On the role of dynamics for the foundations of statistical thermodynamics

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11 June 2009

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Time-dependent specific heat

Birge Nagel PRL

The exchanged heat is defined by

$$\delta Q \stackrel{\text{def}}{=} < E(t) - E(0) >$$

Fluctuation–dissipation theorem gives

$$< E(t) - E(0) > = (C_V - c(t))\delta\beta + \ldots$$

where C_V is the canonical specific heat while

$$c(t) \stackrel{\text{def}}{=} < E(t)E(0) >_\beta - < E(t) >_\beta < E(0) >_\beta$$

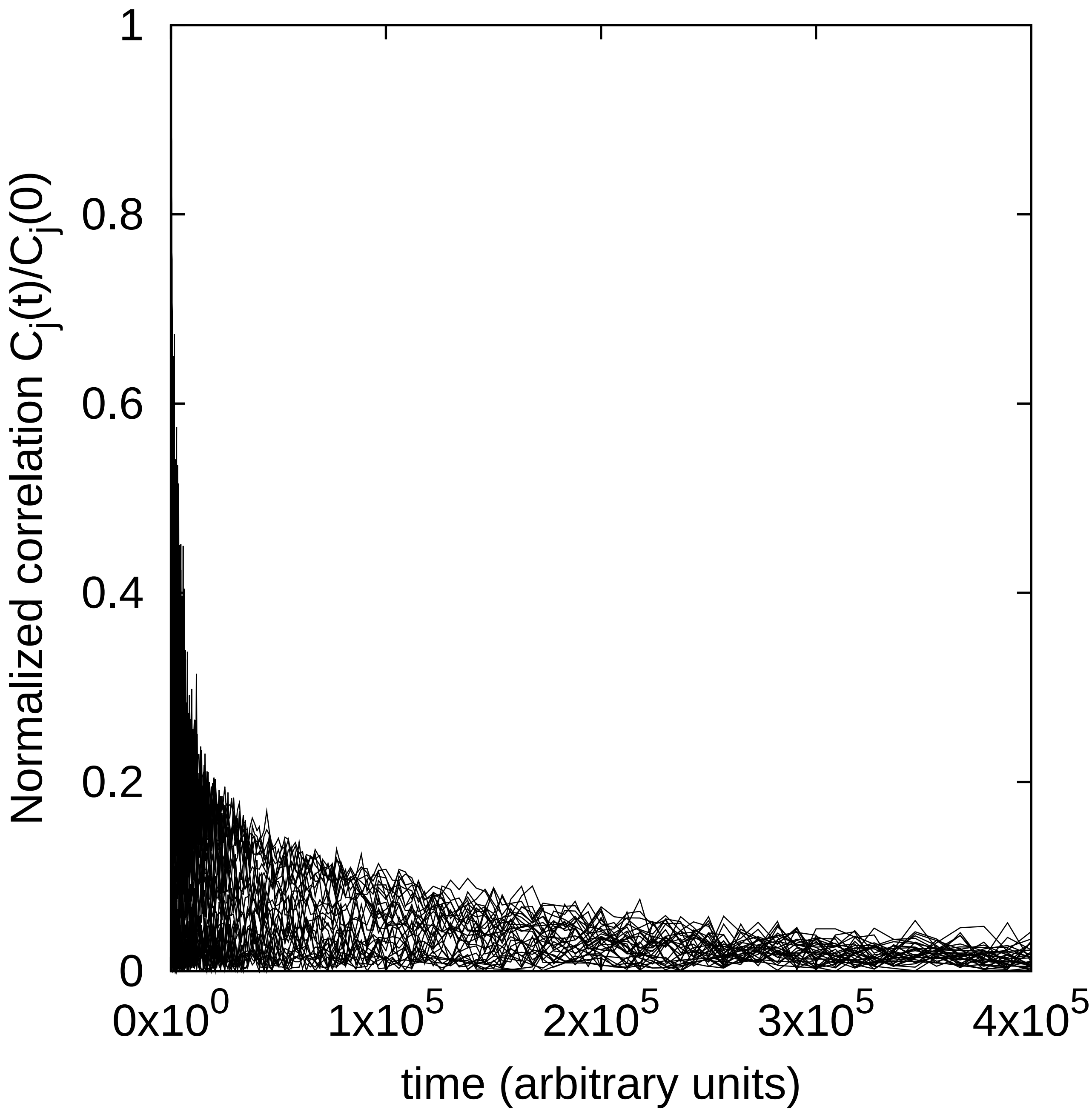
is the autocorrelation function of the energy. This can be proven in the hypothesis that

