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Far from equilibrium: Patterns, fluctuations, and extreme statistics

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We studied two topics within the general framework of statistical physics: i) the control of precipitation patterns and ii) the extreme statistics of correlated systems. The first part aimed at understanding the emergence of spatial patterns built by reaction-diffusion fronts and giving answer to the question: How do external fields and fluctuations influence the formation of precipitation patterns? We have shown, both experimentally and theoretically, that electric fields and currents are effective tools in the control and design of patterns. Furthermore, we have also demonstrated that the presence of noise is essential in the formation of such structures as helicoids and helices. In connection with extreme statistics, we focused on answering the question: How do correlations modify the extreme event statistics?. Building upon our previous work on correlated signals with $1/f^{\alpha}$ power spectrum, we developed a picture gallery of the distribution of the extreme values of the signal for the experimentally relevant case of measuring the maximum with respect to the initial value. It was also shown that the density of near extreme events is related to the extreme value distribution, and this connection allowed us to develop a scaling theory of the order statistics of $1/f^{\alpha}$ signals.

CONTROL OF PRECIPITATION PATTERNS

Introduction

The emergence of spatial order has been a major line of research in non-equilibrium statistical physics during the last decades [1, 2], and the field has matured to the point where one may try to address more practical problems. We have been working along these lines for more than two decades and, building on our previous results, we studied now the following questions: *How do external fields and fluctuations influence the formation of precipitation patterns?*. The relevance of the question arises from recent recognition that precipitation patterns built by reaction-diffusion fronts may be used in the so called bottom-up methods of building structures. Furthermore, this rather inexpensive precipitation processes could be, in principle, used for engineering micro- and nano-scale patterns. Accordingly, the goal of our project was to understand how the reaction-diffusion fronts can be controlled and how to turn this control into methods of designing and realizing precipitation patterns.

Control by electric field and electric current

Reaction-diffusion systems yielding precipitation patterns are well known [3]. It has been also been known that the precipitation patterns can be influenced by appropriately chosen geometry [4], boundary conditions [5], or by a combined tuning of the initial and boundary conditions [6–8]. Although these control methods are straightforward, they are unwieldy, and more flexible approaches are clearly needed. We introduced a novel method based on the use of pre-designed electric fields and currents for regulating the dynamics of the reaction zones in the system.

Our idea of regulation stems from the observation that precipitation patterns are often formed in the wake of moving reaction fronts [1, 3]. Consequently, control over the precipitation pattern can be realized through controlling the properties of the reaction front and, in particular, by controlling the amount of reaction product emerging at a given position and at a given time by employing time-dependent electric fields and currents. The reason for the effectiveness of the method is that the reactions usually take place between ions whose flux can be controlled by electric fields.

The actual realization of control was based on our earlier studies [9] of the importance of the ionic nature of the reagents and on the concurrent calculation of the spatial- and temporal properties of the fronts in the presence of external fields and currents [10, 11]. Combining these results with our earlier theory [12, 13] of precipitation patterns for the case of Liesegang phenomena [3], we arrived at a theoretical framework which allowed us to design patterns by pre-calculating the time-dependence of the field needed for the given pattern [14]. In particular, we showed how to make periodic the quasi-periodic Liesegang patterns, or how to make precipitation bands with a given sequence of distances between them.

The theory was put to test by following the theoretical prescription and manipulating experimental Liesegang patterns [14] as shown in Fig.1. In this case the band pattern emerged from the reaction diffusion process $2AgNO_3 + K_2Cr_2O_7 \rightarrow \underline{Ag_2Cr_2O_7} + 2KNO_3$, and the precipitate bands (formed by $Ag_2Cr_2O_7$) are the dark bands in the picture. The pattern-forming process

