$

$$= \left(1 - \frac{2M}{N}\right)\Big(N_+(t) - N_-(t)\Big)$$

$$\Rightarrow \frac{1}{N}\Big(N_+(t) - N_-(t)\Big) = \left(1 - \frac{2M}{N}\right)^t = <\varepsilon>^t$$

Since

$N_+(0) = N \qquad N_-(0) = 0$

and

$$<\varepsilon> = \left(1 - \frac{2M}{N}\right).$$

(We may assume $\frac{M}{N} < 1/2$).

$\Rightarrow$ EQUILIBRIUM !

BOLTZMANN'S ENTROPY, BY DEFINITION, IS THE LOGARITHM OF THE NUMBER OF MICROSTATES CORRESPONDING TO A GIVEN MACROSTATE

$$S_B(t) = \ln \begin{pmatrix} N \\ N + -(t) \end{pmatrix} = \ln \left(\frac{N!}{N_+(t)!N_-(t)!} \right)$$

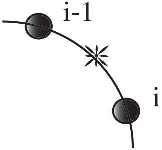
IS MAXIMUM for $N_- = N_+ = \frac{N}{2}$ AND IS THEN APPROXIMATELY EQUAL TO $N \ln 2$.

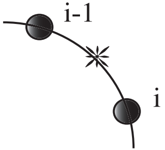
BOLTZMANN'S ENTROPY IS MAXIMAL AT EQUILIBRIUM

MICROSCOPIC THEORY

1. Eq. of MOTION

$$\eta_i(t) = \eta_{i-1}(t-1)\varepsilon_{i-1}$$





$\Rightarrow$ SOLUTION

$$\eta_i(t) = \eta_{i-t}(0)\varepsilon_{i-1}\varepsilon_{i-2}\ldots\varepsilon_{i-t} \quad \text{MOD } N$$

BUT MACROSCOPIC VARIABLES
= FUNCTIONS OF THE MICROSCOPIC ONES

$$\frac{1}{N}(N_+(t) - N_-(t))$$

$$= \frac{1}{N}\sum_{i=1}^{N} \eta_i(t)$$

$$= \frac{1}{N}\sum_{i=1}^{N} \eta_{i-t}(0)\varepsilon_{i-1}\varepsilon_{i-2}\ldots\varepsilon_{i-t}$$

IF we look at $t = 2N$: PROBLEM (PERIODICITY)

TAKE $t << N$, e.g. $t = 10^6$. $N \sim 10^{23}$.

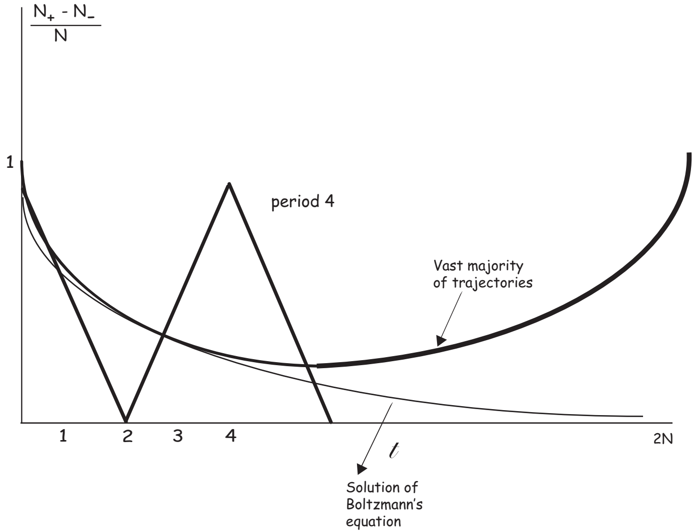
Then, one can show, by the law of large numbers, that, for the overwhelming majority of microscopic initial configurations, i.e. of distributions of crosses,

$$\frac{1}{N}\Big(N_+(t) - N_-(t)\Big) \approx \left(1 - \frac{2M}{N}\right)^t = < \varepsilon >^t,$$

i.e. the macrostate follows the solution of the Boltzmann approximation. So, the microstate does, in the overwhelming majority of cases, move towards larger regions of phase space.

In Kac's model : $S_B(t) = \ln \begin{pmatrix} N \\ N_-(t) \end{pmatrix} = \ln \begin{pmatrix} N \\ N_+(t) \end{pmatrix}$.

$S_0 = 0$, $S_t \to N \ln 2$ as t increases (not too much).



