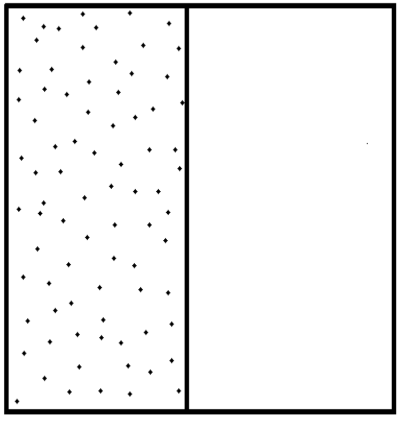
Boltzmannian Statistical Mechanical Foundations of Irreversibility



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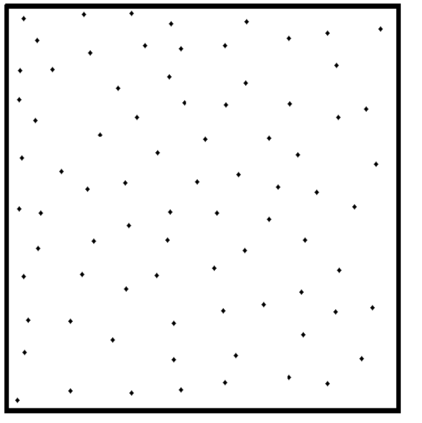

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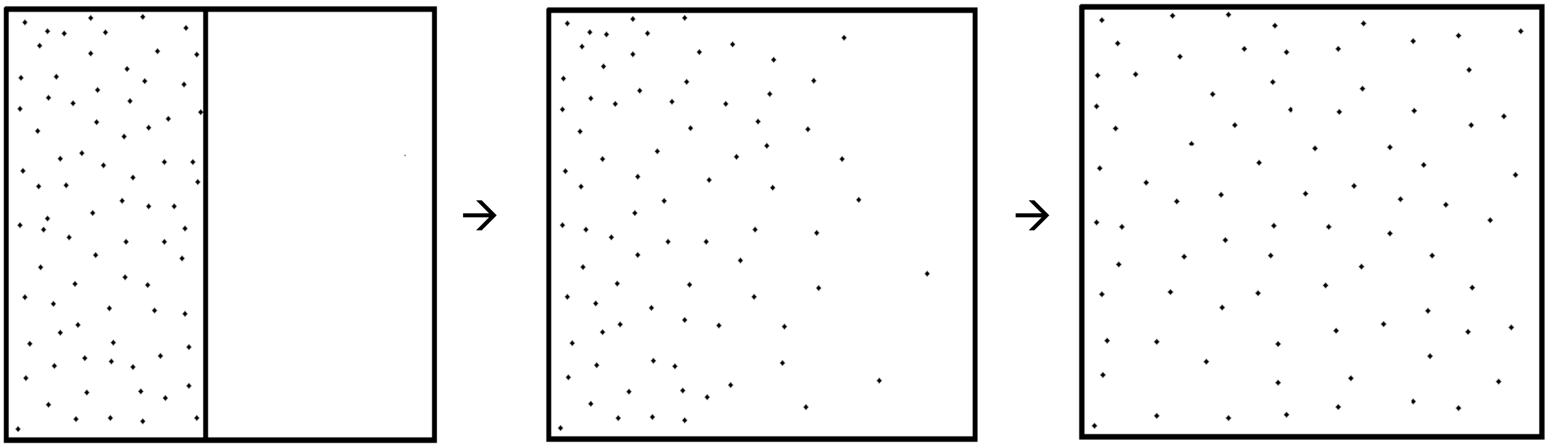


$$S = nc_v \ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}$$

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} > 0$$

2nd Law of Thermodynamics implies:
S will increase for every irreversible process occurring between two equilibrium states of a closed system. → "Thermodynamic Arrow of Time"

Classical Dynamics

Dynamical State:

$$(\mathbf{q},\mathbf{p}) \equiv \{q_1, \dots, q_i \dots ;\ p_1, \dots p_i, \dots\} \in \Gamma \qquad , i = 1, \dots, rN$$

Hamiltonian:

e.g.