1. Gibbs measure is invariant

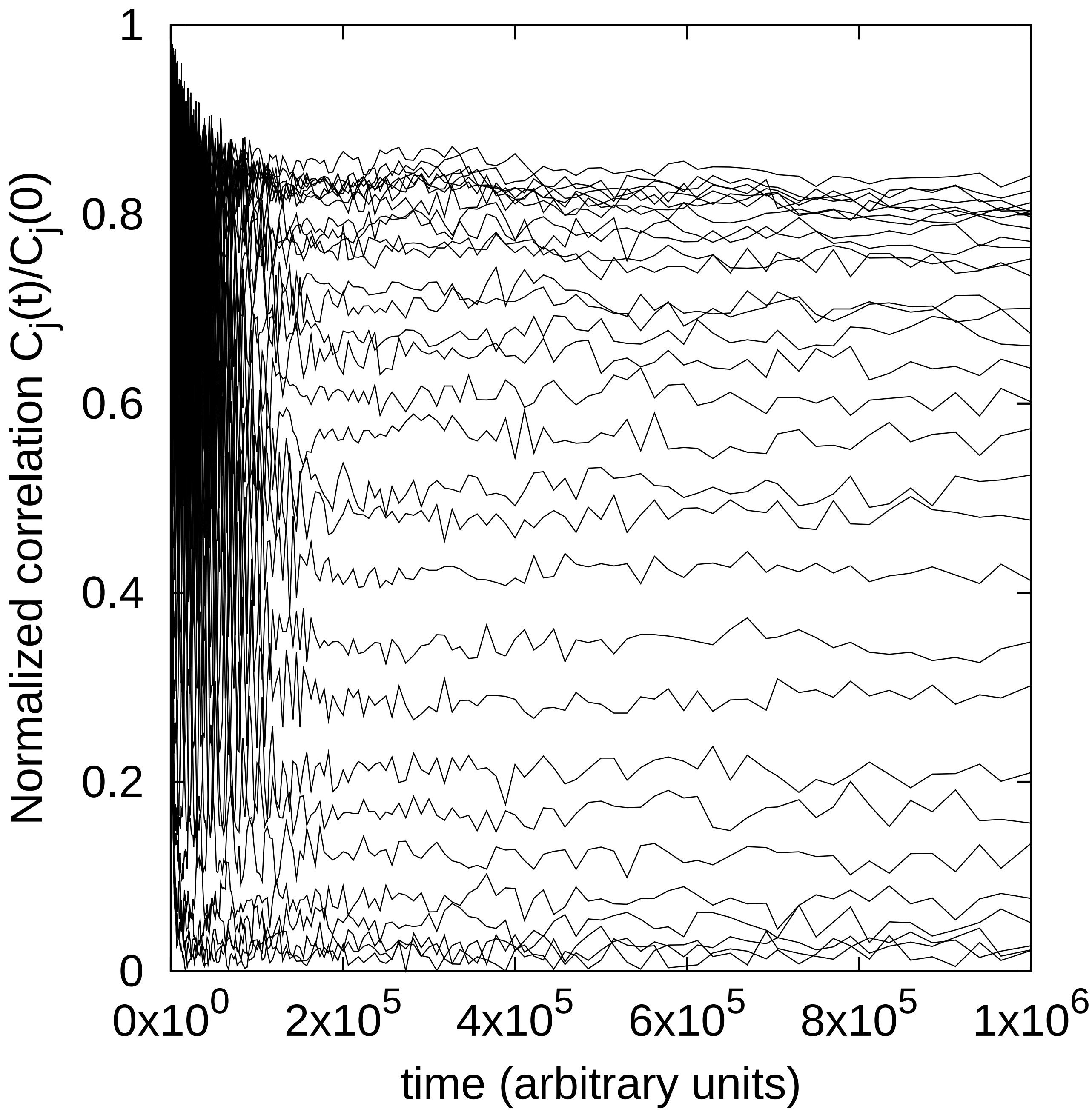
2. The dynamics is time reversible

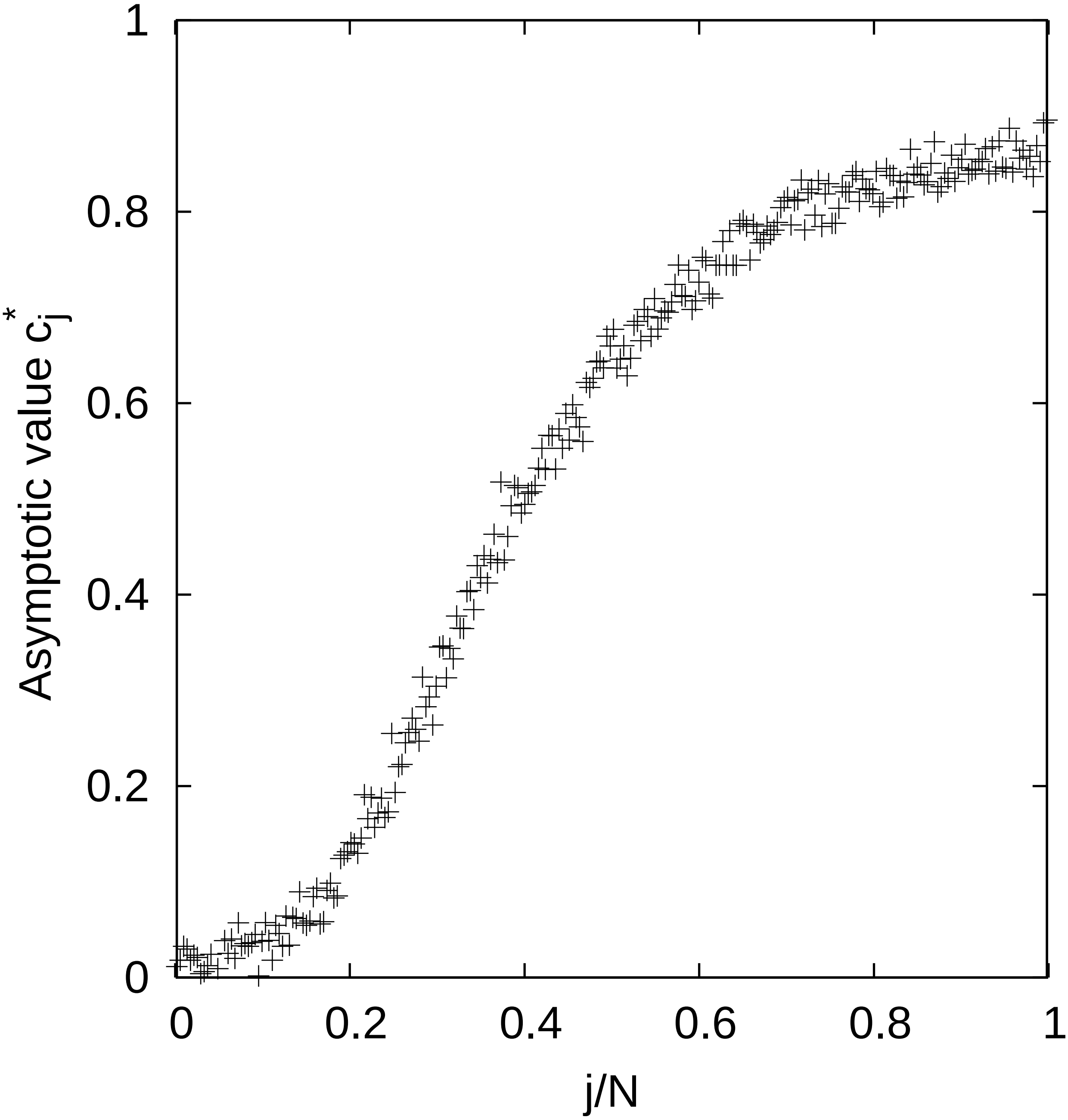
3. Energy interaction can be neglected in computing the averages