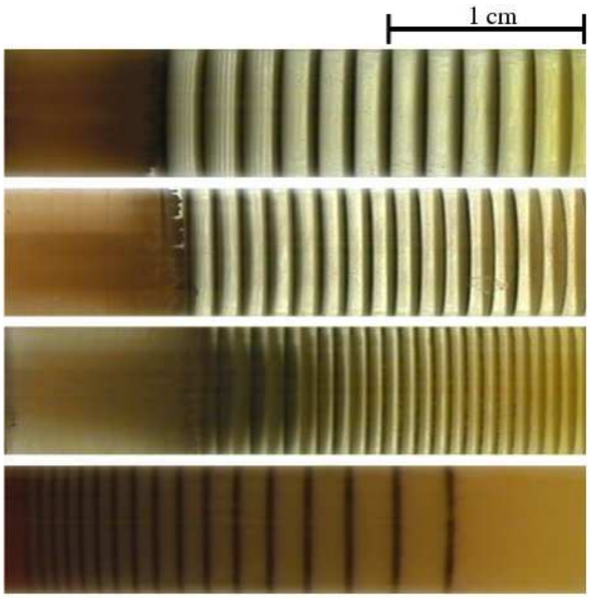

FIG. 1: Experimental precipitation patterns (the precipitates are the dark bands). A quasi-periodic current was used with decreasing characteristic period, respectively, as going down the panels. The lowest panel illustrates the usual Liesegang bands formed without the presence of the current.

took place in the gel columns with the inner electrolyte ($K_2Cr_2O_7$) initially homogeneously distributed in the gel, while the outer electrolyte. $AgNO_3$ was brought into contact with the left end of the gel column at the start of the experiment. As can be seen, the quasi-periodic pattern of Liesegang bands have been replaced by a periodic placement of the bands and the period of the band sequence can be controlled by an appropriate design of the properties of the current.

Once the technicalities of the design and realization of the current was learned [14, 15], we could generate an arbitrary sequence of band position as can be seen in Fig.2 where close agreement between the theoretically expected and the experimentally observed patterns can be seen.

Problems with downscaling

At present, the control of patterns is realized at the 100μ scale and, clearly, these are only the first steps towards controlling precipitation patterns at the micro-scales. Bringing the scale well below the microns would really open the doors to a wide range of industrial applications.

Since the width of the reaction zones is one of the limiting factors in downsizing, it is clear that one should understand how to control it. The studies of the width for neutral reagents [16–18] suggest that the parameter strongly affecting the width is the reaction rate constant.

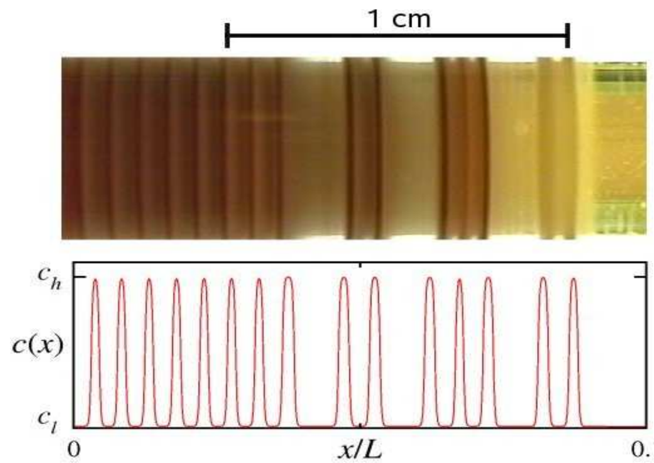

FIG. 2: An example of designer pattern. The dark bands in the upper panel (experiment) are the precipitate which correspond to the high concentration (c_h) in the spatial distribution of the reaction product $c(x)$ in the theoretical calculation (lower panel). The proposed protocol for generating the "2-3-2" structure yields patterns in accord with the experiment and the theory.

It is, however, not a parameter we can adjust, thus other means of control should be found. Since electric currents turned out to be useful in manipulating patterns [14, 15], we asked if the width could also be controlled by them.

We developed a mean-field theory to tackle the problem and found that an electric current may decrease or increase the width of the reaction zone with respect to the neutral case [19]. We found that a decrease takes place when the current drives the reacting ions toward the reaction zone while the width increases in the opposite case. Unfortunately, when estimating the effect from a linear response theory we find that the effect is weak thus a significant (order of magnitude) decrease cannot be reached for a system with usual parameters.

Thus new directions should be sought to solve the problem of the width of reaction zones.

