Understanding Boltzmann's analysis via solvable models

Contents

1   Kac ring model

On a circle we consider n equidistant points $P_1, P_2, \ldots, P_N$, L of which are marked (with a cross).
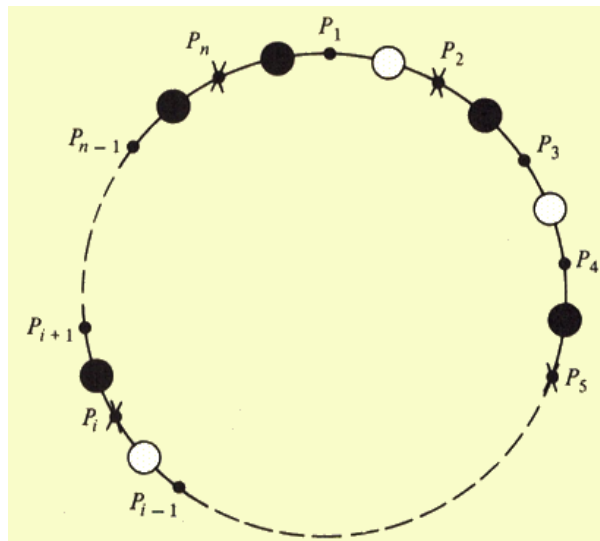
Between successive points there is ball which can be either white (w) or black (b). During an elementary (unit) time interval each ball moves counterclockwise to the nearest site with the following proviso: **when it moves trough a marked point, it changes color, when it passes trough an unmarked one, it doesn't**.

    Suppose that we start with some special initial state, e.g., all white balls, the question is **what happens after a large number of moves**.

1.1   Microstates

The analogy with mechanics is this. The balls are described by their position and by their discrete "velocity," namely their color. One of the simplifying feature of the model is that the "velocity" does not affect the motion. The only reason of the analogy of color with "velocity" is that it changes when the ball collides with a fixed "scatterer." Scattering with fixed objects tend to be easier to analyze than collisions between particles.

Let us write the microscopic equations of motion for the microscopic variable $X(t) = (X_1(t), \ldots X_N(t))$, where

$$X_k(t) = \begin{cases} +1 & \text{if the ball between } P_{k-1} \text{ and } P_k \text{ is black at time } t \\ -1 & \text{if the ball between } P_{k-1} \text{ and } P_k \text{ is white at time } t \end{cases} \tag{1}$$

Let

$$Y_k = \begin{cases} +1 & \text{if there is no marker at point } P_k \\ -1 & \text{if there is a marker at point } P_k \end{cases} \tag{2}$$

Then the "equations of motion" are

$$X_k(t) = Y_{k-1} X_{k-1}(t-1) \tag{3}$$

whose solution is

$$X_k(t) = Y_{k-1} Y_{k-2} \cdots Y_{k-t} X_{k-t}(0) \tag{4}$$

(where the subtractions in the indices are to be taken modulo N). So we have an explicit solution of the equations of motion at the microscopic level. The dynamics is clearly deterministic and reversible: if after a time t we change the orientation of the motion from counterclockwise to clockwise, we return after t steps to the initial state. Moreover the motion is strictly periodic: *after $2N$ steps each point has been crossed twice by each ball, hence they all come back to their original color.* This is analogous to the Poincaré cycles, with the proviso that here the length of the cycle is the same for all states (something that we should not expect in general to be true).
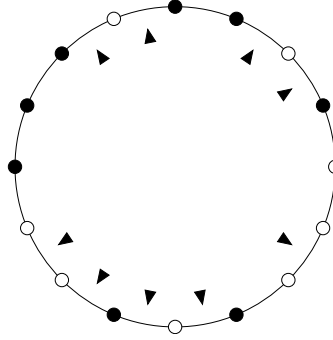
Kac ring with 16 lattice sites and 9 markers