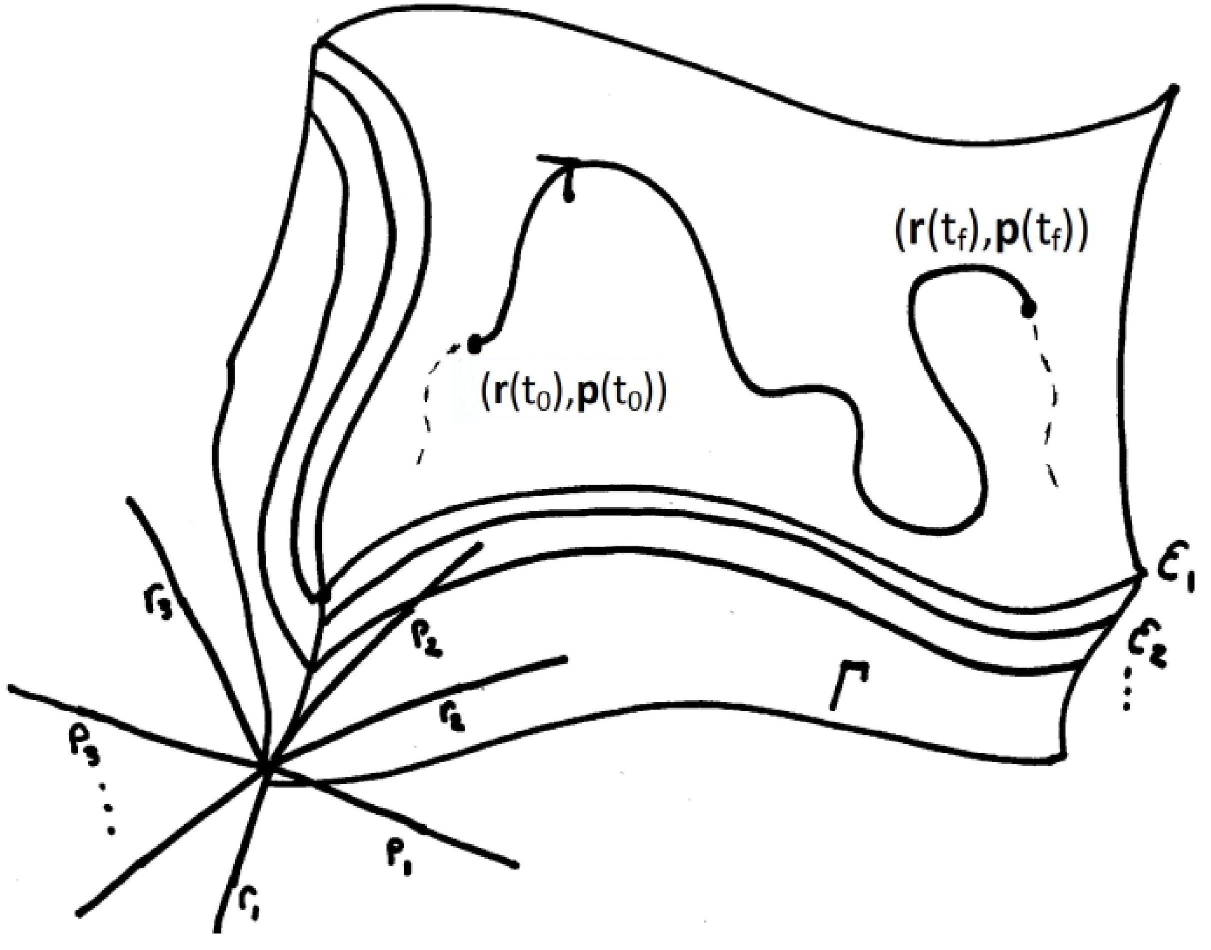
$$H(\boldsymbol{q},\boldsymbol{p}) = \sum_{i=1}^{rN} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=1}^{rN} \sum_{\substack{j=1 \\ i \neq j}}^{rN} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

Eqn's of motion:

$$\left. \begin{aligned} \frac{dq_i}{dt} &= \frac{\partial H(q_1, \dots q_i, \dots ;\ p_1, \dots p_i, \dots)}{\partial p_i} \\ \frac{dp_i}{dt} &= -\frac{\partial H(q_1, \dots q_i, \dots ;\ p_1, \dots p_i, \dots)}{\partial q_i} \end{aligned} \right\} (i = 1, \dots, rN)$$

