# Gradient Pattern Analysis of Structural Dynamics: Application to Molecular System Relaxation

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This paper describes an innovative technique, the *gradient pattern analysis* (GPA), for analysing spatially extended dynamics. The measures obtained from GPA are based on the spatio-temporal correlations between large and small amplitude fluctuations of the structure represented as a dynamical gradient pattern. By means of four gradient moments it is possible to quantify the relative fluctuations and scaling coherence at a dynamical numerical lattice and this is a set of proper measures of the pattern complexity and equilibrium. The GPA technique is applied for the first time in 3D-simulated molecular chains with the objective of characterizing small symmetry breaking, amplitude and phase disorder due to spatio-temporal fluctuations driven by the spatially extended dynamics of a relaxation regime.

## I Introduction

Spatiotemporal systems driven away from thermodynamic equilibrium can form complex structures when forced beyond a critical threshold. The spatiotemporal dynamics of such nonequelibrium structures have been the subject of numerous experimental and theoretical investigations, notably in extended neutral and ionized fluid flows, lasers and optical electronics, oscillated granular layers, molecular clusters and percolative systems [1-5]. There are systems in which the instantaneous patterns are disordered, but they retain sufficient phase coherence that the time-averaged images reveal spatially regular and quasi-periodic structures. In the more general case the global structures can exhibit complex spatio-temporal dependencies reflecting many structural nonlinear properties as spatio-temporal fluctuations, symmetry breaking under energy dissipation, scaling coherence and structural entropy.

Thus, quantitative characterization of spatio-temporal patterns is clearly essential to the understanding of spatio-temporal phenomena. An important question in this problem concerns the long-term evolution of the pattern properties. Usually, the classical measures of complex extended variability do not take into account the directional information contained in a vectorial field: the main source of spatio-temporal variability. Moreover, since spatio-temporal information is even more accessible through high resolution digitized images, the need for sensitive techniques working in the real space is evident [6].

The *gradient pattern analysis* (GPA) is an innovative technique, which characterizes the formation and evolution of extended patterns based on the spatio-temporal correlations between large and small amplitude fluctuations of the structure represented as a gradient field. Here we report, mainly, the performance of this new technique in characterizing nonlinear emergence of ordered structures as from random initial condition, a macroscopic signature called *spatio-temporal relaxation* (STR). Usually, the STR is a complex spatio-temporal regime described by means of the correlation among many localized dynamics. Here we analyze the STR regime observed from a simulated short chain-molecule system [4]. The chain molecules model consists of a sequence of $CH_2$ groups, which are treated as united oscillons. The mass of each molecular oscillon is 14 g/mol and they interact via bonded potentials (bond-stretching, bond-bending, and torsional potentials) and a non-bondend

Lennard Jones potential. The system, at first, is randomly distributed configuration of 100 short chain molecules, each of which consists of 20 oscillons, at 700-300 K bath temperature. The local fluctuation of this molecular system is given by $\tau_{i,j} = 2\pi\left[(I/k_{i,j})^{1/2} + \Delta_{i,j}\right]$ with $\Delta_{i,j} = R/k_{i,j}^2$ where $I$ is the moment of inertia of the system, $k_{i,j}$ is the local term of Lennard-Jones potential and $\Delta_{i,j}$ is the term related to the local fluctuations of the rigidity (R) of the chains. More details on the system simulation is given by Fujiwara et al. [4,7].

In Figure 1 shows the chain of 3D-configurations at various times at T=400 K. At the early time, the spatiotemporal configuration is disordered. As time elapses (mainly after $t \sim 10^2$ps), growth of local orientationally-ordered structures is observed in several positions. At last ($t \sim 10^3$ ps), several clusters coalesce into a large structure and a highly ordered pattern is formed. This 3D STR regime is also well characterized as a similar stepwise behaviour taking the 2D cross section from the middle of the system (See Fig.2). Therefore, it becomes interesting to characterize such extended dynamics by means of measures that produce scalar moments from two-dimensional patterns (operations $\Re^2 \mapsto \Re$), consequently obtaining an easily temporal representation of their corresponding dissipative correlations working under far-from-equilibrium conditions.