1.2 Macrostates

The obvious macrostates are those in correspondence with the different values N_w, the number of white balls or N_b, the number of black balls since they satisfy the conservation law (constraint) $N_w + N_b = N$. Let us choose those in correspondence of N_b. Consider the macrostate $N_b = k$. Since the system is large, the true macrostates are those in correspondence of N and k large. It is then convenient to write $k = pN$ and parametrize the macrostates in terms of $p \in [0, 1]$ (coarse graining and continuum limit). We shall write M_p for the macrostate $N_b = pN$. Let

$$\Gamma_p = \{X \in \Gamma \mid N_b = pN\}$$

the set of points in phase space corresponding to the macrostate M_p. Since N_b is unconstrained, the "volume" of Γ_p is[1]

$$|\Gamma_p| = \binom{N}{pN} \asymp e^{N[-p \log p - (1-p) \log(1-p)] - o(N)} \tag{5}$$

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[1]See the lecture on coin tossing and the lecture on "Statistical analysis of large systems based on the equivalence of ensembles."

The equilibrium macrostate is the one of largest volume in correspondence of the p that maximizes the exponent in the equation above. As expected, this is $p = 1/2$. In correspondence of this value we have

$$\left|\Gamma_{1/2}\right| \asymp 2^{N-o(N)} \asymp 2^N$$

So we find an instance of the general feature we have highlithed in the previous lecture: *the volume of the equilibrium macrostate is almost the volume of the entire phase space[2] and the non equilibrium macrostates ($p \neq \frac{1}{2}$) have a relative volume that is exponentially small in the number of particles*.

1.3   Boltzmann's entropy

The formula for Boltzmann's entropy of our model is

$$\mathcal{S}_B(X) = S_B(p(X)) \tag{6a}$$

with

$$S_B(p) = \log|\Gamma_p| = -N\left[p\log p + (1-p)\log(1-p)\right] - o(N). \tag{6b}$$

1.4   Analog of the classical solution of Boltzmann

Let us look for a plausible description of the dynamics on the macroscopic scale. In addition to the macroscopic variables $N_w(t)$ and $N_b(t)$, the number of white and black balls at time t, let us introduce the variables $N_w(S,t)$ and $N_b(S,t)$, *the number of white and black balls, respectively, with a marked point ahead at time* t. Here S denote the set of marked points and we have made explicit the dependence on this set.

Note that while $N_w(t)$ and $N_b(t)$ are doubtless macroscopic variables, describing a global feature of the system state, $N_w(S,t)$ and $N_b(S,t)$, on the other hand, contain local information about individual sites—*they cannot be computed without knowing the location of each marker and the color of the ball at every site and this information is specified by the set S of marked points*.

The evolution of the variables $N_w(t)$ and $N_b(t)$ is constrained by the global conservations laws

$$N_w(t) + N_b = N \tag{7}$$

$$N_w(S,t) + M_b(S,t) = L \tag{8}$$

and by the local ones (continuity equations)

$$N_w(t+1) = N_w(t) - N_w(S,t) + N_b(S,t) \tag{9}$$

$$N_b(t+1) = N_b(t) - N_b(S,t) + N_w(S,t) \tag{10}$$

We shall study the behavior of

$$D(S,t) = N_b(t) - N_w(t).$$

Clearly, from the above equations,

$$D(S,t+1) = D(t) + 2(N_b(S,t) - N_w(S,t)) \tag{11}$$

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[2]Under the microcanonical constraints, but here there are no constraints.

A key feature of this system (and of the realistic systems) is that the evolution of the global quantities is not computable only from the global and local conservations laws. In other words, it is not possible to eliminate $N_w(S, t)$ and $N_b(S, t)$ from eqs. (7) to (11). This is known as ***the closure problem***.

