

Boltzmann and the Interpretation of Entropy

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Outline

Introduction

The debate on Boltzmann's equation

Boltzmann's expression for the entropy

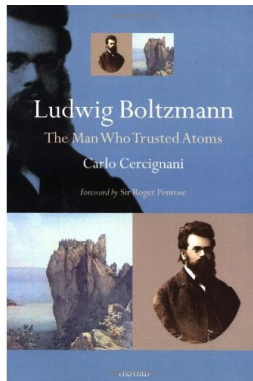
Two Simple Models

Conclusions

Boltzmann's Grave in the Vienna Cemetery



Carlo Cercignani



The debate on Boltzmann's equation

- ▶ Maxwell's distribution
- ▶ Boltzmann's equation
- ▶ Loschmidt's argument
- ▶ Boltzmann's answer
- ▶ Poincaré's theorem and Zermelo's argument
- ▶ Boltzmann's answer

Maxwell's distribution

- ▶ Velocity distribution: $f(\mathbf{v}) = \sum_{i=1}^N \delta(\mathbf{v} - \mathbf{v}_i)$
- ▶ Maxwell distribution: $f^{\text{eq}}(\mathbf{v}) \propto e^{-\lambda(\frac{1}{2}mv^2)}$
- ▶ Via the Bernouilli argument, $\lambda^{-1} = \frac{2}{3}(E/N) = k_B T$

Maxwell's argument (1867):

- ▶ Collisions change $(\mathbf{v}_1, \mathbf{v}_2)$ to $(\mathbf{w}_1, \mathbf{w}_2)$
- ▶ At equilibrium, as many collisions should go from $(\mathbf{v}_1, \mathbf{v}_2)$ to $(\mathbf{w}_1, \mathbf{w}_2)$ as viceversa (detailed balance)
- ▶ The corresponding rates are proportional to $f^{\text{eq}}(\mathbf{v}_1)f^{\text{eq}}(\mathbf{v}_2)$ and $f^{\text{eq}}(\mathbf{w}_1)f^{\text{eq}}(\mathbf{w}_2)$ respectively, so these products must be equal
- ▶ The only connection between the two pairs is that they correspond to the same value of total kinetic energy
- ▶ This can only be satisfied if $\log f^{\text{eq}}(\mathbf{v}) \propto \text{kinetic energy}$

Approach to equilibrium

How does $f(\mathbf{v}, t)$ approach Maxwell's distribution?

Boltzmann's 1872 memoir:

$$\frac{\partial f(\mathbf{v}, t)}{\partial t} = \text{gain}(\mathbf{v}, t) - \text{loss}(\mathbf{v}, t)$$

$$\text{gain}(\mathbf{v}, t) = \int d\mathbf{v}' d\mathbf{w} d\mathbf{w}' \Omega(\mathbf{v}, \mathbf{v}' | \mathbf{w}, \mathbf{w}') f^{(2)}(\mathbf{w}, \mathbf{w}', t)$$

$$\text{loss}(\mathbf{v}, t) = \int d\mathbf{v}' d\mathbf{w} d\mathbf{w}' \Omega(\mathbf{w}, \mathbf{w}' | \mathbf{v}, \mathbf{v}') f^{(2)}(\mathbf{v}, \mathbf{v}', t)$$

Symmetry of the collision kernel (time reversal & space inversion):

$$\Omega(\mathbf{v}, \mathbf{v}' | \mathbf{w}, \mathbf{w}') = \Omega(\mathbf{w}, \mathbf{w}' | \mathbf{v}, \mathbf{v}')$$

Molecular chaos hypothesis (*Stoßzahlansatz*):

$$f^{(2)}(\mathbf{v}_1, \mathbf{v}_2, t) = f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)$$

Boltzmann's equation and the H -theorem

$$\frac{\partial f(\mathbf{v}, t)}{\partial t} = \int d\mathbf{v}' d\mathbf{w} d\mathbf{w}' \Omega [f(\mathbf{w}, t)f(\mathbf{w}', t) - f(\mathbf{v}, t)f(\mathbf{v}', t)]$$

H -theorem:

- ▶ Definition:

$$H(t) = \int d\mathbf{v} f(\mathbf{v}, t) \log f(\mathbf{v}, t)$$

- ▶ If $f(\mathbf{v}, t)$ satisfies Boltzmann's equation

$$\frac{dH}{dt} \leq 0$$

- ▶ H is minimal for the Maxwell distribution:

$$\frac{\delta}{\delta f} \left[H + \lambda \left\langle \frac{1}{2} m v^2 \right\rangle \right] = \log f(\mathbf{v}) + \lambda \frac{1}{2} m v^2 + \text{const.}$$

Observations

- ▶ Boltzmann initially assumed the molecular chaos hypothesis *tacitly*
- ▶ In the 1872 memoir, he used the *kinetic energy* distribution rather than the velocity distribution
- ▶ He also treated the more general nonuniform case with $f(\mathbf{r}, \mathbf{v}, t)$ —which is the most useful for applications
- ▶ One also finds a discussion of polyatomic molecules
- ▶ Boltzmann identifies H with the gas entropy (he used the symbol E in the manuscript)
- ▶ He introduces in this memoir his energy discretization (having to grasp functional equations and the like)

Proof of $dH/dt \leq 0$

- ▶ Consider the effect of $(\mathbf{v}, \mathbf{v}') \longrightarrow (\mathbf{w}, \mathbf{w}')$ collisions:

$$df(\mathbf{v}) = -dt \Omega f(\mathbf{v})f(\mathbf{v}')$$

$$df(\mathbf{v}') = -dt \Omega f(\mathbf{v})f(\mathbf{v}')$$

$$df(\mathbf{w}) = dt \Omega f(\mathbf{v})f(\mathbf{v}')$$

$$df(\mathbf{w}') = dt \Omega f(\mathbf{v})f(\mathbf{v}')$$

- ▶ Overall effect on H : since $dH \simeq \log f df$,

$$dH = dt \Omega f(\mathbf{v})f(\mathbf{v}') \log \frac{f(\mathbf{w})f(\mathbf{w}')}{f(\mathbf{v})f(\mathbf{v}')}$$

- ▶ Considering also the reverse collision

$$dH = dt \int \Omega [f(\mathbf{v})f(\mathbf{v}') - f(\mathbf{w})f(\mathbf{w}')] \log \frac{f(\mathbf{w})f(\mathbf{w}')}{f(\mathbf{v})f(\mathbf{v}')} \leq 0$$