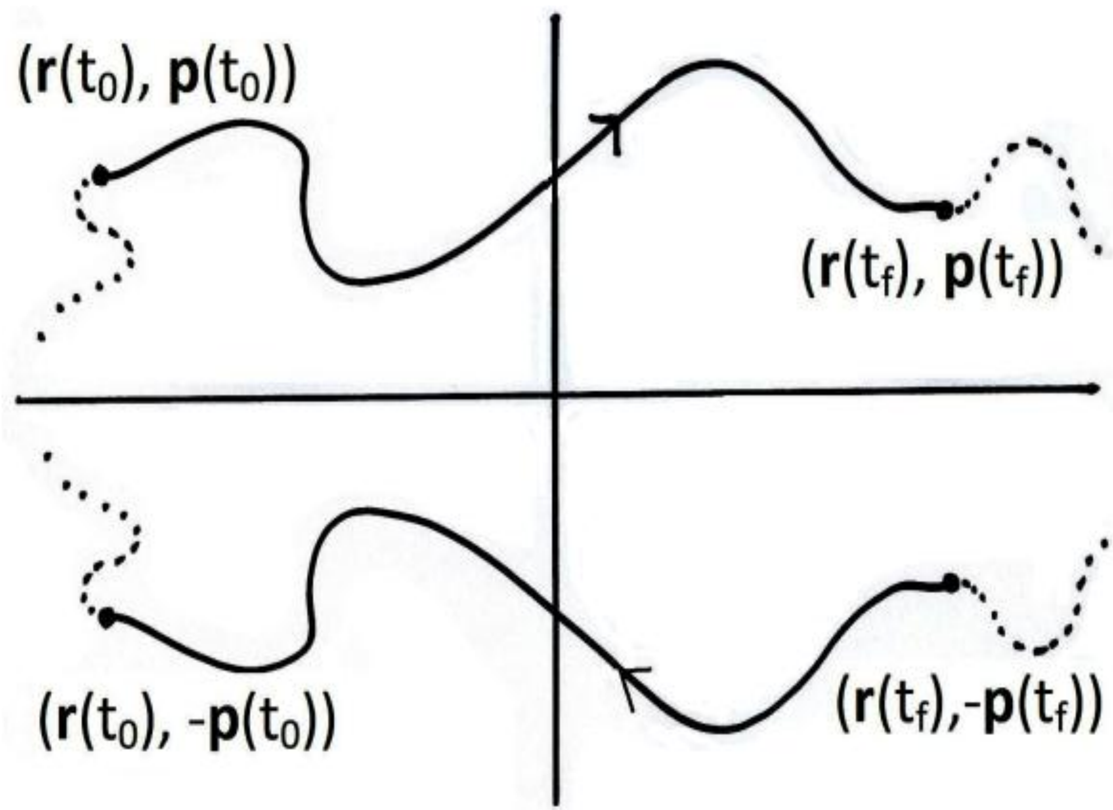
$\rightarrow [q_i(t), p_i(t)]$

G-path in Γ (Phase Space)



Two solutions to dynamical equations due to "time symmetry"

$[\mathbf{r}_j(t), \mathbf{p}_j(t)]$ and $[\tilde{\mathbf{r}}_j(t), \tilde{\mathbf{p}}_j(t)] = \mathbf{r}_j(-t), -\mathbf{p}_j(-t)]$

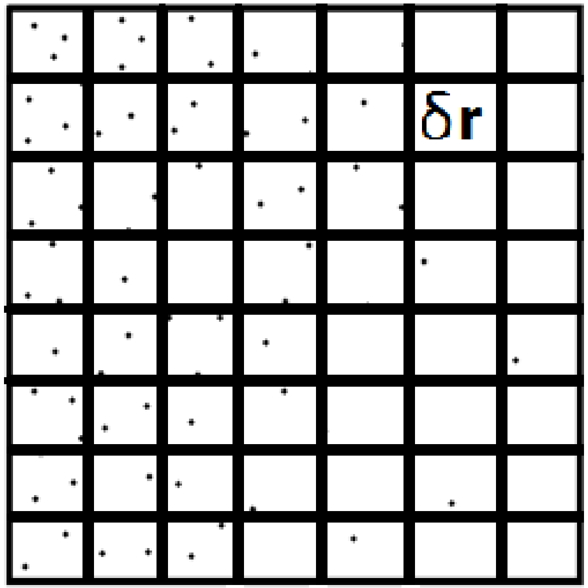


Statistical Mechanics

(q,**p)** → $6\text{x}10^{23}$ variables!