If the autocorrelation stabilizes, on a certain time–scale (undercooled liquid for example), and does not vanish, the specific heat is not the canonical one. Next figures show what happens in the case of a perfect crystal, i.e. a FPU system (the number of particle ranges from 512 to 4024).

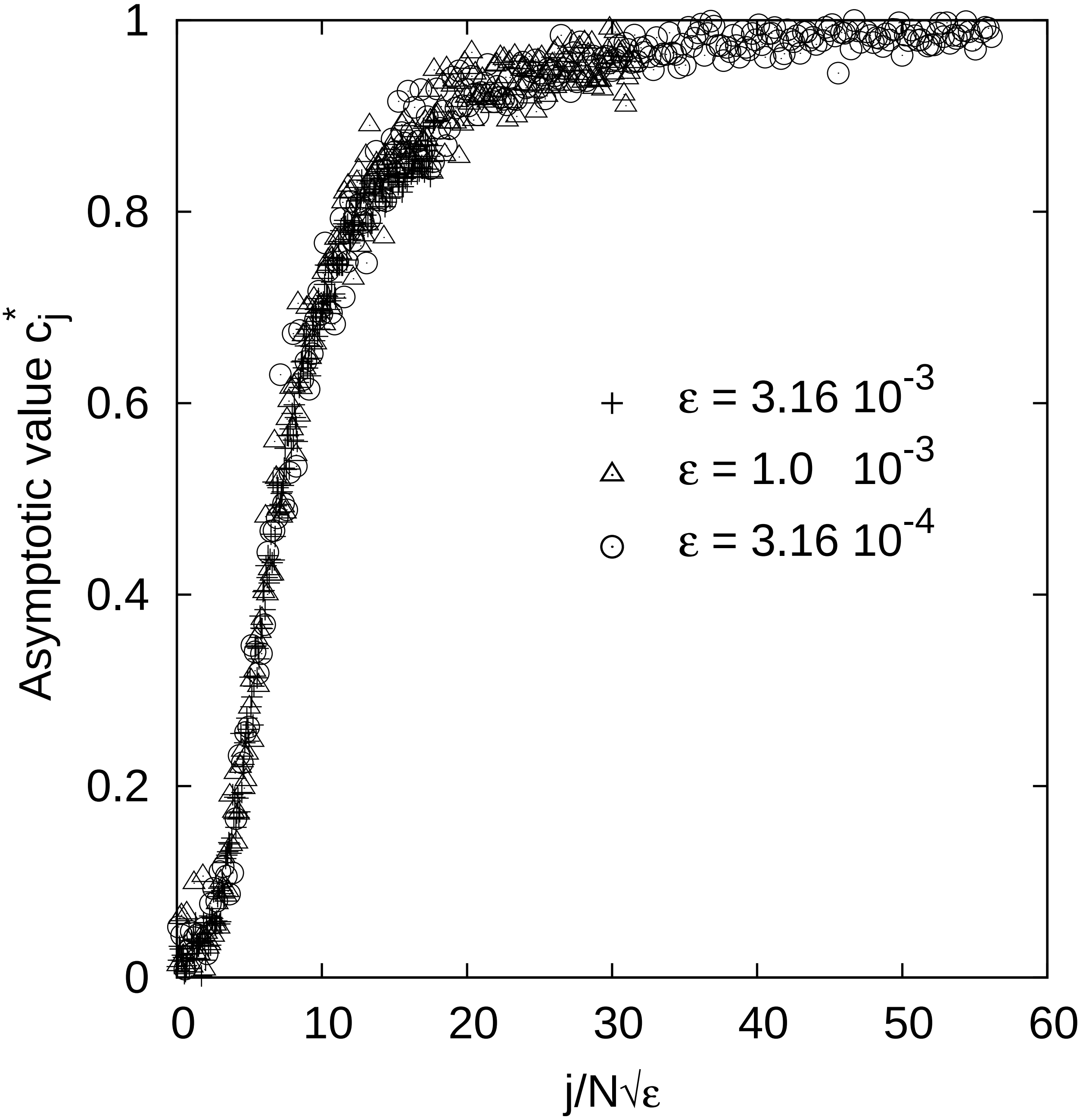


1
0.8
0.6
0.4
0.2
0
Normalized correlation $C_j(t)/C_j(0)$
$0x10^0$
$1x10^5$
$2x10^5$
$3x10^5$
$4x10^5$
time (arbitrary units)