Following Boltzmann, we introduce the assumption ("Stosszahlansatz" =collision number hypothesis, or "hypothesis of molecular chaos"): Let $\mu = L/N$ be the density of market points, we assume that

$$N_w(S, t) = \mu N_w(t) \tag{12}$$
$$N_b(S, t) = \mu N_b(t) \tag{13}$$

The intuitive justification is that each ball is "uncorrelated" with the event "the point ahead of time is marked," and so we write

$$N_w(S, t) = \text{[number of white balls]} \times \text{[density of marked points]} = N_w(t) \times \mu$$

Though this assumption looks completely reasonable, it may raise some questions: ***what does "uncorrelated" exactly mean? Why we do introduce a statistical assumption in a mechanical model?*** Moreover, for an actual set S of marked points these relations will generally not be satisfied. However, we hope that this assumption represents, in some sense, the ***typical behavior of large sized rings***.

Under this "Stosszahlansatz," we obtain

$$D(t + 1) = (1 - 2\mu) \, D(t) \,, \tag{14}$$

whose solution is

$$D(t) = (1 - 2\mu)^t \, D(0) \tag{15}$$

and hence if

$$2\mu < 1$$

(as we shall henceforth assume) $D(t) \to 0$ monotonically as $t \to \infty$. So, there is a ***monotonic*** approach to equipartition of white and black balls, that is to equilibrium for which $D = 0$. Note that we get a monotonic approach for ***all*** initial conditions $D(0)$ of the balls. For our model, eq. (14) takes the role of ***Boltzmann equation*** in the kinetic theory of gases.

Clearly, this equation cannot describe the dynamics of one particular ring exactly. For instance, $D(t)$ is generically not an integer anymore. Moreover, $D(t)$ is monotonically decreasing and therefore not time-reversible contrary to what we know about the microscopic dynamics. Thus, we have here an instance of ***Loschmidt's paradox***. Moreover, it is easy to find special microstates which obviously do not tend to equilibrium: start with all white balls and every other point P marked (with $M = N/2$); then after two steps, all balls are black, after four steps they are all white, etc.—the motion is periodic with period 4. More generally, the microscopic dynamics has a recurrence time of at most $2N$. But according to eq. (15) the initial state cannot recur. Thus, we have here an instance of ***Zermelo's paradox***.

1.5   Increase of entropy

Consider

$$p = \frac{N_b(t)}{N} = \frac{\frac{1}{2} + \frac{1}{2}D(t)}{N} = \frac{1}{2} \left[1 + (1 - 2\mu)^t \right] \frac{D(0)}{N} \,.$$

Then, for $t \to \infty$, $p(t)$ will tend monotonically to the value $1/2$. Thus the entropy, given by eq. (6b),

$$S_B(p) = -N \left[p \log p + (1 - p) \log(1 - p) \right] \,,$$

will **increase monotonically** with time and reach in the limit $t \to \infty$ its equilibrium value

$$S_B(1/2) = N \log 2$$

1.6 Statistical analysis of the microscopic model

Since the microscopic model is solvable, with solution of the equations of motion given by eq. (4),

$$X_k(t) = Y_{k-1}Y_{k-2} \cdots Y_{k-t}X_k(0)$$

we can express the macroscopic variables in terms of this solution:

$$D(t) = \frac{1}{N}\sum_{k=1}^{N} X_k(t) = \frac{1}{N}\sum_{k=1}^{N} Y_{k-1}Y_{k-2} \cdots Y_{k-t}X_{k-t}(0) \tag{16}$$

(recall (1)). We want to compute $D(t)$ for large N, for various choices of the initial conditions $X_k(0)$ and various sets S of marked points (determining the Y_ks). It is here that a **statistical assumption** enter. It is the following:

> *Fix an arbitrary initial condition $X(0) = (X_1(0), \ldots, X_N(0))$ and consider all possible set S of marked points with fixed density $\mu = |S|/N$.* **(SA)**

(N. B. one can think of the choice of S as being part of the choice of the initial conditions.)

We shall then switch to our standard notation and write

$$D(t) = \sum_{k=1}^{N} X_k(t) = \sum_{k=1}^{N} Y_{k-1}Y_{k-2} \cdots Y_{k-t}X_{k-t}(0) \tag{17}$$

to emphasize that the only the Y_ks are considered as random variables according to (**SA**).