→F(**r**,**v**,*t*) Reduced Dynamical Description

F(**r**,**v**,*t*)δ**r**δ**v** = # of .'s with ~ **r** and **v**



$$F_{\mathrm{eq}}(\mathbf{r},\mathbf{v}) = F_{MB}(v) \equiv N\sqrt{\frac{2}{\pi}\left(\frac{m}{kT}\right)^{3}}\,v^{2}e^{\frac{-mv^{2}}{2kT}}$$

Boltzmann's Transport Equation:

$$\frac{\partial F(\mathbf{r},\mathbf{v},t)}{\partial t} = -\mathbf{v}\ \cdot \nabla_{\mathbf{r}} F(\mathbf{r},\mathbf{v},t) + \iiint d\boldsymbol{v}_{\mathbf{1}} b\ db\ d\epsilon\ |\mathbf{v}_{\mathbf{1}} - \mathbf{v}|[F' F_1' - F_1 F]\ + \Gamma_w,$$

Boltzmann's *H*-theorem:

If *F* satisfies the BE, the functional

$$H[F] \equiv \int d\mathbf{r} \int d\mathbf{v} F(\mathbf{r},\mathbf{v},t) \log F(\mathbf{r},\mathbf{v},t) \ = H(t)$$

never decreases, i.e. $\frac{dH(t)}{dt} \leq 0$

Boltzmann further showed:

dH(t)/dt = 0 only when $F = F_{MB}(v)$

And for an ideal gas $\Delta S = -k\Delta H!$

Implies *S(F(**q**,**p**))*

and S*(t)*

Loschmidt’s Paradox:

How can we derive irreversible behavior from time-reversible dynamics?

Specifically, for every G-path which increases S, there is one that decreases it!

Indicated original BE derivation (using Stosszahlansatz) was not strictly mechanical