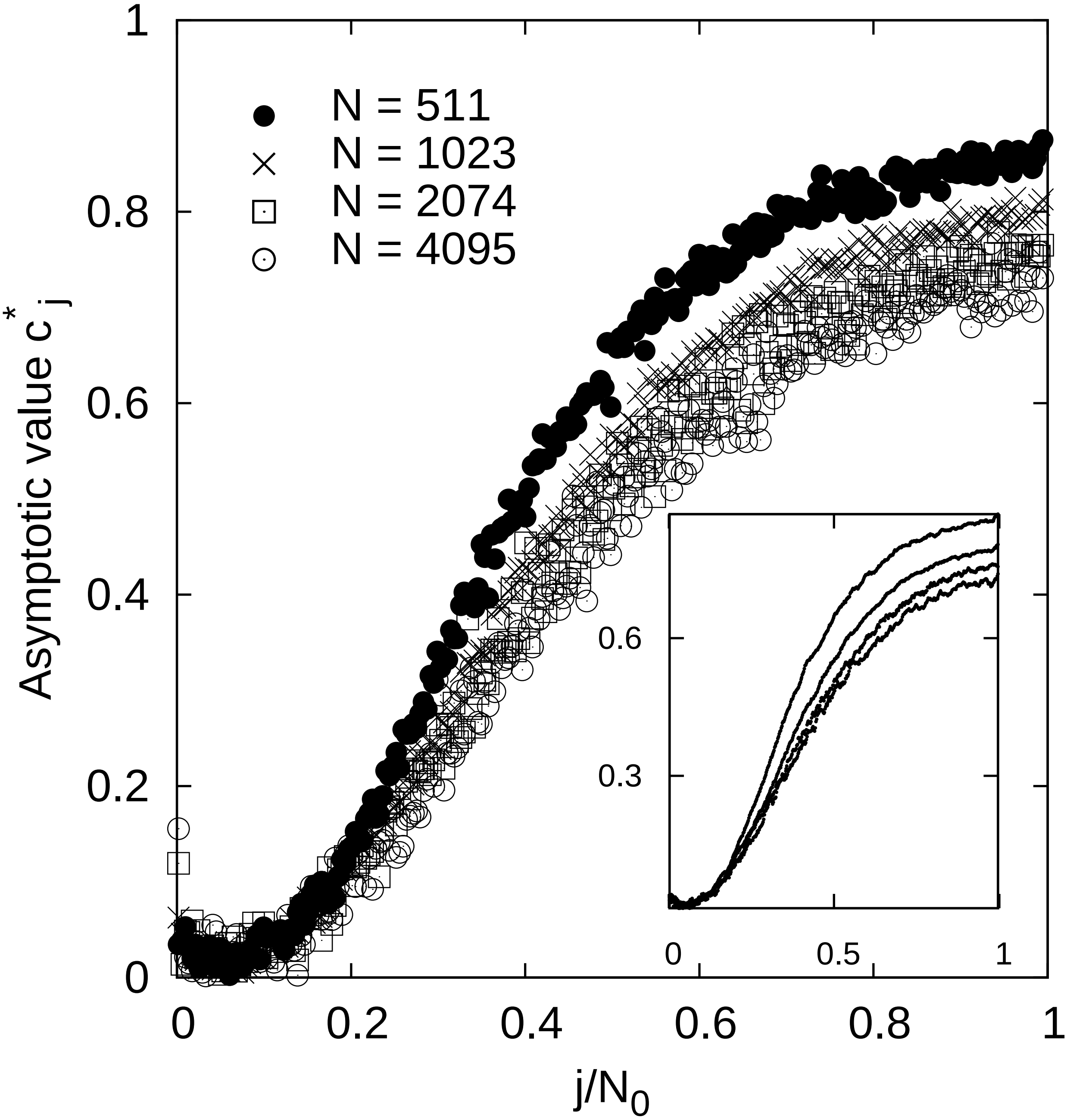

1
0.8
0.6
0.4
0.2
0
Normalized correlation $C_j(t)/C_j(0)$
0x10^0
2x10^5
4x10^5
6x10^5
8x10^5
1x10^6
time (arbitrary units)



1
0.8
0.6
0.4
0.2
0
Asymptotic value c*j
0
0.2
0.4
0.6
0.8
1
j/N



1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
Asymptotic value c*j
j/N√ε
ε = 3.16 10-3
ε = 1.0 10-3
ε = 3.16 10-4



N = 511
N = 1023
N = 2074
N = 4095
Asymptotic value c^*_j
j/N_0
0
0.2
0.4
0.6
0.8
1
0.3
0.6
0.5

There is a PARADOX.