We shall now compute the sample mean

$$\langle D(t) \rangle = \sum_{k=1}^{N} \mathbb{E}\{Y_{k-1}Y_{k-2} \cdots Y_{k-t}\}X_{k-t}(0) \tag{18}$$

Since according to (**SA**) all equidistant points have equal probability of carrying a marker, the average in eq. (18) must be invariant under index shifts. In particular,

$$\mathbb{E}\{Y_{k-1}Y_{k-2} \cdots Y_{k-t}\} = \mathbb{E}\{Y_1Y_2 \cdots Y_t\},$$

so that

$$\langle D(t) \rangle = \mathbb{E}\{Y_1Y_2 \cdots Y_t\} \sum_{k=1}^{N} X_{k-t}(0) = \mathbb{E}\{Y_1Y_2 \cdots Y_t\}\, D(0) \tag{19}$$

Our remaining task is to find an explicit expression for $\mathbb{E}\{Y_1Y_2 \cdots Y_t\}$, a quantity which only depends on the distribution of the markers, but not on the balls. We distinguish two cases.

$$\text{(a)} \quad 0 \le t \le N$$
$$\text{(b)} \quad N \le t \le 2N$$

(a) When $0 \leq t \leq N$ there are no periodicities, which means that all factors $Y_1, Y_2, \ldots, Y_t$ are independent and the only global condition is that $\mu = M/N$. Thus[3]

$$\mathbb{E}\{Y_1 Y_2 \cdots Y_t\} = \mathbb{E}\{Y\}^t$$

and

$$\mathbb{E}\{Y\} = (+1)(1-\mu) + (-1)\mu = 1 - 2\mu \,,$$

whence

$$\mathbb{E}\{Y_1 Y_2 \cdots Y_t\} = (1-2\mu)^t \tag{20}$$

Inserting this expression into eq. (19), we obtain

$$\langle \mathsf{D}(t) \rangle = (1-2\mu)^t \langle \mathsf{D}(0) \rangle \tag{21}$$

the same expression (15) we obtained through our "molecular chaos assumption". This result is encouraging, because it shows that the relatively crude "molecular chaos assumption" may be related to the average over a statistical ensemble.

(b) When $N \leq t \leq 2N$, it can be shown that (exercise)

$$\langle \mathsf{D}(t) \rangle = (1-2\mu)^{2N-t} \langle \mathsf{D}(0) \rangle \tag{22}$$

As the exponent on the right hand side is negative on the interval $N \leq t \leq 2N$, the sample mean $\langle \mathsf{D}(t) \rangle$ increases on this interval and, in particular, recurs to its initial value for $t = 2N$. This behavior is called *anti-Boltzmann*.

1.7   Law of large numbers and typicality

We have seen that he average behavior, over the sets S of marked points with the same density, for times $t \leq N$, behaves as prescribed by "Boltzmann's equation" (14). But this does not, by itself, imply that the ensemble average represents in some way the typical behavior of the members of the sample, or that it is even close to any individual system trajectory. For example, at the half-recurrence time $t = N$, each ball is back at its initial position with a possible global change of color whenever the total number of markers is odd, so that $\mathsf{D}(N) = \pm\mathsf{D}(0)$, while, by eq. (21), $\langle D(N) \rangle$ is close to zero (see fig. below).