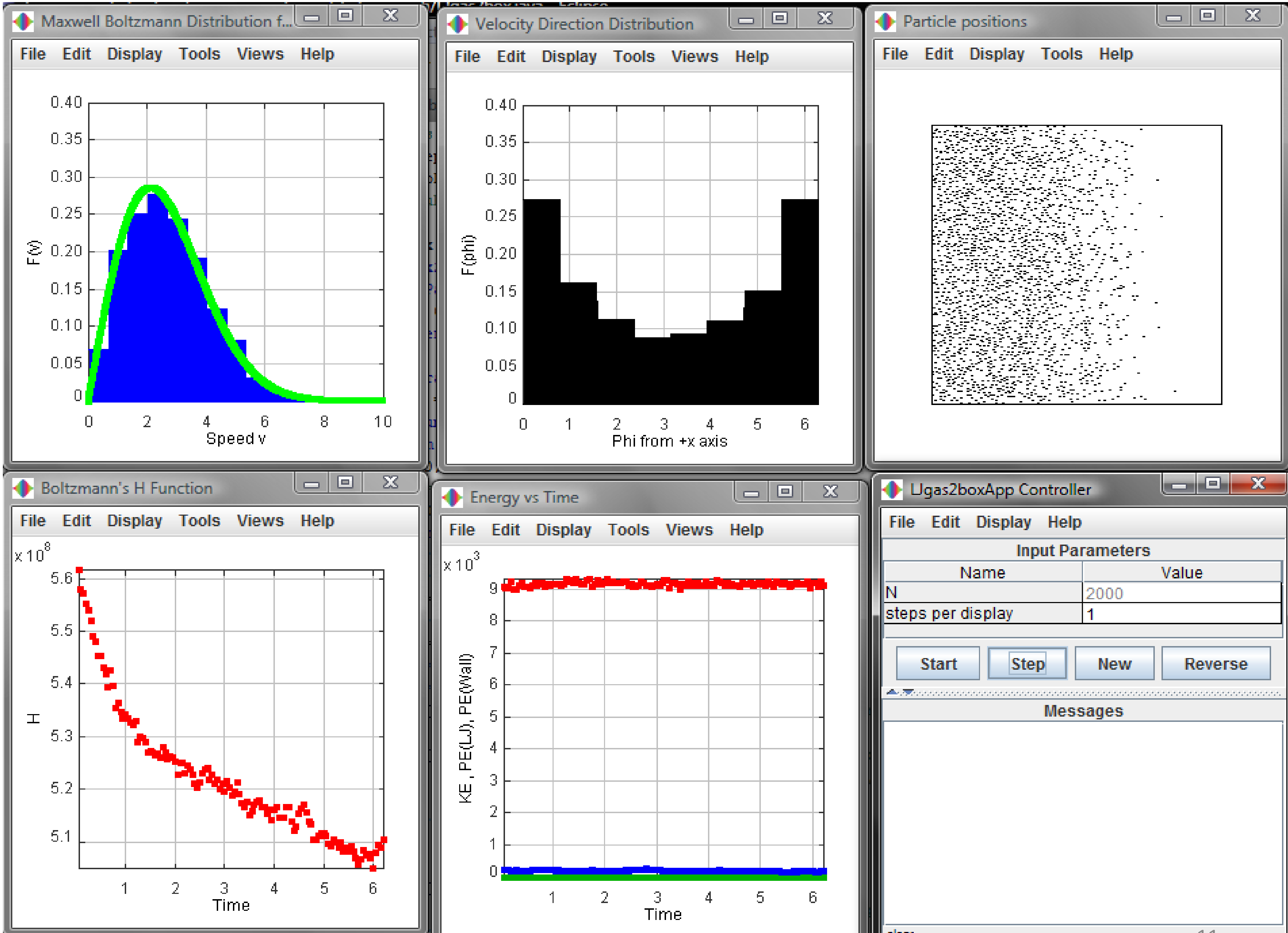
Loschmidt's Paradox Resolution

1. # of microstates for F_{MB} > than all others combined