One starts up with an invariant measure, but this is not the right ones to do Thermodynamics. (Poincaré 1906, Nernst 1916)

How can this happen?

Does there exist an ensemble adapted to such a situation?

General Setting

Given a map $\Phi : \mathcal{M} \to \mathcal{M}$ and an orbit $x_{n+1} = \Phi(x_n)$, $n = 0, \ldots, N$, one is interested in computing the time–average of a dynamical variable $A : \mathcal{M} \to \mathbf{R}$. If $\mathcal{M} = \cup \mathcal{Z}_j$ is a partition of $\mathcal{M}$ in K cells one has

$$\bar{A} \stackrel{\text{def}}{=} \frac{1}{N} \sum_{n=0}^{N} A(x_n) \simeq \frac{1}{N} \sum_{j=1}^{K} n_j(x_0) A_j$$

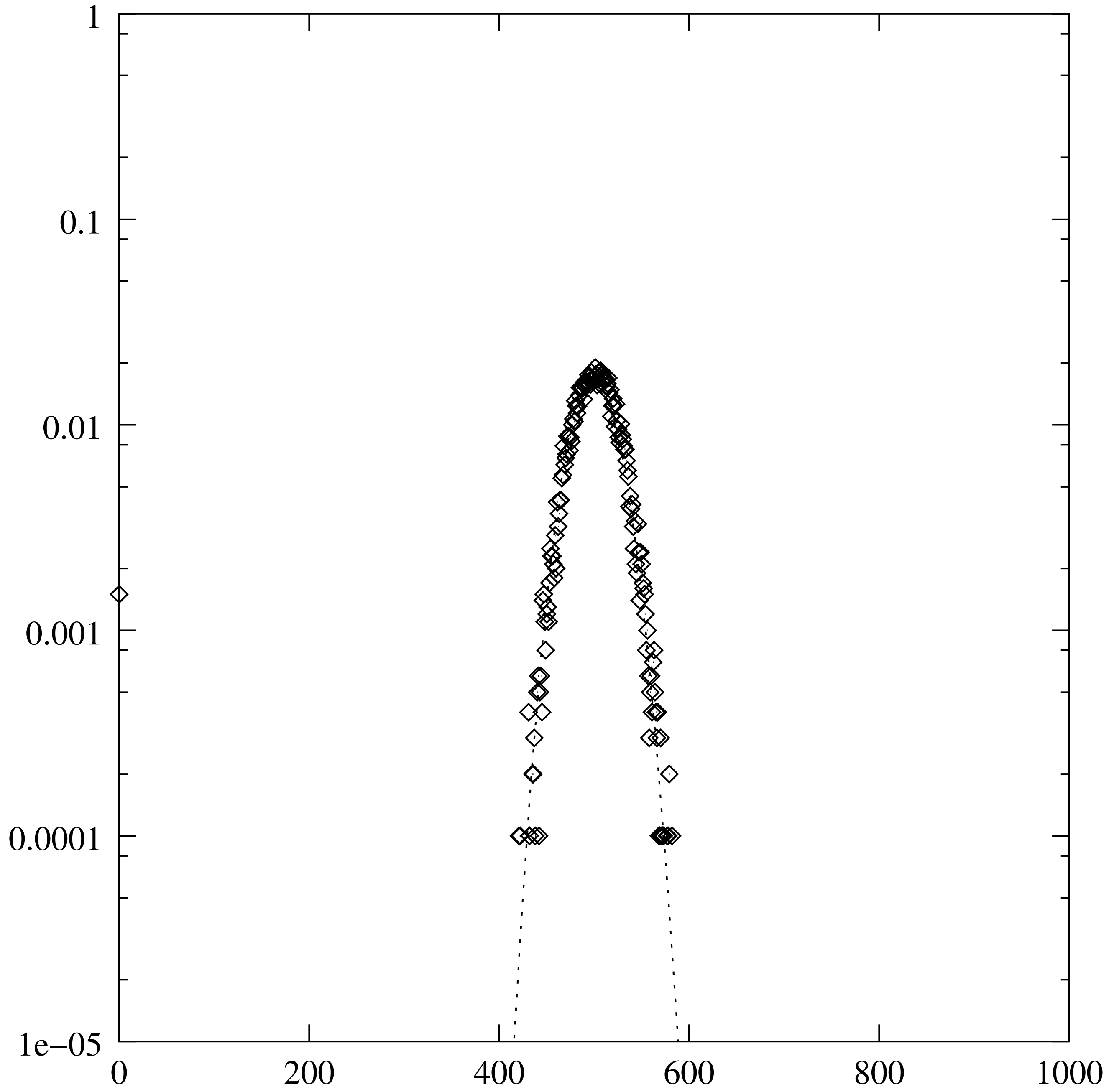
where n_j is the *sojourn time*. If one assigns a p.d.f. for the initial data x_0 (for example Lebesgue) and averages one gets