Transverse patterns (patterns within the reaction zone)

We have explored an idea for downscaling the precipitation patterns by considering possible patterning within the reaction zones in the direction perpendicular to its motion [20]. At first, the experiments appeared to be promising because patterns significantly smaller scale than the width of the reaction zone could be observed in various Liesegang type experiments. These patterns, however, did not stay stationary. A well defined coarsening stage set in, and the characteristic scale grew with time t as $\sqrt{t}$. The coarsening can be seen in Fig.3 where precipitation in a two-dimensional moving front is shown.

In this example $NaOH$ was diffusing into a gel containing $AlCl_3$ and the time evolution of the precipitate $Al(OH)_3$ was observed (remarkably, the observation of a narrow region is possible since the precipitate redissolves in the excess outer electrolyte $NaOH$ and thus it exists only in a narrow optically accessible region of the reaction front).

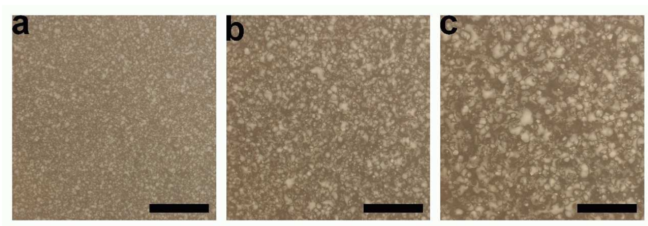

FIG. 3: Time evolution of the precipitation pattern in the reaction zone for the samples with [NaOH] = 2.5M (outer electrolyte) and [$AlCl_3$] = 0.52M (inner electrolyte). The front moves perpendicularly to the plane of the picture and the pictures were taken at $t_1 = 180$s (a), $t_2 = 480$s (b), and $t_3 = 960s$ (c) after the initiation of the reaction. The length of the scale-bars is 1cm.

Theoretical study of the above problem [20] led to the same conclusion about growing coarsening scale of the pattern. It is clear that it would be an important step in the solution of downscaling if one could find an effective and experimentally realizable way of arresting the phase separation process. Work in this direction is in progress.

Effect of noise

In principle, the noise (thermal, chemical, compositional, etc.) should be counterproductive to designing and realizing well defined structures. We found, however, that for complex structures such as helicoids and helices, the presence of finite-amplitude noise was a necessary condition for their emergence.

We got interested in helical structures since they are present from nano- to macro-scale and the precipitation helices [21–23] are known to have remarkable properties from material research point of view. Thus they may be important elements in the bottom-up building strategy.

Generally, the emergence of such structures raises the question whether the symmetry breaking occurring in the formation process is spontaneous (intrinsic property) or induced by initial or boundary conditions. We studied this question both experimentally and theoretically [24] by investigating precipitation patterns formed in the wake of planar reaction-diffusion fronts (examples of helicoidal structures can be seen in Fig.4). Our experiments showed that helices/helicoids emerged with well defined probabilities controlled by experimental conditions (e.g., by the initial concentration of the reagents) which do not break the chiral symmetry. The probabilities were rather large, reaching 50-60% probabilities for some parameter range. As simulations and theoretical consideration also confirmed, the probabilities are an intrinsic property determined by a delicate interplay among the time- and length-scales related to the front motion and to the growth of the unstable modes of the precipitation process and, furthermore, the noise amplitude also plays an important role. In the theoretical model we studied (reaction-diffusion process combined with Cahn-Hilliard type precipitation plus noise), it was found that there is a threshold in the noise amplitude below which no helices form and the system always evolves into the usual Liesegang patterns. The presence of noise threshold appears to be a rather interesting phenomena, its experimental study is presently under way.