2. Ergodic Hypothesis→ a time spent by a microstate in a region is proportional to its volume

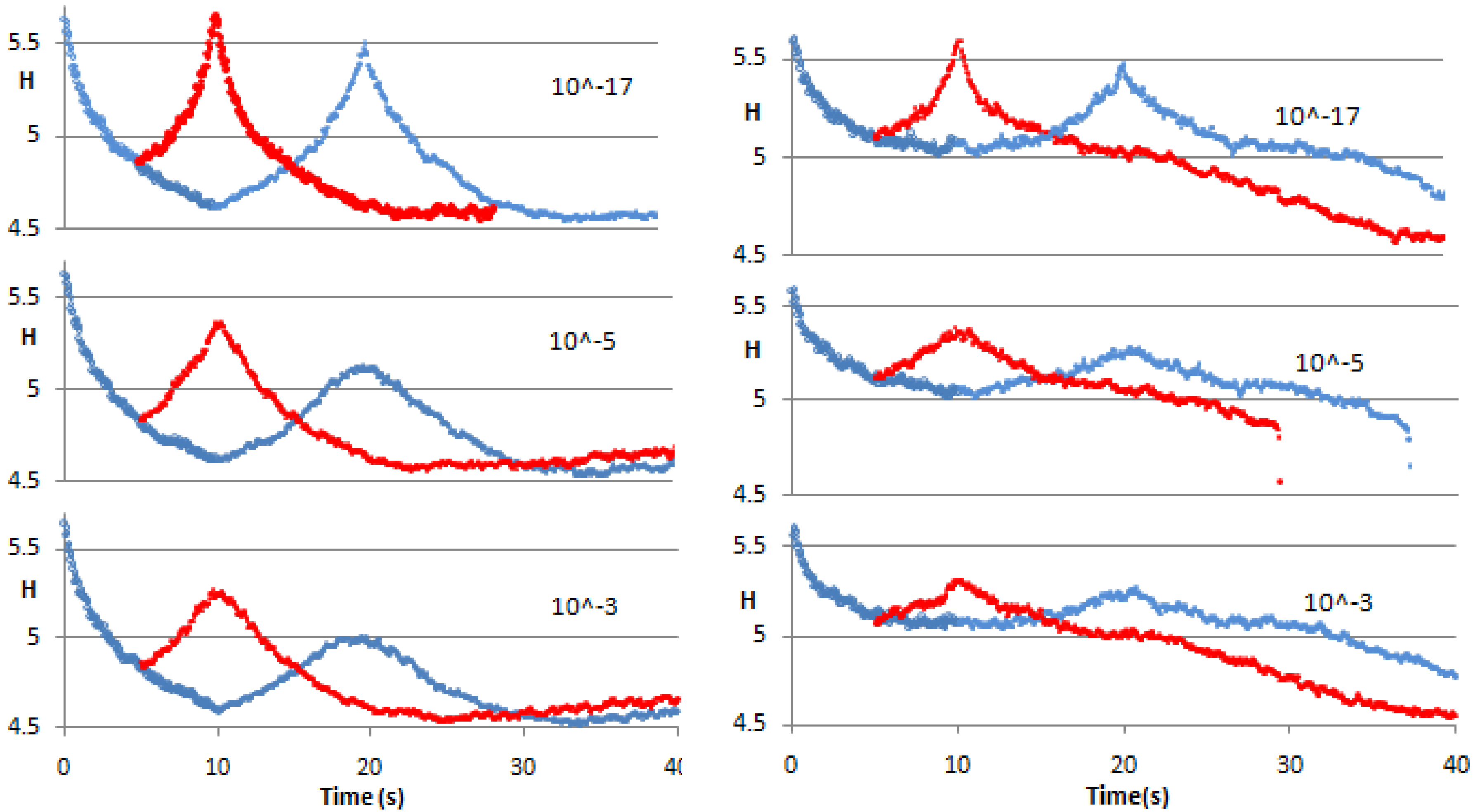
→Equlibrium is "the rule"