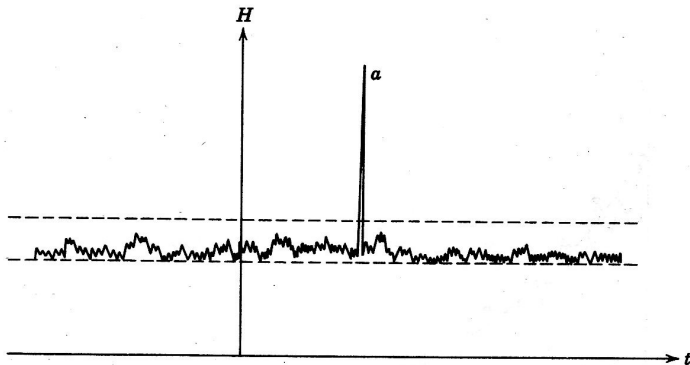
Loschmidt's objection

- ▶ Hamilton's equations are time-reversal invariant
- ▶ What happens if we reverse all velocities?

Low's argument (cf. Huang, *Statistical Mechanics*):

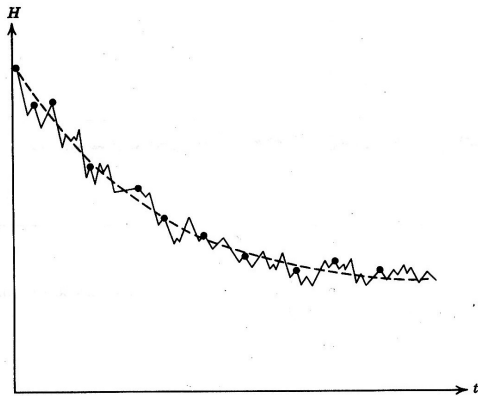
- ▶ Assume that at $t = 0$ the system exhibits molecular chaos and $f(\mathbf{v}, 0)$ is non-Maxwellian, but depends only on $|\mathbf{v}|$: then $dH/dt < 0$ for $t = \epsilon > 0$
- ▶ Consider a system with all velocities reversed: also for it $dH/dt < 0$ for $t = \epsilon$
- ▶ The future of the second system is the past of the first one: hence $dH/dt > 0$ for $t = -\epsilon$
- ▶ Thus H is at a local peak whenever molecular chaos is satisfied

The behavior of $H(t)$



K. Huang, Statistical Mechanics

The behavior of $H(t)$



K. Huang, Statistical Mechanics

Boltzmann's answer

Introduces the **probability** of obtaining the distribution $f(\mathbf{r}, \mathbf{v}, t)$:

One therefore cannot prove that, whatever may be the positions and velocities of the spheres at the beginning, the distribution must become uniform after a long time; rather we can only prove that infinitely many more initial states will lead to a uniform one after a definite length of time than to a non-uniform one.

[Approach to equilibrium] is in fact a consequence of probability theory, for any non-uniform distribution of states, no matter how improbable it may be, is still not absolutely impossible.

A new research program

- ▶ Consider an **ensemble** of systems, with the same initial value of $f(\mathbf{v}, t)$
- ▶ Define $\bar{f}(\mathbf{v}, t)$ as the **ensemble average** of $f(\mathbf{v}, t)$
- ▶ Will it obey Boltzmann's equation and satisfy the H -theorem?

Developments

Carleman, 1933: Existence and uniqueness of $\bar{f}(\mathbf{v}, t)$ for a hard-sphere gas, is special conditions

Grad, 1949: Definition of the Boltzmann-Grad limit: $N \rightarrow \infty$, $\sigma \rightarrow 0$, $N\sigma^2 = \text{const.}$

Cercignani, 1972: Conjecture about the convergence to the Boltzmann equation in the Boltzmann-Grad limit

Lanford, 1973: Proof of the convergence to the solution of the Boltzmann equation for a finite (and short!) time interval

DiPerna and Lions, 1989: Existence and weak stability for the Boltzmann equation (Field medal)

Villani, 2003: Cercignani's conjecture is sometimes true and sometimes almost true (Field medal)

Poincaré's theorem and Zermelo's argument

Poincaré's theorem (1890):

If a system obeys the canonical equations of motion, and is bound to evolve in a limited region of space and with bounded values of the velocity, for almost all initial conditions the system will visit an infinite number of times any arbitrary neighborhood of the initial condition.

Zermelo's argument:

From this it follows directly that there can be no single-valued continuous function $S = S(x_1, x_2, \dots, x_n)$ of the states that always increases for all initial states in some region, no matter how small the region.

Boltzmann's answer

... I have also emphasized that the second law of thermodynamics is from the molecular viewpoint merely a statistical law. Zermelo's paper shows that my writings have been misunderstood; nevertheless it pleases me for it seems to be the first indication that these writings have been paid any attention in Germany.

Boltzmann's answer

It should indeed be obvious that if a trillion tiny spheres, each with a high velocity, are initially collected together in one corner of a container with absolutely elastic walls, then in a very short time they will be uniformly distributed through the container; and that the time required for all their collisions to have compensated each other in such a way that they all come back to the same corner, must be so large that no one will be present to observe it.

The nature of the second law

The second law will be explained mechanically by means of the assumption A (which is of course improvable) that the universe, considered as a mechanical system—or at least a very large part of it which surrounds us—started from a very improbable state and still is in an improbable state.

The nature of the second law

... if we do not make any assumption about the present state of the universe, then of course we cannot expect to find that a system isolated from the universe, whose initial state is completely arbitrary, will be in an improbable state initially rather than later.

The nature of the second law

An answer to the question—how does it happen that at present the bodies surrounding us are in a very improbable state—cannot be given, any more than one can expect science to tell us why phenomena occur at all and take place according to certain laws.

Is the “arrow of time” absolute?

[An alternative hypothesis is that] there must then be in the universe, which is in thermal equilibrium as a whole and therefore dead, here and there relatively small regions of the size of our galaxy [...] which during the relatively short time of eons deviate from equilibrium. [...] For the universe as a whole the two directions of time are indistinguishable, just as in space there is no up or down. However, just as at a certain place on the earth's surface we can call “down” the direction towards the centre of the earth, so a living being that finds itself in such a world at a certain period of time can define the time direction as going from less probable to more probable states. . .

Entropy vs. probability

The “great memoir” of 1877:

- ▶ In an isolated system of bodies, the probability of a (macroscopic) state cannot but increase
- ▶ On the other hand, the same applies for the entropy
- ▶ Thus the entropy must be a monotonically increasing function of the probability

Questions:

- ▶ What does B. understand for state? and for probability?
- ▶ How does he evaluate this relation?