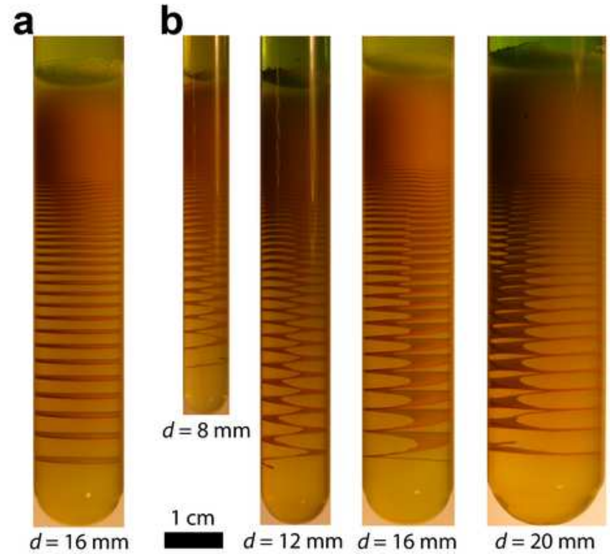

FIG. 4: Regular Liesegang (a) and helocoidal patterns (b) in agarose gel emerging in the reaction $Cu^{2+}(aq) + CrO_4^2(aq) \rightarrow CuCrO_4(s)$. Experimental conditions (T = 22.0 ± 0.3 ^{0}C, initial concentrations: $[Cu^{2+}]$ = 0.5 M, and $[CrO_4^2]$ = 0.01 M) were the same except for the test tube radii (R) in all the cases.

EXTREME STATISTICS OF CORRELATED SYSTEMS

Introduction

Extreme value statistics (EVS) is important in science and engineering [25], as well as at the societal level since the frequency of catastrophic events (floods, earthquakes, financial breakdowns) is a much wanted information [26, 27]. At present, EVS is mainly limited to ensembles of independent, identically distributed (i.i.d) random variables though natural phenomena (e.g. climatic data on temperature series, wind strength, precipitation) often display strong correlations. Our main goal was to expand our knowledge about EVS to correlated data. For this purpose we considered systems where, in accord with natural time-series, the power spectrum of the measured signal was $1/f^\alpha$ type. Such signals are remarkable in that the strength of correlations can be tuned by the parameter α and, furthermore, they are mathematically more easily handled and occasionally allow not only numerical but exact calculations as well. Our choice also followed from the fact that we have accumulated much experience with $1/f^\alpha$ noise through earlier studies of fluctuation distributions of such signals [28, 29], and we have already made the first steps in the direction of understanding their extreme properties [30] as well.

Distribution of the maximum relative to the initial value

Our earlier investigations of systems displaying correlations with $1/f^\alpha$ type power spectrum showed that these systems should be considered as critical since boundary-condition effects emerge in their limit distributions [29, 30]. This leads to problems in the case of studying time-series (such as the ones in climatic phenomena) where the boundary conditions are unknown. In order to come closer to the experimentally investigated extreme-value statistics, we introduced a quantity – *the maximum of a signal relative to the initial value* – and found that the distribution of this quantity is markedly different [31] from that of the usual *maximum relative to the average* studied in [30]. To illustrate the dramatic differences, we display the scaled maximum distribution $\Phi(x) = \langle h_m\rangle P(x\langle h_m\rangle)$ (where the maximum value of the signal h_m is scaled by its average $x = h_m/\langle h_m\rangle$) for the cases of $\alpha = 2$ and $\alpha = 4$ in Figs. 5 and 6, respectively.

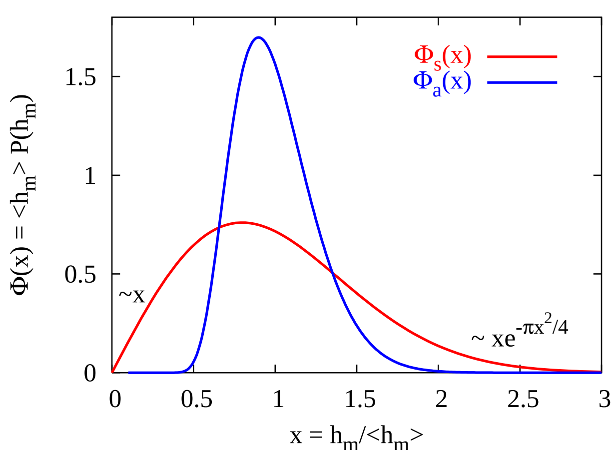

FIG. 5: The exact EV limit distributions for $\alpha = 2$. The case of the maximum measured from the average, $\Phi_a(x)$ [32], is compared to the distribution $\Phi_s(x)$ obtained by us for the distribution of the maximum measured from the initial value.