Deviations are the exceptions

- H:



Maxwell Boltzmann Distribution f...
File Edit Display Tools Views Help
F(v)
Speed v
0.40 0.35 0.30 0.25 0.20 0.15 0.10 0.05 0
0 2 4 6 8 10
Velocity Direction Distribution
File Edit Display Tools Views Help
F(phi)
Phi from +x axis
0 1 2 3 4 5 6
Particle positions
File Edit Display Tools Help
Boltzmann's H Function
File Edit Display Tools Views Help
x 10^8
H
5.6 5.5 5.4 5.3 5.2 5.1
Time
1 2 3 4 5 6
Energy vs Time
File Edit Display Tools Views Help
x 10^3
KE , PE(LJ), PE(Wall)
9 8 7 6 5 4 3 2 1 0
Time
LJgas2boxApp Controller
File Edit Display Help
Input Parameters
Name
Value
N
2000
steps per display
1
Start
Step
New
Reverse
Messages
clear

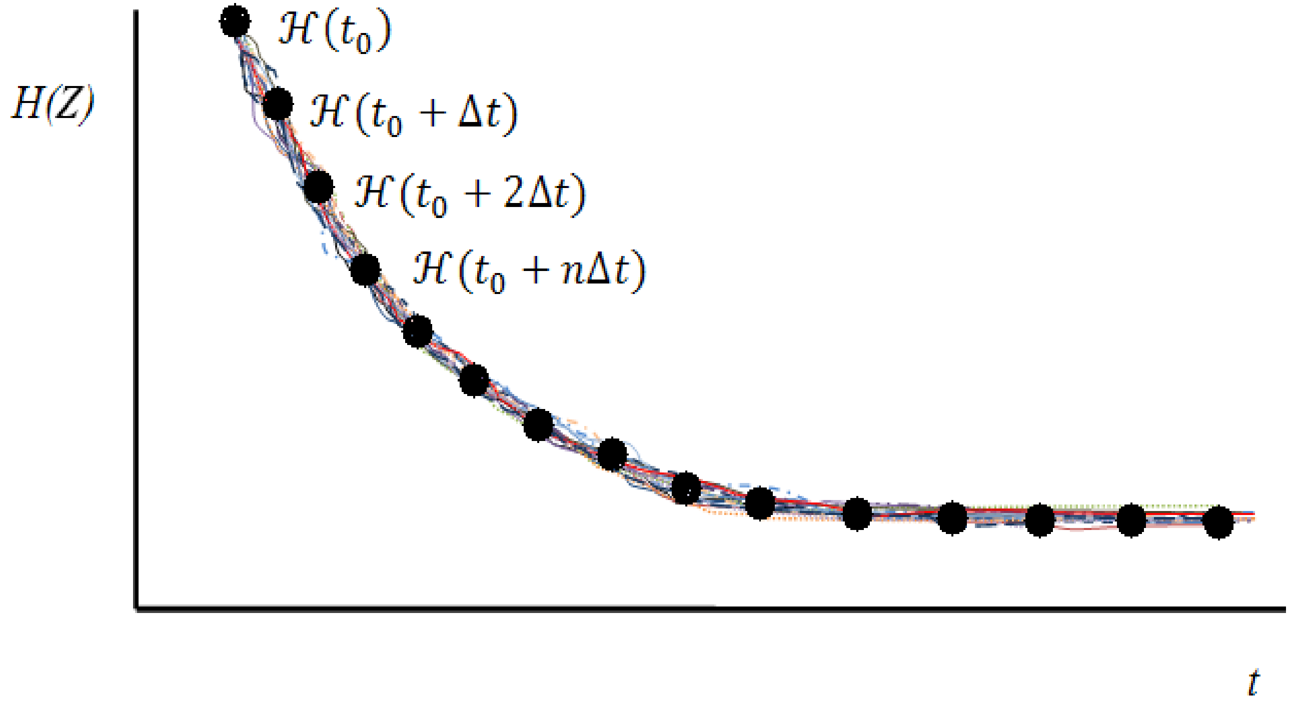

5.5
H
5
4.5
10^-17
10^-5
10^-3
0
10
20
30
40
Time (s)
Time(s)

Conclusions

1. Anti-kinetic evolutions exist, as indicated by Loschmidt.
2. These evolutions are unstable to small perturbations.
3. Statistical Interpretation:
   1. At each later time *t*, the value of *H* for <u>nearly</u> every element is equal to each other, or very near each other. This *H* value at each time corresponds to a point on a curve which is claimed to monotonically decrease until it reaches its minimum value, from which it never departs, just as observed for entropy (with a sign change) for a single system in reality
   2. This "concentration curve" exactly corresponds to the BE *H* curve.

While neither claim 1 or 2 have been proven, they could in principle, using only mechanical means, thus giving the Boltzmann Equation and *H* a rigorous mechanical—albeit statistical—foundation.

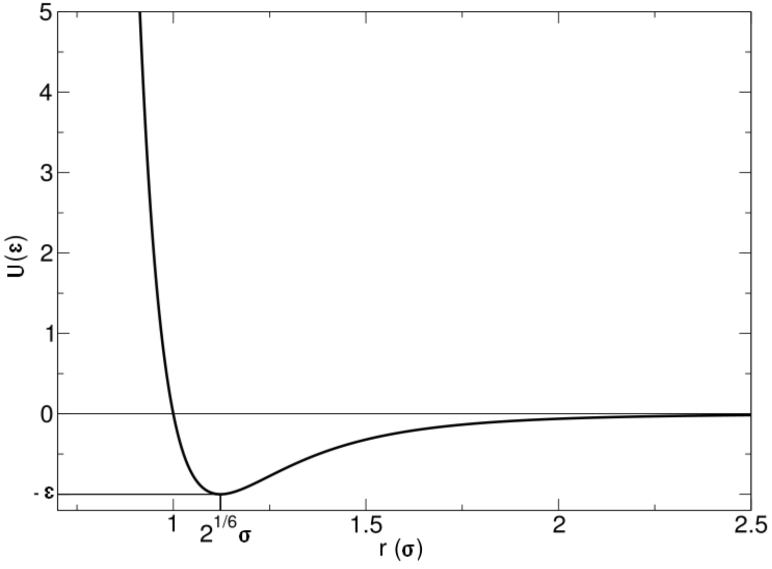
Thank you for you time.



Questions?