Energy repartition

A first example:

- ▶ Single particle energies:

$$E \in \{0, \epsilon, 2\epsilon, \dots, p\epsilon\}$$

- ▶ Repartition: $(w_0, w_1, w_2, \dots, w_p)$: w_k is the number of particles with energy equal to $k\epsilon$
- ▶ Complexion: $i \longrightarrow E_i, i = 1, \dots, n, E_i \in \{0, \dots, p\epsilon\}$
- ▶ Number of complexions

$$\mathfrak{P} = \frac{n!}{w_0! w_1! \dots w_p!}$$

- ▶ Probability:

$$W = \frac{\mathfrak{P}}{J}; \quad J = \text{number of all complexions}$$

Maximal probability

- ▶ Asymptotic expression:

$$\log \mathfrak{P} \simeq n \log n - w_0 \log w_0 - w_1 \log w_1 - \cdots - w_p \log w_p$$

- ▶ Constraints:

$$\sum_k w_k = n; \quad \sum_k k w_k = \lambda$$

- ▶ Constrained extremum (via Lagrange multipliers) (for $p \rightarrow \infty$)

$$\log w_k = -(\mu + k\nu)$$

A comment

Boltzmann's calculation of the asymptotic behavior of multinomial probabilities in terms of relative entropy was carried out in 1877 as a key component of his paper that gave a probabilistic interpretation of the Second Law of Thermodynamics. This fundamental calculation represents a revolutionary moment in human culture during which both statistical mechanics and the theory of large deviations were born.

R. S. Ellis, 1999

Generalization

Point-like particles: divides velocity space into cells of volume $\epsilon\zeta\eta$ and obtains

$$\begin{aligned}\Omega &= \log \mathfrak{P} = n \log n - (p + q + r + 1) \log 2\pi - n \log(\epsilon\zeta\eta) \\ &\quad - \sum_{a=-p}^{+p} \sum_{b=-q}^{+q} \sum_{c=-r}^{+r} (\epsilon\zeta\eta) f(a\epsilon, b\zeta, c\eta) \log f(a\epsilon, b\zeta, c\eta) \\ &= \text{const.} - \iiint dv_x dv_y dv_z f(v_x, v_y, v_z) \log f(v_x, v_y, v_z)\end{aligned}$$

Polyatomic molecules and external forces: *phase space*
 (p_i^α, q_i^α) (α is the kind of particle)

$$\Omega = - \left[\sum_{\alpha} \iint \cdots f(p_1^\alpha, p_2^\alpha, \dots, q_r^\alpha) \log f(p_1^\alpha, p_2^\alpha, \dots, q_r^\alpha) \right. \\ \left. dp_1^\alpha dp_2^\alpha \cdots dq_r^\alpha \right]$$

Relation between $\mathfrak{P}$ and the entropy

Ideal gas: $\Omega = \log \mathfrak{P}$

$$\Omega = - \iiint \iiint \iiint f(x, y, z, u, v, w) \log f(x, y, z, u, v, w) dx dy dz du dv dw$$

N.B.: Boltzmann's T corresponds to $\frac{3}{2} k_B T$:

$$f(x, y, z, u, v, w) = \frac{N}{V \left(\frac{4\pi T}{3m} \right)^{\frac{3}{2}}} e^{-\frac{3m}{4T} (u^2 + v^2 + w^2)}$$

$$\Omega = \frac{3N}{2} + N \log \left[V \left(\frac{4\pi T}{3m} \right)^{\frac{3}{2}} \right] - N \log N$$

$$d\Omega = N \frac{dV}{V} + \frac{3N}{2} \frac{dT}{T}$$

$$dQ = NdT + \frac{2N}{3V} T dV = \frac{2}{3} T d\Omega$$

Comments

- ▶ B. associates entropy to the macroscopic state of a complex, isolated system
- ▶ Entropy is proportional to the logarithm of the probability of this macroscopic state: the “Gibbs paradox” does not apply ($-N \log N$ term!)
- ▶ B.’s entropy is an *observable*, i.e., a function of the *microstate*: it can fluctuate, and surely does not obey Liouville’s theorem
- ▶ B. explicitly evaluates entropy only for an aggregate of independent particles, but can also (in principle) consider interacting systems (equation for polyatomic molecules)
- ▶ He does not attempt the generalization to other aggregation states because “the nature of these aggregation states is too little known and their theory has not yet been worked out mathematically”

Boltzmann's vs. Gibbs entropies

- ▶ Boltzmann: X is the microstate; $M(X)$ the corresponding macrostate; $W(M)$ its probability (ratio of phase space to the whole available phase space)

$$S_B(X) = \log W(M(X))$$

- ▶ Gibbs: *ensemble* distribution $\rho(X)$

$$S_G[\rho] = - \int \rho(X) \log \rho(X) dX$$

- ▶ At equilibrium, if M is a macrostate and $\rho(X)$ is its corresponding microcanonical ensemble

$$S_B^{\text{eq}} = S_G^{\text{eq}}$$

- ▶ Out of equilibrium: S_G is constant, while S_B will typically increase

Approach to equilibrium in the ideal gas

Frisch, Swendsen

- ▶ **Free expansion:** An ideal gas is initially at equilibrium in a cylinder of length L_0 and section S ; the available volume is suddenly extended to length L
- ▶ One-dimensional model: Expansion in the x direction, independence of the y and z directions
- ▶ Initial distribution factorizes: each particle evolves independently

Solution of the dynamics:

- ▶ Let $x \in [-L, +L]$; when the particle hits the boundary at $x = +L$ it reenters (with the same velocity) at $x = -L$ (and viceversa); crossing $x = 0$ corresponds to impact at the origin
- ▶ We set the mass $m = 1$, $k_B T = 1$

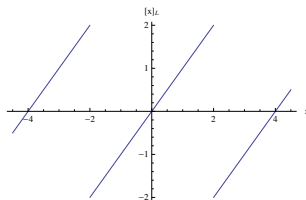
Dynamics

Initial condition:

$$\rho(x, p, 0) = \frac{e^{-p^2/2}}{\sqrt{2\pi}} \theta(L_0 - |x|)$$

Distribution at time t :