$\frac{N_+ - N_-}{N}$
1
period 4
Vast majority of trajectories
1
2
3
4
2N
t
Solution of Boltzmann's equation

For the model on the line, again by the strong law of large numbers, one can show that, with

$$M(t) = \frac{1}{2N+1} \sum_{i=-N}^{N} \eta_i(t)$$

$$\lim_{N\to\infty} M(t) =< \varepsilon >^t \lim_{N\to\infty} M(0) =< \varepsilon >^t m$$

almost surely with respect to the product of Bernoulli measures with average m for the η variables (signs) and average $< \varepsilon >$ for the ε variables (crosses).
This means that

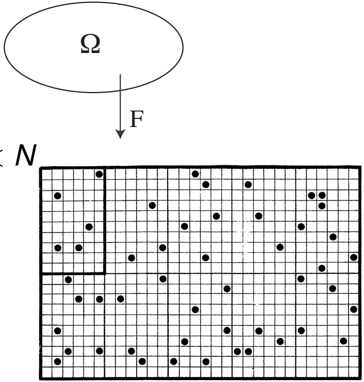
$$\lim_{t\to\infty} \lim_{N\to\infty} M(t) = 0,$$

i.e. convergence to equilibrium (BUT NOT if we inverse the limits !).

GOING BACK TO THE GENERAL SITUATION

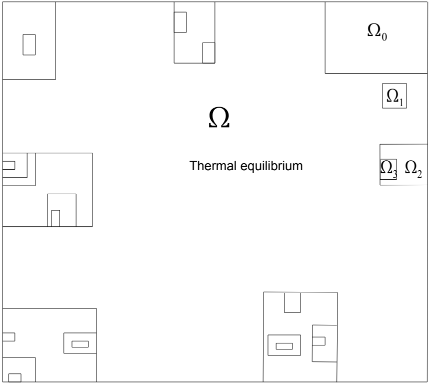
Ω = "BiG" PHASE SPACE $\subset \mathbb{R}^{6N}$
$N \sim$ AVOGADRO

$n << N$
Ex :

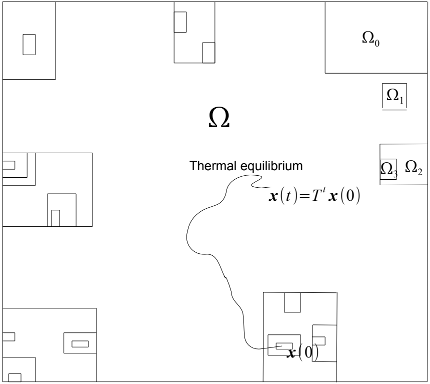


n CELLS

$F(\mathbf{x})$ = $(F_1(\mathbf{x}), ...; F_n(\mathbf{x})) \in \mathbb{R}^n =$ fraction of particles in each cell
$U(x)$ in diffusion equation is a continuous approximation to F.



Ω_0
Ω_1
Ω
Thermal equilibrium
Ω_3 Ω_2



As time evolves, the phase-space point enters compartments of larger and larger volume.

Solution to the reversibility paradox, in general

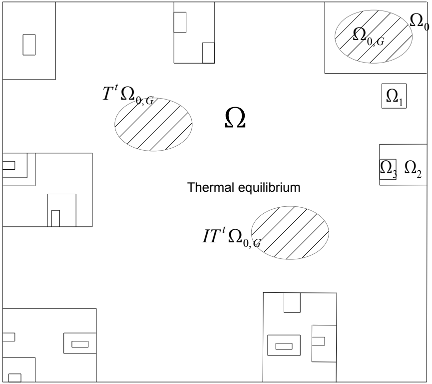
$\Omega_0 = F^{-1}(F_0)$, given F_0

$\Omega_{0,G} \subset \Omega_0$ "good" configurations, meaning that

$\forall\ x \in \Omega_{0,G}$

$F_0 = F(\mathbf{x}) \longrightarrow F_t$

ACCORDING TO THE MACROSCOPIC LAW



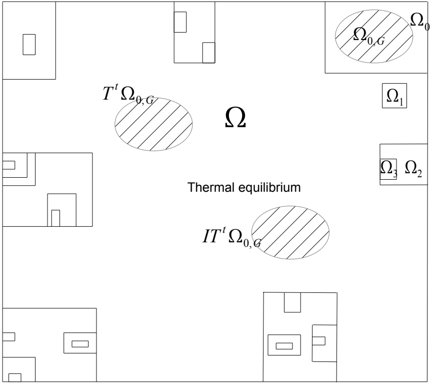
Ω_0 are the initial non equilibrium configurations. $\Omega_{0,G}$ are the good configurations in Ω_0 whose evolution reaches equilibrium at time t : $T^t(\Omega_{0,G}) \subset \Omega_t$;

In Kac's model : $\Omega_0 =$ all signs are $+$ and all configurations of scatterers.

$\Omega_{0,G} =$ all signs are $+$ and the scatterers belong to that overwhelming majority of configurations of scatterers, discussed above.

$|\Omega_t| \uparrow$ with time
$S_t = k \, \ln |\Omega_t| \uparrow$ BOLTZMANN'S ENTROPY
In Kac's model : $S_t = k \, \ln |\Omega_t| = \ln \begin{pmatrix} N \\ N_-(t) \end{pmatrix} = \ln \begin{pmatrix} N \\ N_+(t) \end{pmatrix}$.