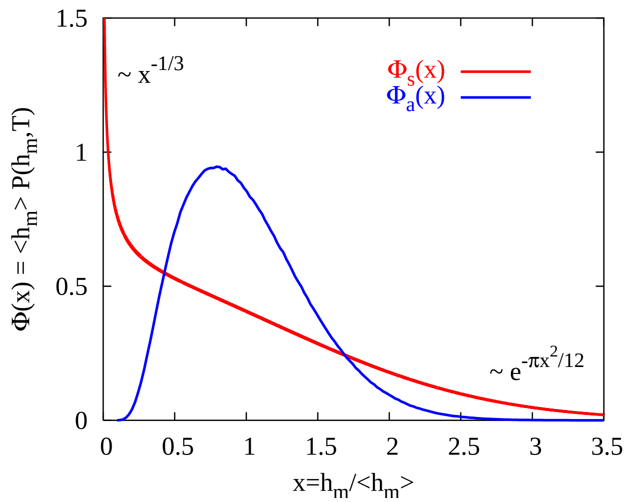

FIG. 6: The same as in Fig.5 but for $\alpha = 4$. Note that the exact form has been calculated only for $\Phi_s(x)$, the function $\Phi_a(x)$ is obtained by numerical methods.

Apart from the obvious difference from the limit distributions related to the unphysical periodic boundary conditions, the distributions of the extreme values measured from the initial value have two distinguishing features which may help in recognizing the underlying system. First, the distributions have large weights at small values of the relative maximum, and second, the distributions diverge for zero arguments for $\alpha \geq 3$. The divergence is of power-law type with a characteristic exponent determined by the value of α.

Order statistics for $1/f^\alpha$ signals

The extreme value in a batch of data is important, but its study makes use of only a small fraction of the available information. Accordingly, there have been various attempts to extend studies towards near-extreme characteristics, such as the density of states near extremes, first-passage and return-time statistics, persistence, and record statistics. A natural extension which we studied [33] is the order statistics which means that we considered not only the extreme, but the sequence $x_1, x_2, ..., x_k, ...$ of the 1st, 2nd, . . . , kth, . . . largest. It should be clear that the information content of this sequence is larger than that of the EV distribution.

Order statistics has been much studied in mathematics [34, 35] and all relevant quantities are known for independent, identically distributed (i.i.d.) variables. The novel aspect of our work is the extension of order statistics to $1/f^\alpha$ signals. Our main result concerns the average gap $d_k = \langle x_k - x_{k+1}\rangle$ between the k^{th} and $(k+1)^{st}$ largest.

We found that it scales with k as

$$d_k \sim \begin{cases} k^{-1} & \text{for } 0 \le \alpha < 1\,, \\ k^{(\alpha-3)/2} & \text{for } 1 < \alpha < 5\,, \\ k & \text{for } 5 < \alpha \le \infty\,. \end{cases} \quad (1)$$

As can be seen, there are three regimes and the scaling exponents match at the borderline values $\alpha = 1$ and 5. The above results were first obtained from simulations of the $1/f^\alpha$ signals and then phenomenological arguments were also used to derive the exponents. The phenomenology is based on a beautiful connection that can be made between the density of near extreme states (which, in turn, can be related to the extreme value distributions for translationally invariant signals [31]) and the order statistics.

Applications and finite-size scaling for i.i.d. variables

When trying to apply ideas from EVS [36, 37], one usually runs into the problem of the finite size of the database. The convergence to limit distribution in EVS is usually slow (logarithmic) and it often becomes premature to think about investigating the correlation effects when they cannot be distinguished from finite size corrections in an i.i.d. sample. This is why we returned to i.i.d. systems and rederived (by an easily applicable method which can be understood by physicists) all the the finite-size corrections for both the amplitude and the shape of the correction to the limit distributions [38, 39] which have been scattered all over the mathematics literature.

Our method is based on the similarity between the critical point distributions and the EVS limit distributions, which allows the use of the renormalization group formalism for the calculation of the corrections due to the finite size of data sets. As a result, one could show with some clarity how the EVS universality classes can be subdivided according to the exponent of the finite-size convergence. Furthermore, it also became transparent that the exponent also determines the shape corrections to the limit distribution.

We made the first steps towards the calculation of the finite-size corrections for $1/f^\alpha$ signals as well. In particular, we found that for strongly correlated systems ($\alpha > 1$), the shape correction can be expressed in terms of the limit distribution itself [38].