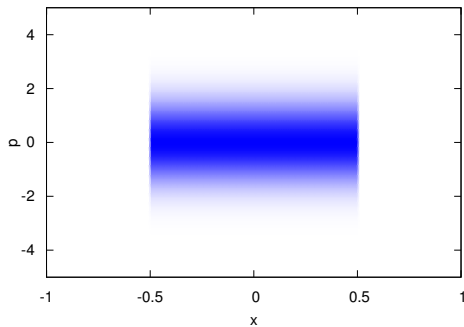
$$[x]_L = 2L \left[\text{frac} \left(\frac{L+x}{2L} \right) - \frac{1}{2} \right]$$



$$\rho(x, p, t) = \frac{e^{-p^2/2}}{\sqrt{2\pi}} \theta(L_0 - [x - pt]_L)$$

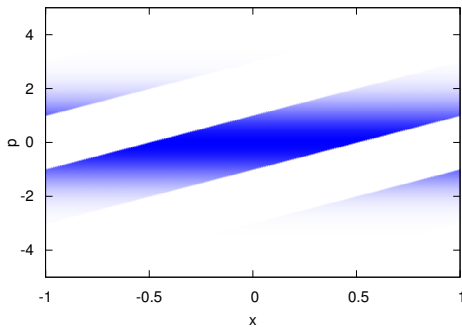
Evolution of the phase-space distribution

$t = 0$



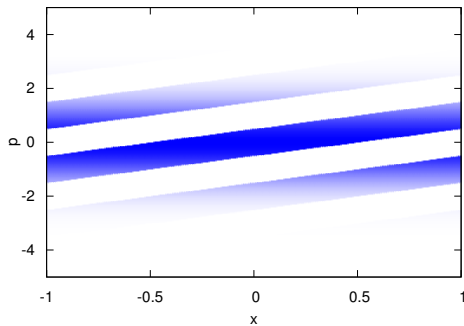
Evolution of the phase-space distribution

$$t = 0.5$$



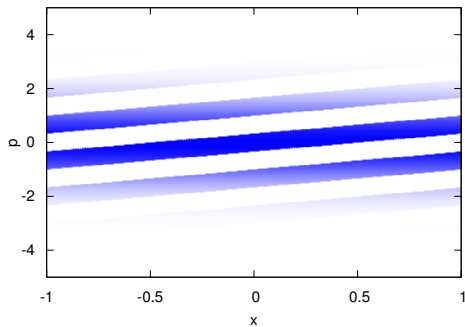
Evolution of the phase-space distribution

$t = 1$



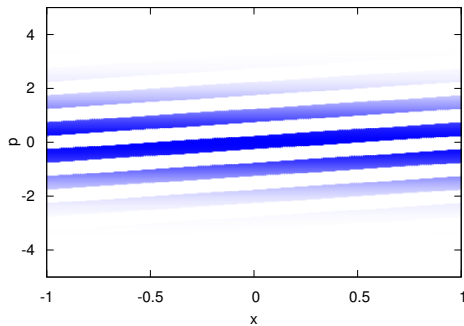
Evolution of the phase-space distribution

$t = 1.5$



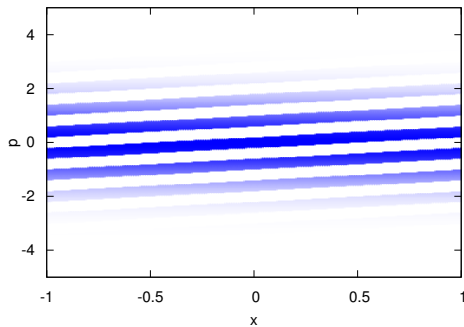
Evolution of the phase-space distribution

$$t = 2$$



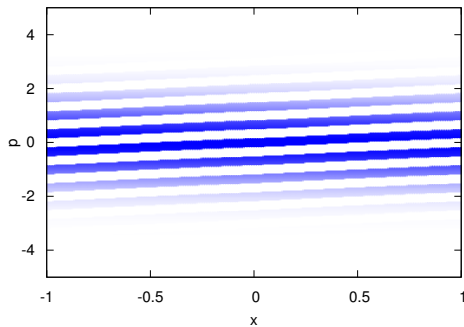
Evolution of the phase-space distribution

$t = 2.5$



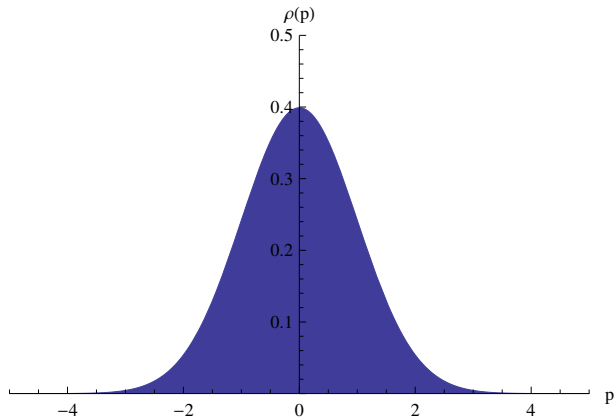
Evolution of the phase-space distribution

$t = 3$



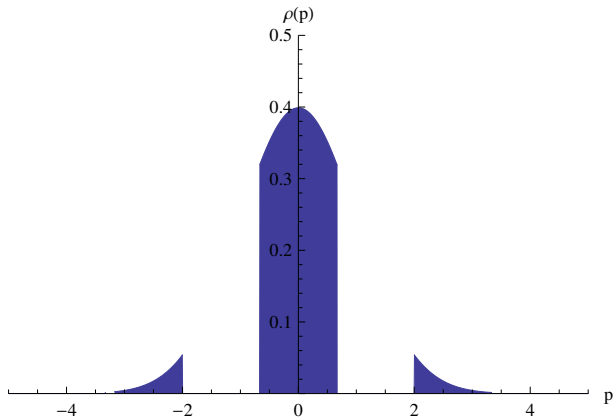
Evolution of the p -distribution at $x = 0$

$$t = 0$$



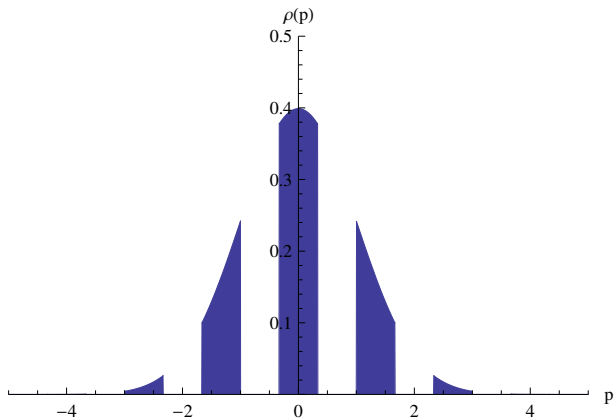
Evolution of the p -distribution at $x = 0$