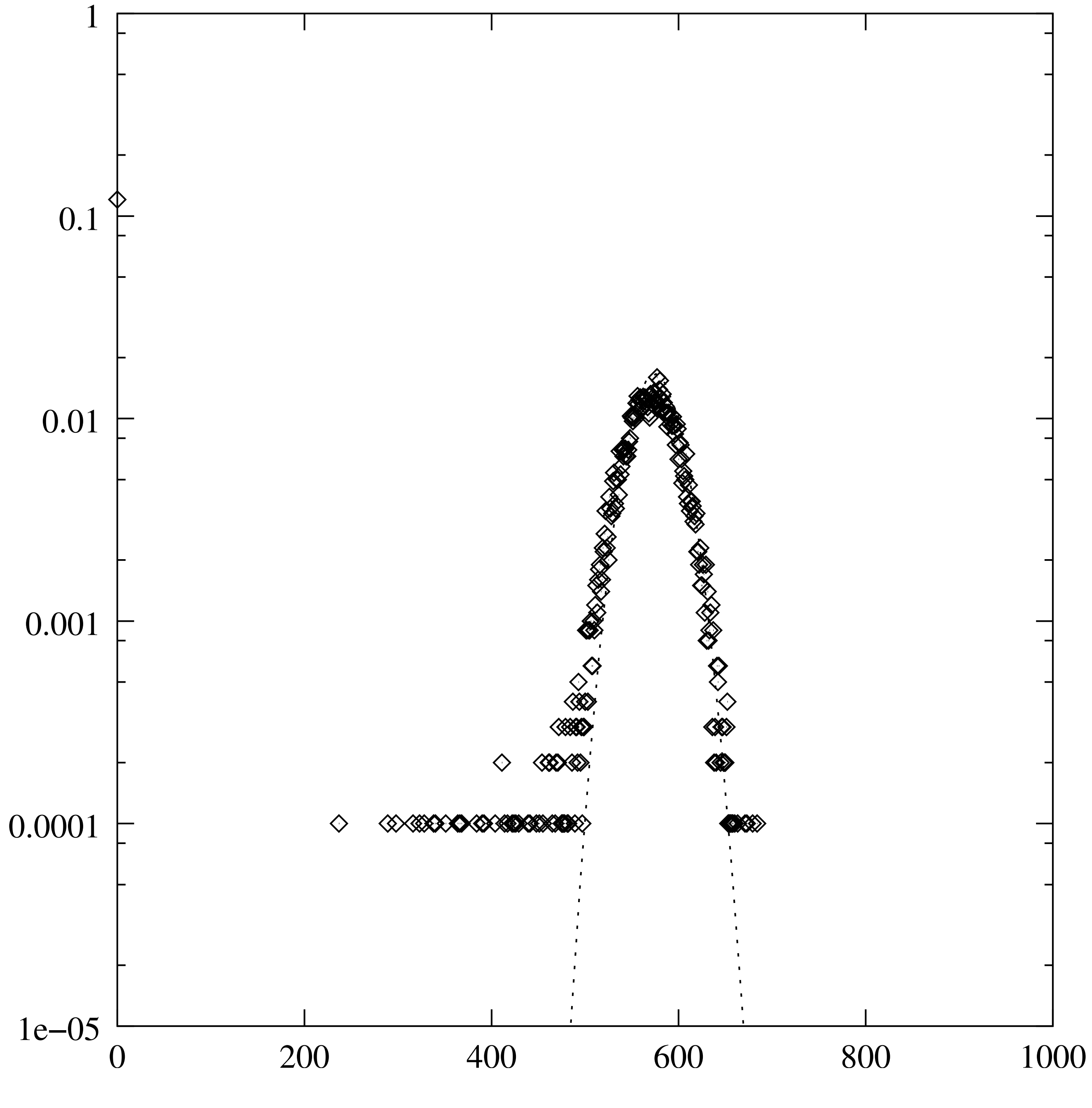
$$< \bar{A} > = \frac{1}{N} \sum_{j=1}^{K} < n_j > A_j$$

Given a p.d.f for the initial data, n_j turns out to be a RANDOM VARIABLE with a p.d.f $F_j(n)$ (i.e. $F_j(n)$ is the probability that $n_j < n$).

Hypothesis One assumes that the random variables n_j are independent, except for

$$\sum_j n_j = N$$


1
0.1
0.01
0.001
0.0001
1e−05
0
200
400
600
800
1000



1
0.1
0.01
0.001
0.0001
1e−05
0
200
400
600
800
1000

In thermodynamics one has the condition that the time average of energy has a given value U, i.e.

$$\frac{1}{N}\sum n_j\varepsilon_j \equiv U \left(\text{and } U \neq < E > \stackrel{\text{def}}{=} \frac{1}{N}\sum < n_j > \varepsilon_j\right)$$

So, one has the problem to compute the conditional probability, i.e. to compute

$\bar{\nu}_j \equiv$ mean sojourn time when mean energy is U

Knowing $\bar{\nu}_j$ one gets

$$< \bar{A} >_U = \frac{1}{N}\sum_{j=1}^{K} \bar{\nu}_j A_j$$

Notice that $\bar{\nu}_j$ has to satisfy the relations

$$N = \sum_{j=1}^{K} \bar{\nu}_j \ , \quad U = \frac{1}{N}\sum_{j=1}^{K} \bar{\nu}_j \varepsilon_j$$