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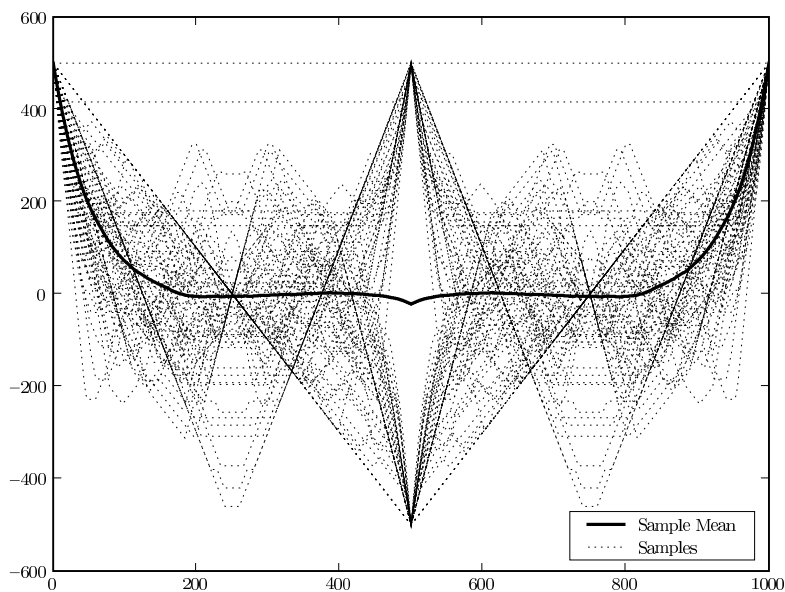
[3]See last section of the lecture "Statistical analysis of large systems based on the equivalence of ensembles."

Sampling on 400 Kac rings with $N = 500$ initially all occupied by black balls. Time in abscissa and $D(t)$ in ordinate (From "G. A. Gottwald, M. Olivier, Boltzmann's dilemma — an introduction to statistical mechanics via the Kac ring (2009)").

For small t, on the other hand, most members of the sample stay close to the sample mean. Both these regimes are clearly visible in the figure above. How can we quantify this observed behavior? We will answer this question by estimating the variance of the ensemble as a function of t.

It can be shown that (exercise) that for $t < N/2$ we have the following bound

$$\text{Var}\left[\mathsf{D}(t)\right] \leq N\left[\frac{1 - (1 - 2\mu)^{2t}}{2\mu(1-\mu)} - 1 - (2t-1)(1-2\mu)^{2t}\right] \tag{23}$$

and that the bound is strictly increasing on $0 \leq t \leq N/2$ (provided that $0 < \mu < 1/2$). We also leave as an exercise to compute the analogous bound for $N/2 \leq t \leq N$.

The most important consequence we can draw from the above bound is that the variance scales like N, the standard deviation thus like $\sqrt{N}$ so long as we remain some distance away from the half-recurrence time $t = N$. This behavior indicates that as N gets large, the tube of the solution curves about $\langle \mathsf{D}(t) \rangle$ with a width of one standard deviation, as depicted in the figure below, becomes narrow relative to $D_{\max} = N$. Thus, for short times and large N we can conclude that **_the average behavior is typical_**.

In the figure below (From "G. A. Gottwald, M. Olivier, op. cit.") there is a magnified view of the time window $0 \leq t \leq N$ where the solution depicted in the figure above has "Boltzmann behavior." Also depicted is the neighborhood with the radius of one standard deviation about the predicted ensemble mean.
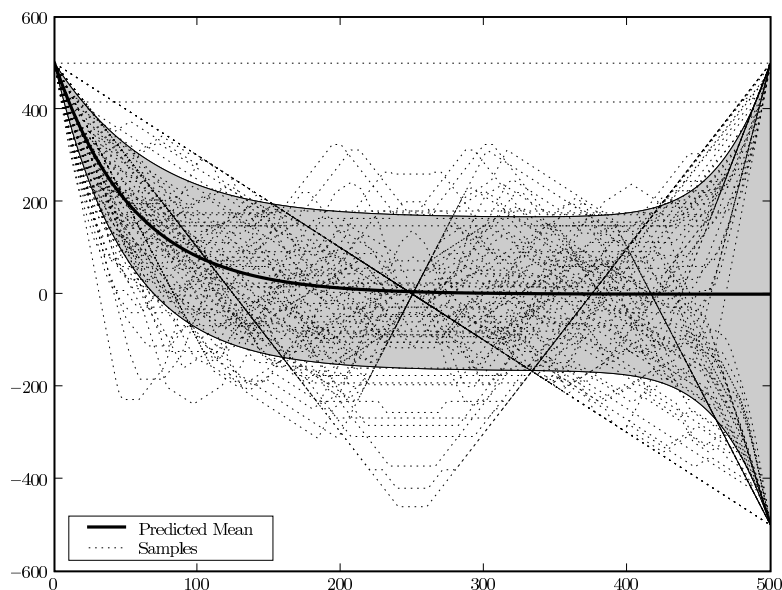
Next, we shall make this asymptotic regime more precise.