$$t = 0.5$$



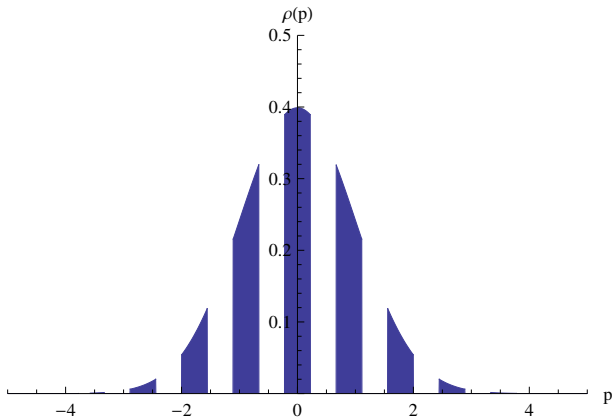
Evolution of the p -distribution at $x = 0$

$$t = 1$$



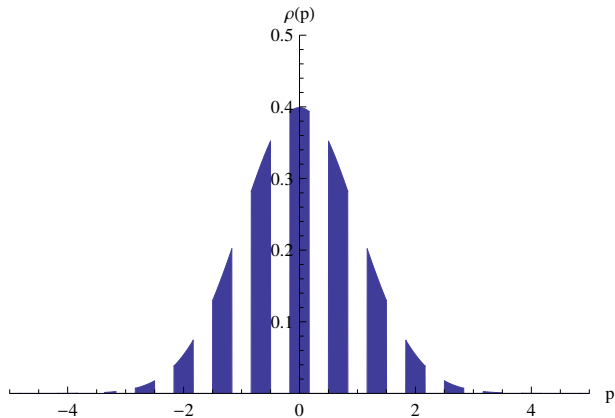
Evolution of the p -distribution at $x = 0$

$$t = 1.5$$



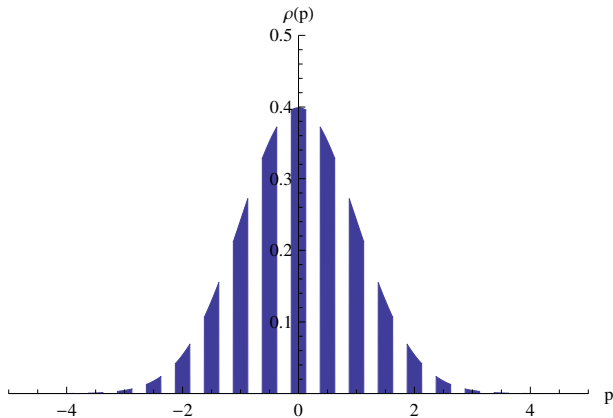
Evolution of the p -distribution at $x = 0$

$$t = 2$$



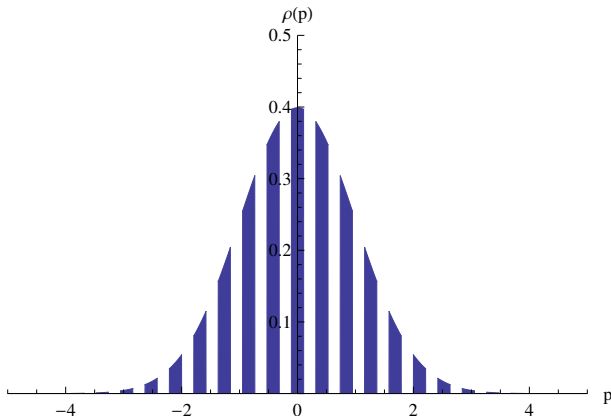
Evolution of the p -distribution at $x = 0$

$t = 2.5$



Evolution of the p -distribution at $x = 0$

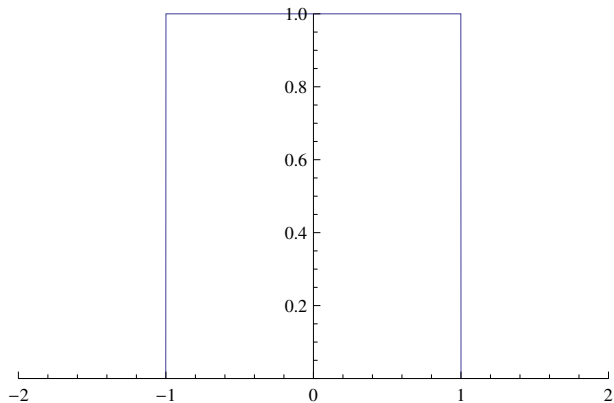
$t = 3$



- ▶ The distribution never reaches equilibrium
- ▶ *Observables* reach equilibrium pretty fast!

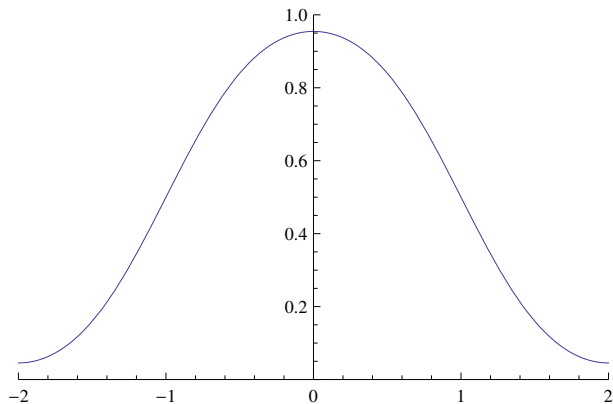
Evolution of the densities

Particle density



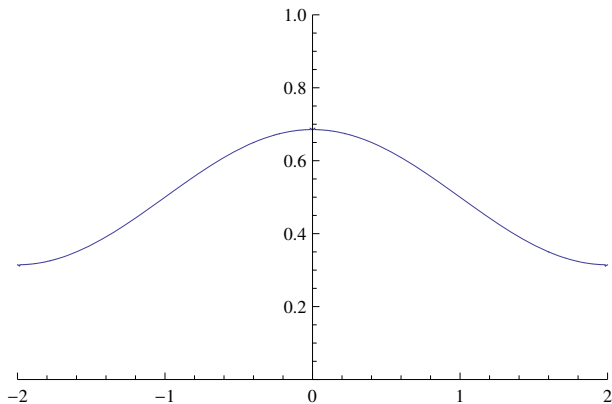
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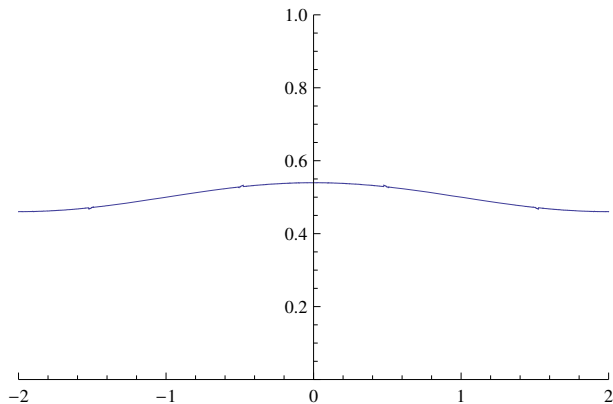
Evolution of the densities