MISCELLANEOUS

As usual with scientific projects, we followed some sidelines in our research which may not have been directly connected to the main goals of the project but nevertheless they were originated in it. For us, such a side-branch was the general study of non-equilibrium steady states and, in particular, the calculating of non-equilibrium Casimir effect on the example of a one-dimensional spin chain [40]. The importance of our approach was in the possibility of the *exact* calculation of the Casimir force in the presence of energy flux. Our result show that the presence of the energy flux weakens the Casimir force. This result can be understood if we take into account that the Casimir force emerges from fluctuations, and the fluctuations are known to decrease (at least in the XX model) in the presence of an energy flux. It is believed, however, that the decrease of fluctuation in the presence of a flux is a general phenomenon and thus the Casimir force is expected to decrease in non-equilibrium situations quite generally.

BIBLIOGRAPHY

Publications produced within the framework of the present OTKA grant and carrying the corresponding grant number (K 68109) are set in bold letters.

[1] M.C. Cross and P.C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1994).

[2] B. Schmittmann and R.K.P. Zia, in *Phase Transitions and Critical Phenomena* eds. C. Domb and J.L. Lebowitz, vol. 17 (Academic Press, London, 1995).

[3] H.K. Henisch, *Periodic precipitation* (Pergamon Press, New York, 1991).

[4] O. Giraldo et al., Nature **405,** 38 (2000).

[5] I.T. Bensemann, M. Fialkowski, and B.A. Grzybowski, J. Phys. Chem. B **109,** 2774 (2005).

[6] M.I. Lebedeva, D.G. Vlachos, and M. Tsapatsis, Phys. Rev. Lett. **92,** 088301 (2004).

[7] T. Antal, I. Bena, M. Droz, K. Martens, and Z. Rácz, Phys. Rev. E **76**, 046203 (2007).

[8] I. Bena, M. Droz, K. Martens, and Z. Rácz, J. Phys. C **19**, 065103 (2007).

[9] T. Unger and Z. Rácz, Phys.Rev.E **61**, 3583 (2000).

[10] I. Bena, F. Coppex, M. Droz, and Z. Rácz, J. Chem. Phys. **122**, 024512 (2005).

[11] I. Bena, M. Droz, and Z. Rácz, J. Chem. Phys. **122**, 204502 (2005).

[12] T. Antal, M. Droz, J. Magnin, and Z. Rácz, Phys. Rev. Lett. **83**, 2880 (1999).

[13] Z. Rácz, Physica A **274**, 50 (1999).

[14] **I. Bena, M. Droz, I. Lagzi, K. Martens, Z. Rácz, and A. Volford**
Designed Patterns: Flexible Control of Precipitation through Electric Currents
Phys. Rev. Lett. 101, 075701 (2008).

[15] **K. Martens, I. Bena, M. Droz, and Z. Rácz**
Encoding information into precipitation structures
J. Stat. Mech. Theory and Exp. P12003 (2008)

[16] L. Gálfi and Z. Rácz, Phys. Rev. A **38**, 3151 (1988).

[17] Cornell, B. Chopard, and M. Droz, Physica A **188**, 322 (1992); S. Cornell and M. Droz, Phys. Rev. Lett. **70**, 3824 (1993).

[18] E. Ben-Naim and S. Redner, J. Phys. A **25**, L575 (1992).

[19] **K. Martens, M. Droz, and Z. Rácz**
Width of reaction zones in $A + B \rightarrow C$ type reaction-diffusion processes: Effects of an electric current
J. Chem. Phys. 130, 234506 (2009)

[20] **A. Volford, I. Lagzi, F. Molnár Jr., and Z. Rácz**
Coarsening of precipitation patterns in a moving reaction-diffusion front
Phys. Rev. E 76, 055102(R) (2009).

[21] S. C. Müller, S. Kai, and J. Ross, Science **216**, 635-637 (1992).

[22] R. V. Suganthi, E. K. Girija, S. N. Kalkura, H. K. Varma, A Rajaram, J. Mater. Sci.-Mater M. **20**, 131-136 (2009).

[23] O. Giraldo, S. L. Brock, M. Marquez, S. L. Suib, H. Hillhouse, and M. Tsapatsis, Nature **405**, 38-38 (2000).