1.8 Continuum limit

So far, everything we have talked about was fully discrete and finite. We shall now pass to the **_continuum limit_** $N \to \infty$ in a rigorous and precisely defined sense. The key idea is (like in the thermodynamic limit) is to identify quantities which neither diverge nor go to zero and can thus carry nontrivial information about the system behavior into the limit.

- The first of such quantities is obvious:

$$\mathsf{d}(t) = \frac{\mathsf{D}(t)}{N}$$

Though for a ring of a fixed size, d takes only a discrete set of values, every real value of d(t) in the interval $[-1, 1]$ can be approximated arbitrarily closely by a state of a finite Kac ring of sufficiently large size. In terms of d, eqs. (21) and (23) read

$$\langle \mathsf{d}(t) \rangle = (1 - 2\mu)^t \langle \mathsf{d}(0) \rangle \qquad (24)$$

$$\mathrm{Var}\left[\mathsf{d}(t)\right] \le \frac{1}{N}\left[\frac{1}{2\mu(1-\mu)} - 1\right] \quad (t < N) \qquad (25)$$

- Second, we want the system within one unit of macroscopic time to be affected by very many steps of the underlying microscopic Kac ring dynamics. This is achieved by introducing a macroscopic time variable τ which relates to microscopic time t via a scaling law of the form

$$\tau = \frac{t}{N^\alpha} \qquad (26)$$

for some exponent $\alpha > 0$.

- Third, the behavior of the system within one unit of macroscopic time should be nontrivial as $N \to \infty$.

Substituting τ into eq. (24), we obtain

$$\langle \mathsf{d}(N^\alpha \tau) \rangle = (1 - 2\mu)^{N^\alpha \tau} \langle \mathsf{d}(0) \rangle$$

and thus see that it is necessary to have $\mu \to 0$ in this limit ("Boltzmann-Grad limit"). To be definite, we set

$$2\mu = \frac{1}{N^\beta} \qquad (27)$$

for some exponent $\beta > 0$. We shall also require that $\beta < 1$, for else there would be, on average, less than one marker per ring so that, in the limit, most realizations would be uninteresting. With $\beta \in (0, 1)$, the scaling law (27) expresses that the average number of markers $N\mu = (1/2)N^{1-\beta}$ goes to infinity, but at a lesser rate than the size of the ring.

Plugging the scaling assumptions into eq. (24), we find that

$$(1 - 2\mu)^t = \left(1 - \frac{1}{N^\beta}\right)^{\tau N^\alpha} \quad \to \quad \begin{cases} 0 & \text{if} \quad \beta < \alpha \\ e^{-\tau} & \text{if} \quad \beta = \alpha \\ 1 & \text{if} \quad \beta > \alpha \end{cases}$$

as $N \to \infty$ for any fixed $\tau > 0$. Hence, the condition $\alpha = \beta$ is necessary for obtaining a nontrivial large system limit.

Under this assumption, the limit Kac ring dynamics becomes

$$\langle \mathsf{d}(\tau) \rangle = e^{-\tau} \langle \mathsf{d}(0) \rangle \qquad (28)$$

$$\mathrm{Var}\left[\mathsf{d}(t)\right] \le \frac{1}{N}\left[\frac{1}{2\mu(1-\mu)} - 1\right] \sim \frac{1}{N}\frac{1}{2\mu} = N^{\beta-1} \to 0 \text{ as } N \to \infty. \qquad (29)$$

(recall that $\beta < 1$). This proves that, in the limit, for almost all sets S of given density, the solutions follow the average dynamics; the macroscopic equation (28) describes the macroscopically observable behavior of the overwhelming majority of the solution curves.