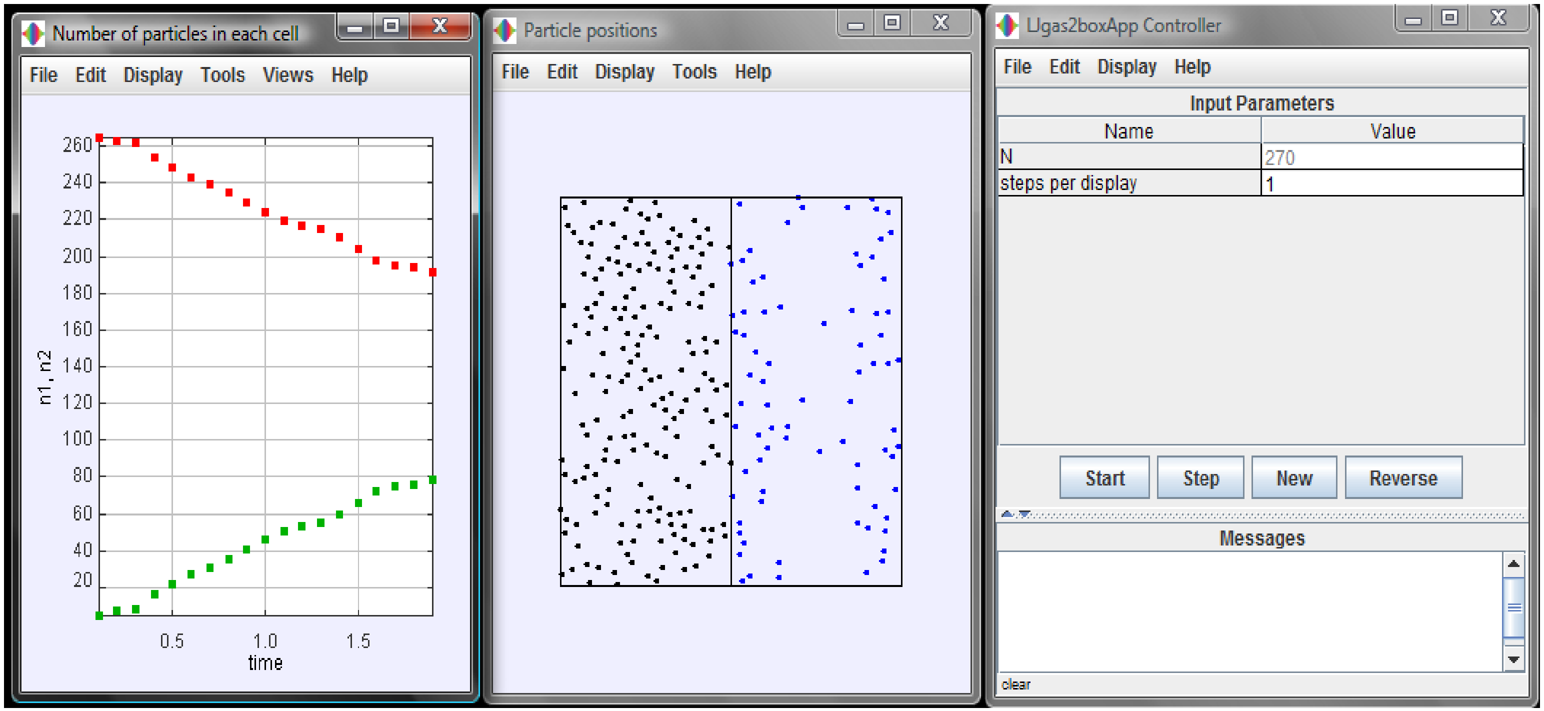
Potential

- Intermolecular, Lennard Jones



- Wall:

$$U_{x_i}^{\mathrm{wall}} = \mathrm{C}\left(\frac{1}{\mathrm{x}_i^{\alpha}} + \frac{1}{(\mathrm{a}-\mathrm{x}_i)^{\alpha}}\right), i = 1,2$$



Number of particles in each cell
File Edit Display Tools Views Help
260
240
220
200
180
160
140
120
100
80
60
40
20
n1, n2
0.5
1.0
1.5
time
Particle positions
File Edit Display Tools Help
Ugas2boxApp Controller
File Edit Display Help
Input Parameters
Name
Value
N
270
steps per display
1
Start
Step
New
Reverse
Messages
clear

To restate the above, let us consider (as the Ehrenfests do) three values of H much above H_{eq} $\equiv H_0$ such that $H_a < H_b < H_c$. If we consider a very long segment of the $H(t)$ curve (a.k.a. "H-curve") and look at all intersections it has with the $H = H_b$ line, Loschmidt demands that we should observe the time sequence

$$\begin{array}{ccccccc} & & H_c & \text{as often as} & H_c & & \\ & H_b & & & & H_b & \\ H_a & & & & & & H_a \end{array}$$

where our implied axes are $+t$ pointing right, and $+H$ pointing up. However, the sequence

$$\begin{array}{ccc} & H_b & \\ H_a & & H_a \end{array}$$

can still be expected to occur much more often since for any $H>H_0$ one expects H to decrease due to the very large $[Z_{eq}]$ and indecomposability. Finally, the smallest fraction of H_b instances should occur like

$$\begin{array}{ccc} H_c & & H_c \\ & H_b & \end{array}$$