[24] **S. Thomas, F. Molnár Jr., I. Lagzi, and Z. Rácz**
Emergence of helices and helicoids in precipitation processes
Submitted for publication in PNAS.

[25] R.A. Fisher and L.H.C. Tippett, Cambridge Phil. Soc. **28**, 180 (1928); E. J. Gumbel, *Statistics of Extremes* (Columbia University Press, 1958).

[26] R.W. Katz, M. B. Parlange, and P. Naveau, Adv. Water Resour. **25**, 1287 (2002).

[27] P. Embrecht, C. Klüppelberg, and T. Mikosch, *Modelling Extremal Events for Insurance and Finance* (Springer, Berlin, 1997).

[28] T. Antal, M. Droz, G. Györgyi and Z. Rácz, Phys. Rev. Lett. 87, 240601 (2001).

[29] T. Antal, M. Droz, G. Györgyi, and Z. Rácz, Phys. Rev. E **65**, 046140 (2002).

[30] G. Györgyi, N. Moloney, K. Ozogány, and Z. Rácz, Phys. Rev. E **75**, 021123 (2007).

[31] **T. W. Burkhardt, G. Györgyi, N. Moloney, and Z. Rácz,**
Extreme statistics for time series: Distribution of the maximum relative to the initial value,
Phys. Rev. E 76 041119 (2007).

[32] S. N. Majumdar and A. Comtet, Phys. Rev. Lett. **92**, 225501 (2004).

[33] **N. Moloney, K. Ozogány, and Z. Rácz,**
Order statistics of $1/f^{\alpha}$ signals,
Phys. Rev. E 84, 061101 (2011).

[34] M. R. Leadbetter, G. Lindgren, and H. Rootzen, *Extremes and Related Properties of Random Sequences and Processes* (Springer-Verlag, New York, 1982).

[35] J. Pickands, Annals of Statistics **3**, 119 (1975).

[36] **T. Antal, F. Sylos Labini, N. L. Vasilyev, and Y. V. Baryshev,**
Galaxy distribution and extreme-value statistics,
EPL, 88, 59001 (2009).

[37] **M. Taghizadeh-Popp, K. Ozogány, Z. Rácz, E. Regős, and A. S. Szalay,**
Distribution of Maximal Luminosity of Galaxies in the Sloan Digital Sky Survey
ApJ, under review.

[38] **G. Györgyi, N. Moloney, K. Ozogány, and Z. Rácz,**
Finite Size Scaling in Extreme Statistics,
Phys. Rev. Lett. 100, 210601 (2008).

[39] **G. Györgyi, N. Moloney, K. Ozogány, Z. Rácz, and M. Droz,**
Renormalization-group theory for finite-size scaling in extreme statistics,
Phys. Rev. E 81, 041135 (2010).

[40] **D. L. González-Cabrera, Z. Rácz, and F. van Wijland,**
Casimir effect in the nonequilibrium steady state of a quantum chain,
Phys. Rev. A 81, 052512 (2010).

INVITED TALKS

Z. Rácz
Control of precipitation patterns by currents
Pattern Formation in Reaction-Diffusion Systems
International Workshop, Budapest, March 2008

Z. Rácz
Stochastic resonance and glacial climatic changes
Climate Variability and Climate Change
International Summer School, Visegrád, June 2009

Z. Rácz
Controlling precipitation through electric currents
Middle European Cooperation in Statistical Physics
Conference, Leipzig, March-April, 2009

Z. Rácz
Control of precipitation patterns: I. Theory
Self-organization in Chemical and Biological Systems
International Workshop, Tokyo, July 2009

Z. Rácz
Precipitation patterns in moving reaction-diffusion fronts
Pattern formation in Chemical and Biological Systems
International Workshop, Budapest, October 2010

Z. Rácz
Order statistics of 1/f(alpha) signals
Extremes and Records
Itzykson Meeting, Saclay, June 2011

Z. Rácz
Order statistics and applications to astrophysics
Extreme Value Statistics in Mathematics, Physics and Beyond
Lorentz Workshop, Leiden, July 2011

Z. Rácz
Finite-size corrections to limit distributions
Large Fluctuations in Non-Equilibrium Systems
Workshop, Dresden, July 2011