The figure below (From "G. A. Gottwald, M. Olivier, op. cit.") illustrates the relation between scaled and unscaled variables, and the resulting limiting behavior of the ensemble.
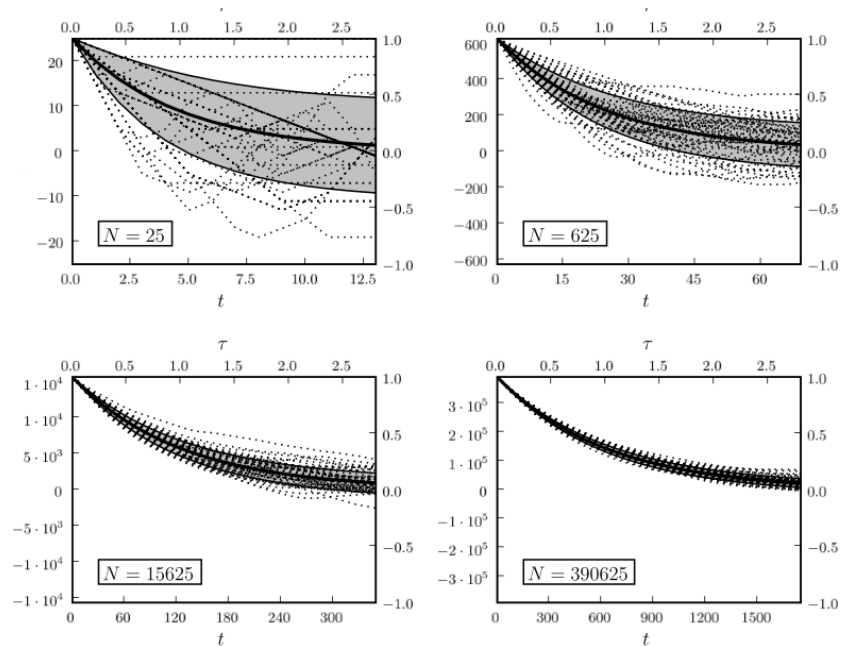
Convergence of trajectories to the ensemble average as the size of the Kac ring grows large. The two axes are labeled both in unscaled and scaled variables with $\alpha = \beta = 1/2$.

N.B. The scaling laws for t and μ may look arbitrary. This is correct in the sense that such scalings are generally outside the scope of the fundamental laws of physics and lack uniqueness in any strict mathematical sense. It is rather up to the ingenuity of the modeler to come up with a scaling which induces a mathematically tractable and well-behaved limit —as in our example above—and, when modeling real-world systems, is consistent with the relevant physical parameters.

(We use limits, as the thermodynamic limit or the continuum limit not because we are mathematically sophisticated, but on the contrary because we are not sufficiently mathematically sophisticated to understand what is going on in a large finite system on the microscopic time scale)

1.9   Morals

- The Poincaré recurrence is easily solved: each solution curve is periodic. So that if we did not fix t, **and then** letting $N \to \infty$, we would not observe "irreversible" behavior. But this limit is correct. The recurrence time is enormous compared to any physically accessible time.

- The same is true for the reversibility objection. Let us consider as initial condition a reversed microstate after time t. Then we now that, for that microstate and that set S, $\mathsf{d}(t)$ will not be close to $(1 - 2\mu)^t$ at time t (since it will be back to its initial value, say 1, corresponding to all particles black). But all we are saying is that for the vast majority of Ss this behavior will be seen. For the reversed microstate, the original set S happens to be exceptional.

- The model, although perfectly "irreversible," is not ergodic. Indeed, since it is periodic, no trajectory can visit more than $2N$ microstates. But the phase space contains 2^N microstates. So, only a very small fraction of phase space is visited by a trajectory.

- This nicely illustrates that ergodicity is not necessary for the foundations of statistical mechanics. What is used here is only the fact that the overwhelming majority of microsates give to the macroscopic variables a value close to their equilibrium value.