The quantities $\bar{\nu}_j$ are computed as follows. Define the function

$$\exp\Big(\chi_j(z)\Big) \stackrel{\text{def}}{=} \int\limits_0^{+\infty} e^{-nz}\, \mathrm{d}F_j$$

then one has

$$\bar{\nu}_j = -\chi_j'\Big(\frac{\theta}{N}\varepsilon_j + \alpha\Big)$$

where θ and α are determined by imposing that U is the mean energy, and the number of total visits is N. So the time-average of A turns out to be given by

$$< \bar{A} >_U = -\frac{1}{N}\sum_{j=1}^{K} A_j \chi_j'\Big(\frac{\theta}{N}\varepsilon_j + \alpha\Big)$$

Define the exchanged heat as the difference

$$\delta\mathcal{Q} = \mathrm{d}U - \delta\mathcal{W}$$

where $\delta\mathcal{W}$ is the mean work performed by changing the external parameter. Then one finds

$$\delta\mathcal{Q} = \frac{1}{N}\sum_j \varepsilon_j \mathrm{d}\bar{\nu}_j$$

One then finds that this expression admits θ/N as an *integrating factor*. In fact, introducing

$$\nu_j \stackrel{\text{def}}{=} -\chi_j'(z)$$

as an independent variable one indeed has

$$\delta\mathcal{Q} = \frac{N}{\theta}\mathrm{d}\Big(\frac{1}{N}\sum h_j(\bar{\nu}_j)\Big)$$

where $h_j(\nu)$ is the Legendre transform of the function $\chi_j(z)$. As a consequence the quantity

$$S = \sum_j h_j(\bar{\nu}_j)/N$$

can be identified with entropy, and

$$\beta = \theta/N$$

with inverse temperature.

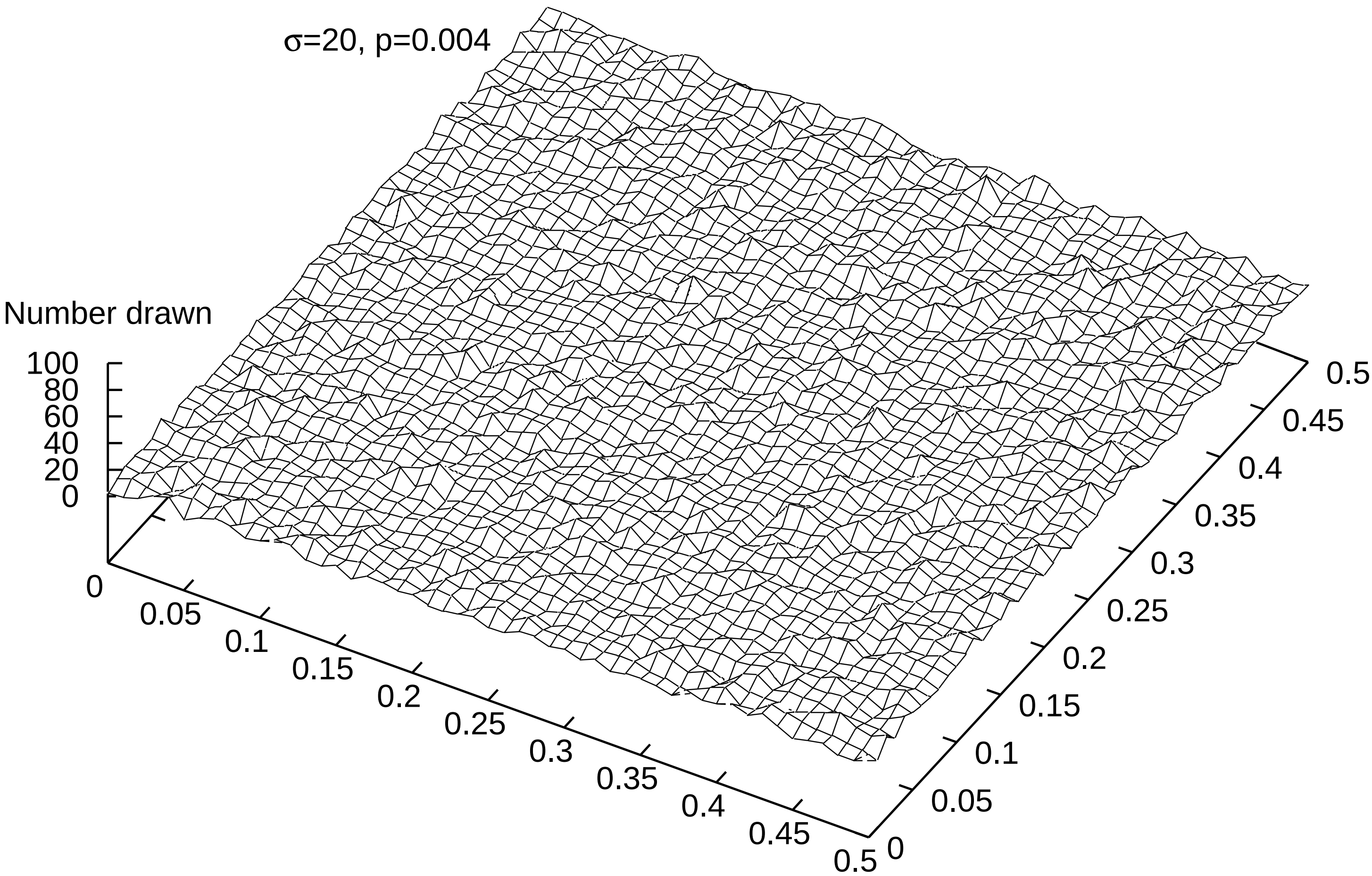
Now, if the p.d.f. $F_j(n)$ is a Poisson distribution, it turns out that