Particle density



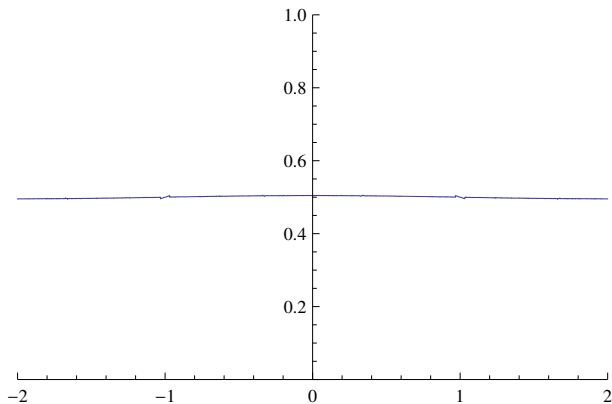
Evolution of the densities

Particle density



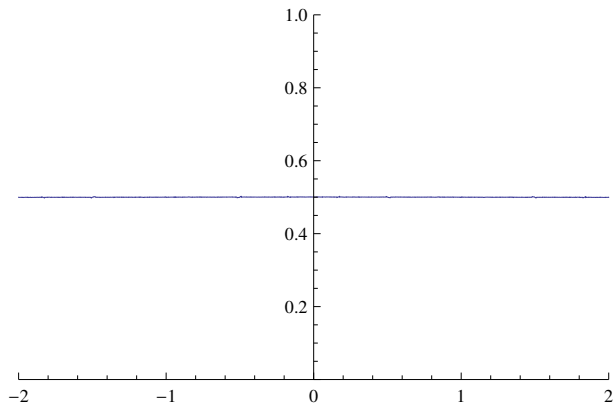
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Particle density