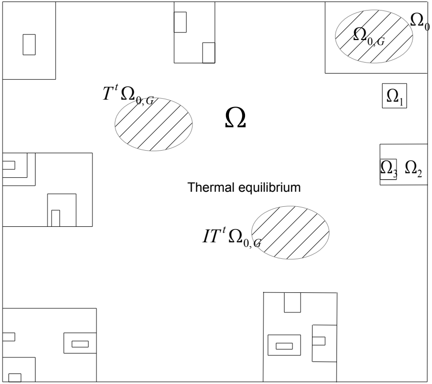
Reversibility paradox



$I(T^t(\Omega_{0,G}))$ are the configurations with velocities reversed of $T^t(\Omega_{0,G})$.

We have :

- $T^t\ \Omega_{0,G} \subset \Omega_t$.



BUT

$\mathrm{I}\ T^t\ \Omega_{0,G} \not\subset \Omega_{t,G}$ BECAUSE $\quad T^t\ \mathrm{I}\ T^t\Omega_{0,G} \subset \Omega_0$

Since $\quad \mathrm{I}T^t\ \mathrm{I}\ T^t\Omega_{0,G} = \Omega_{0,G}$, by reversibility.

BUT THERE IS NO PARADOX BECAUSE, BY LIOUVILLE'S THEOREM :

$|\mathrm{I}\ T^t\ \Omega_{0,G}| = |\Omega_{0,G}| << |\Omega_t|$.

We know that $\mathrm{I}\ T^t\ \Omega_{0,G} \subset \Omega_t \setminus \Omega_{t,G}$.

BUT THAT WE CAN STILL HAVE

$|\Omega_t \setminus \Omega_{t,G}|$ very small.

OF COURSE, THAT REMAINS TO BE PROVEN IN NON TRIVIAL EXAMPLES !

Often misunderstood

Irreversibility is either true on all levels or on none : It cannot emerge as out of nothing, on going from one level to another

I. PRIGOGINE and I. STENGERS

Irreversibility is therefore a consequence of the explicit introduction of ignorance into the fundamental laws

M. BORN

Gibbs was the first to introduce a physical concept which can only be applied to an object when our knowledge of the object is incomplete.

W. HEISENBERG

It is somewhat offensive to our thought to suggest that, if we know a system in detail, then we cannot tell which way time is going, but if we take a blurred view, a statistical view of it, that is to say throw away some information, then we can.

H. BONDI

In the classical picture, irreversibility was due to our approximations, to our ignorance.

I. PRIGOGINE

Misleading ‘solution’

Appeal to ergodicity

(Almost) every trajectory in the ‘big’ phase space Ω will spend in <u>each</u> region of that space a fraction of time proportional to its ‘size’ (i.e. Lebesgue volume).

Shows too much and too little !

Too much : we are not interested in the time spent in every tiny region of the phase space Ω !

Too little : ergodicity, by itself says nothing about time scales. We want the *macroscopic* quantities (and only them !) to ‘reach equilibrium’ reasonably fast.

DOES THIS EXPLAIN
IRREVERSIBILITY
AND THE SECOND LAW ?

WHAT DO YOU MEAN BY "EXPLAIN" ?

IN A DETERMINISTIC FRAMEWORK :

IF THE LAWS IMPLY THAT A STATE A AT TIME ZERO YIELDS A STATE B AT TIME t,

THEN B AT TIME t IS “EXPLAINED” BY THE LAWS AND BY A AT TIME ZERO.

OF COURSE, IT REMAINS TO EXPLAIN A.

IN A PROBABILISTIC FRAMEWORK :

IF F_0 IS A MACROSTATE AT TIME ZERO, THEN THERE IS A "NATURAL" MEASURE ON THE CORRESPONDING SET $F^{-1}(F_0)$ OF MICROSTATES $\mathbf{x}_0$.

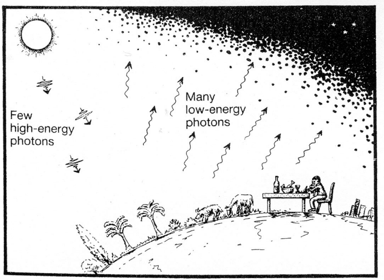
IF, WITH LARGE PROBABILITY WITH RESPECT TO THAT MEASURE, THE MACROSTATE $F(\mathbf{x}_t)$ OBTAINED FROM THE EVOLUTION OF THE MICROSTATE $\mathbf{x}_t$ EQUALS F_t, THEN F_0 AND THE LAWS "EXPLAIN" F_t.

WHY DOESN'T THIS ARGUMENT

APPLY TO THE PAST ?

REAL PROBLEM

ORIGIN of the LOW ENTROPY STATES



The sun and the cycle of life

“ God ” choosing the initial conditions of the universe, in a volume of size $10^{-10^{123}}$ of the total volume (according to R. Penrose).
Possible answer to *that* problem in other talks.