$$\chi_j(z) = p\,\mathrm{exp}(-z) - p$$

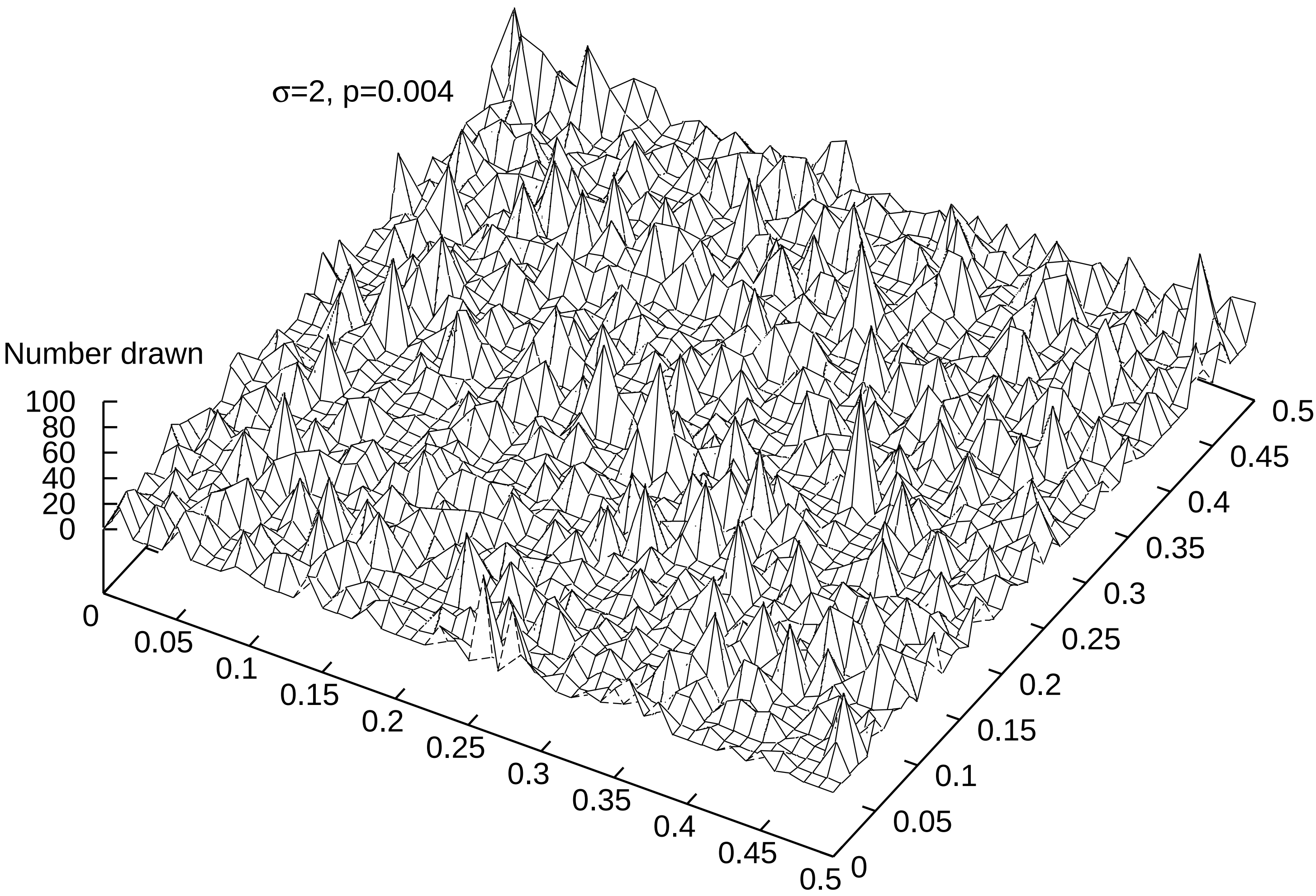
and the measure turns out to be equal to the **Gibbs** distribution (and the specific heat turns out to be the canonical one). Instead if

$$\chi_j(z) = p(1 + \frac{z}{\sigma})^{-\sigma} - p$$

the measure becames equal to the so called $q-$**Tsallis** distribution. Here q is given by $\sigma = \frac{1}{1-q}$.



σ=20, p=0.004
Number drawn
100
80
60
40
20
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5


σ=2, p=0.004
Number drawn
100
80
60
40
20
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5

Return Times

DEFINITION. If $x_0 \in \mathcal{Z}_j$, the return time $t_j(x_0)$ is defined as

$$t_j(x_0) = \min\{\, n > 0 \,\text{s.t. } x_n \in \mathcal{Z}_j\}$$

In the following hypothesis

HYPOTHESIS: *The subsequent visits of the orbit to the same cell are* recurrent events.

between the p.d.f $G(t_j)$ of the return times and the p.d.f. $F_j(n)$ of the sojourn times one has the relation stated in the following

Theorem(Feller, 1949): Defining $\widehat{G}_j(s) = \sum G_j(n)s^n$, then the function $\exp(\chi_j(z))$ is the N-th coefficient of the series expansion of the function

$$F_j(s) \stackrel{\text{def}}{=} \frac{1}{1 - e^{-z}\widehat{G}_j(s)} \frac{1 - \widehat{G}_j(s)}{1 - s}$$

in powers of s.