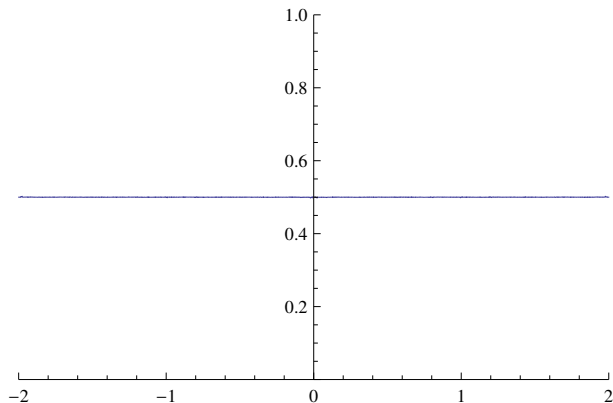
Evolution of the densities

Particle density



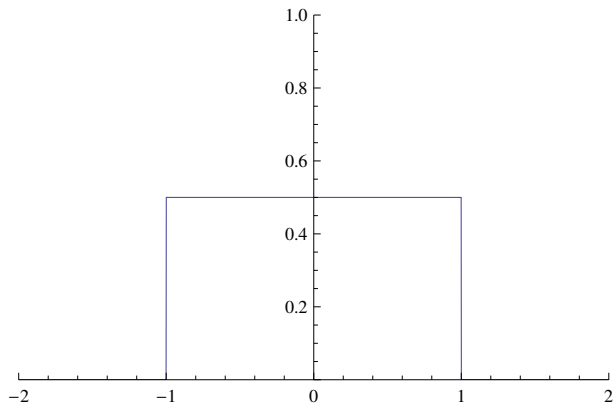
Evolution of the densities

Particle density



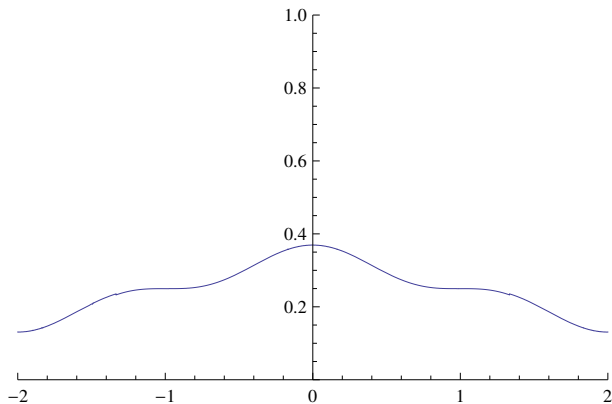
Evolution of the densities

Energy density



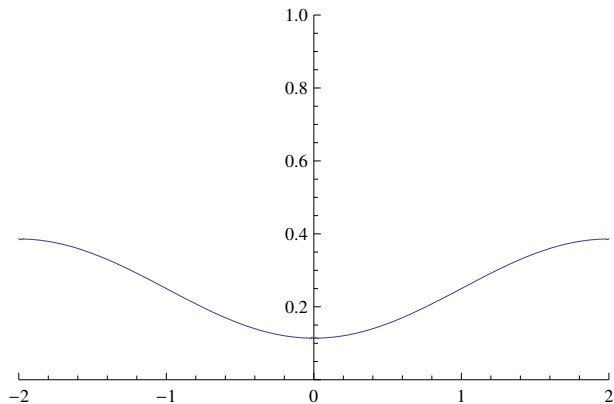
Evolution of the densities

Energy density



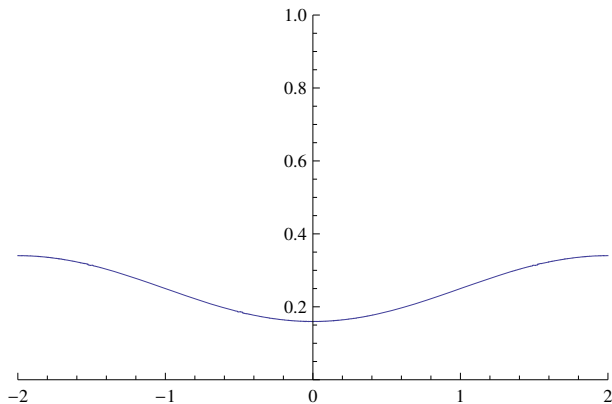
Evolution of the densities

Energy density



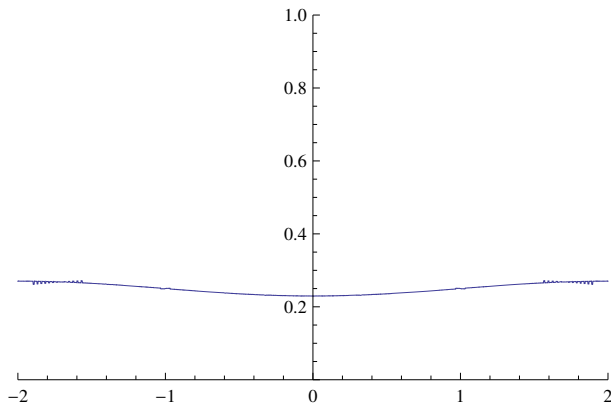
Evolution of the densities

Energy density



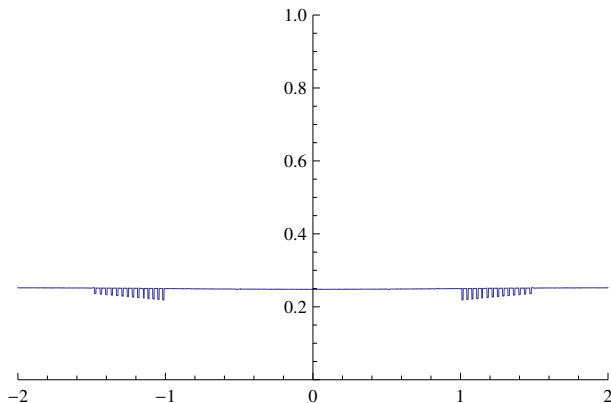
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Energy density



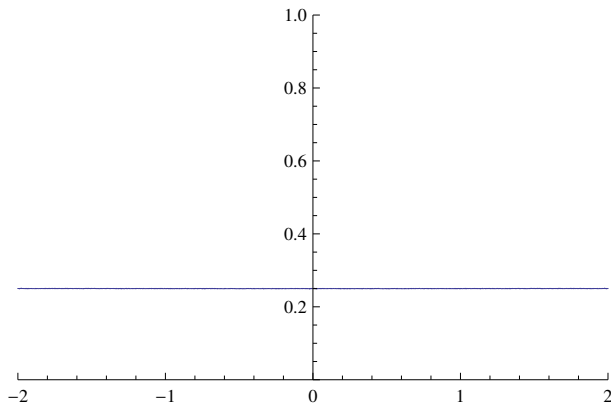
Evolution of the densities

Energy density



Evolution of the densities

Energy density



Kac's Ring Model

- ▶ A ring contains N sites: in each there is a particle that can be white ($\sigma = +1$) or black ($\sigma = -1$)
- ▶ M “barriers” are disposed on fixed bonds in the ring
- ▶ At each time step, all the particles move counterclockwise by one site
- ▶ If a particle crosses a barrier, it changes color

Properties of the dynamics:

Reversibility: Just turn the particles **clockwise**

Recurrence: After $2N$ steps (N if M is even) the system goes back to the initial state

Approximate analysis

- ▶ $W(t)$: number of white particles at time t
- ▶ $B(t)$: number of black particles at time t
- ▶ $w(t)$: number of white particles before a barrier
- ▶ $b(t)$: number of black particles before a barrier
- ▶ Exact evolution equation:

$$W(t+1) = W(t) + b(t) - w(t)$$

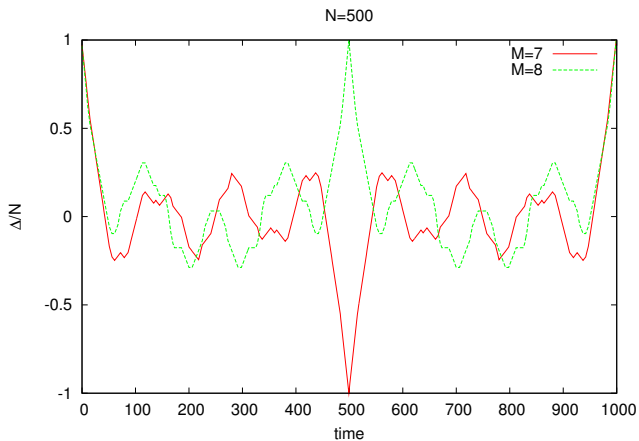
- ▶ “Molecular chaos”: $w(t) = W(t)M/N$, $b(t) = B(t)M/N$
- ▶ $\Delta(t) = W(t) - B(t)$, $\mu = M/N$, $B(t) = N - W(t)$

$$\Delta(t+1) = (1 - 2\mu)\Delta(t)$$

- ▶ $0 < \mu < \frac{1}{2}$, $\tau = -1/\log(1 - 2\mu)$

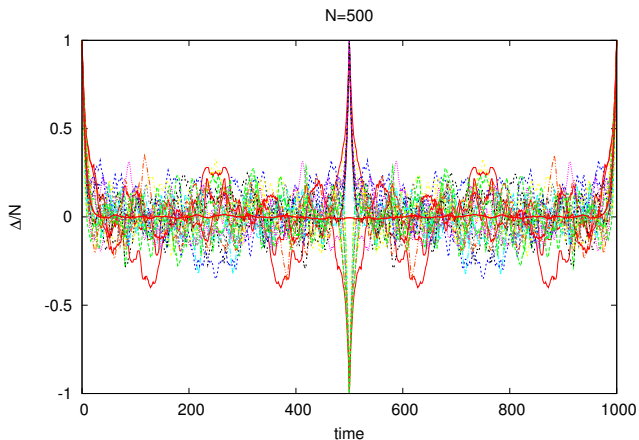
$$\Delta(t) = \Delta(0)e^{-t/\tau}$$

Simulations



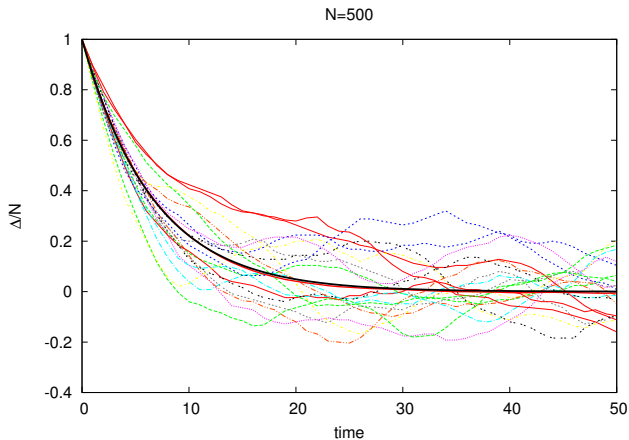
$$\mu = M/N = 0.07$$

Simulations



Continuous line: average over 400 samples

Simulations



Continuous lines: average and $e^{-t/\tau}$

Microscopic Analysis

► $\sigma = (\sigma_1, \dots, \sigma_N), \sigma_i = \pm 1$

► $\epsilon = (\epsilon_1, \dots, \epsilon_N), \epsilon_i = \pm 1,$

$$\epsilon_i = \begin{cases} -1, & \text{if } \exists \text{ barrier between } i \text{ and } i+1 \\ 1, & \text{otherwise} \end{cases}$$

► Liouville operator

$$\sigma(t+1) = \mathcal{L}_\epsilon \sigma(t)$$

$$(\mathcal{L}_\epsilon \sigma)_{i+1} = \epsilon_i \sigma_i$$

► Expression for $\Delta(t)$ (i 's are taken modulo N):

$$\begin{aligned} \Delta(t) &= \sum_{i=1}^N \sigma_i(t) = \sum_{i=1}^N \epsilon_{i-1} \sigma_{i-1}(t-1) \\ &= \sum_{i=1}^N \epsilon_{i-1} \cdots \epsilon_{i-t} \sigma_{i-t}(0) \end{aligned}$$

ϵ averages

- Averages over ϵ :

$$\langle \Delta(t) \rangle = \sum_{i=1}^N \langle \epsilon_{i-1} \cdots \epsilon_{i-t} \rangle \sigma_{i-t}(0)$$

- For $t < N$, all ϵ factors are independent:

$$\langle \epsilon_{i-1} \cdots \epsilon_{i-t} \rangle = \sum_k (-1)^k p_k$$

$$p_k = \binom{t}{k} \mu^k (1 - \mu)^{t-k}$$

$$\langle \epsilon_{i-1} \cdots \epsilon_{i-t} \rangle = (1 - 2\mu)^t$$

- $\langle \Delta(t) \rangle = (1 - 2\mu)^t \Delta(0)$

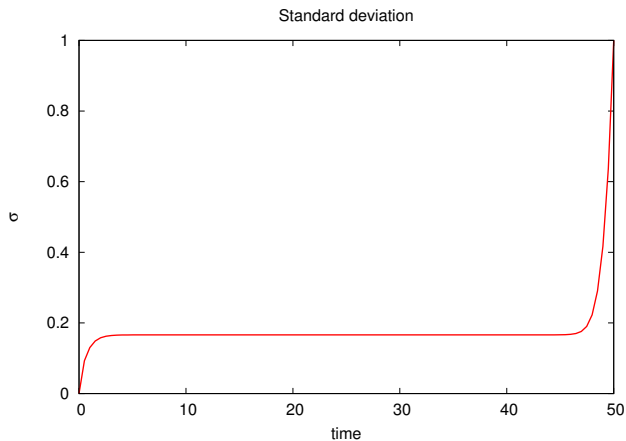
Recurrence

- ▶ For $N \leq t \leq 2N$, some ϵ 's occur twice ($\epsilon^2 = 1$)
- ▶ Only $N - (t - N) = 2N - t$ are independent
- ▶ Thus $\langle \Delta(t) \rangle = (1 - 2\mu)^{2N-t} \Delta(0)$
- ▶ “Anti-Boltzmann” behavior!
- ▶ Variance:

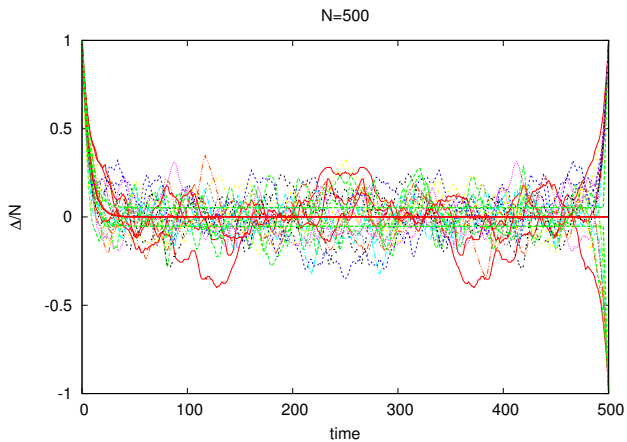
$$\text{Var}[\Delta(t)] \leq NV(t)$$

$V(t)$ grows from 0 to $(1 - (1 - 2\mu)^{2N})\Delta^2(0)$ as t grows from 0 to N

Standard Deviation

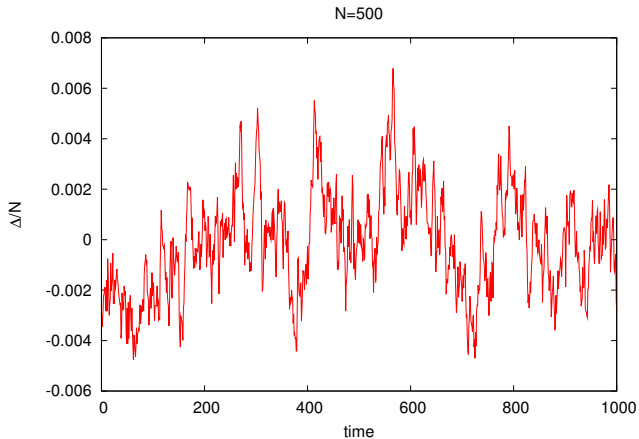


Standard Deviation



Initial conditions

$$W(0) = N/2$$



Conclusions

- ▶ It is worthwhile to go back to Boltzmann's original writings, and not to rely on the Ehrenfests' *Encyclopaedia* article
- ▶ The concept of entropy in B.'s writing is more subtle than the caricature we are accustomed to; it is hard to evaluate, but can be helpful (Swendsen, Lebowitz)
- ▶ The link between irreversibility and cosmology was first envisaged by B., and is still under investigation

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