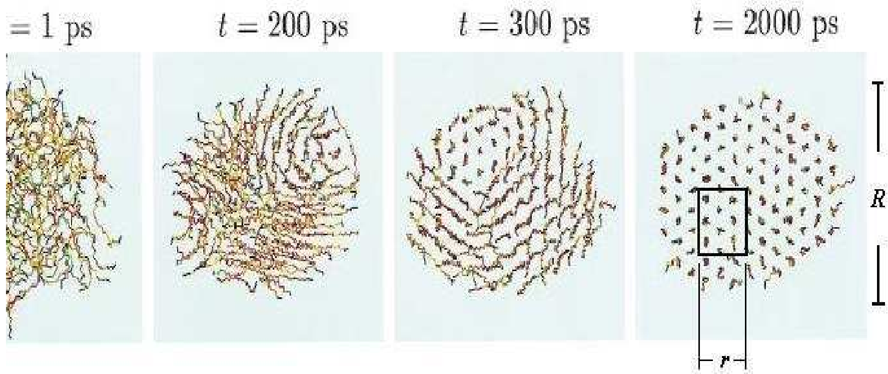


Figure 1. A spatio-temporal sequence, visualized from the top of the structure, of 100 small chains for T=400K at several instants. $R$ and $r$ are, respectively, the global scale and an arbitrary local scale.

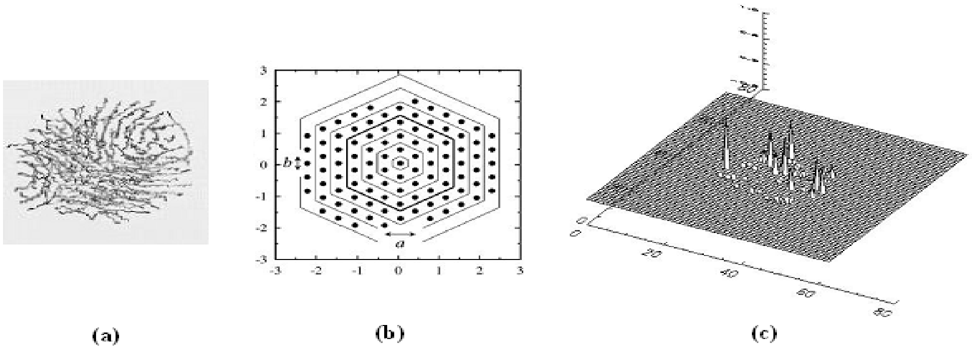


Figure 2. (a) Interacting $CH_2$ chains (b) A straight section of the model, (c) Fluctuation field of the chain rigidity (values of $\Delta_{i,j}$ in z).

# II The gradient pattern analysis formalism

### II.1 The gradient moments

A spatially square extended pattern in two dimensions $(x, y)$ is represented by the square matrix of amplitudes $\mathcal{M} = \mathcal{L}^{\ell\times\ell}\{M(1,1), ..., M(i,j), ..., M(\ell,\ell)\} \mid M \in \Re$, essentially a square lattice, $\mathcal{L}$, if the two dimensions, $x$ and $y$, are discretized into $\ell \times \ell$ pixels, with $i = 1, ..., \ell$ and $j = 1, ..., \ell$. Thus, a dynamical sequence of $N$ lattices, $\mathcal{L}_0, \mathcal{L}_1, ..., \mathcal{L}_N$, is related to the temporal evolution of a visualized amplitude envelope $\mathcal{M}_{x,y,t}$. Usually, each amplitude intensity $\mathcal{E}(i,j)$ reflects a local measurement of spatially distributed energy, as for example scalar relative velocity, concentration rate, etc. The spatial fluctuation of the global pattern $\mathcal{M}(x, y)$, at a given instant $t$, can be characterized by its gradient vector field $\mathcal{G}_t = \nabla[\mathcal{M}(x, y)]_t$. The local spatial fluctuations, between a pair of pixels, of the global pattern is characterized by its gradient vector at corresponding mesh-points in the two-dimensional space. In this representation, the relative values between pixels ($\Delta\mathcal{M} \equiv |\mathcal{M}(i,j) - \mathcal{M}(i+n, j+n)|$) are dynamically relevant, rather than the pixels absolute values. Note that, in a gradient field such relative values, $\Delta\mathcal{M}$, can be characterized by each local vector norm and its orientation.

In view of GPA formalism a gradient vector field $\mathcal{G}_t = \nabla[\mathcal{M}(x, y)]_t$, is composed by $V$ vectors $\mathbf{r}$ where a vector $\mathbf{r}_{i,j}$ is represented, besides its location (i,j) in the lattice, by its norm ($r_{i,j}$) and phase ($\phi_{i,j}$), so that associated to each position in the lattice we have a respective vector ($\mathbf{r}_{i,j} = (r_{i,j}, \phi_{i,j})$). Thus, a given scalar field of absolute values can be represented by a gradient field for the local amplitude fluctuations, and this gradient pattern can be represented by a pair of matrices, one for the norms and another for the phases. A natural subsequent representation is by means of a complex matrix, where each element corresponds to the respective complex number $z_{i,j}$ representing each vector from the gradient pattern. Thus, a given matricial scalar field can be represented as a composition of four gradient moments: first order, $g_1$, is the global representation of the vectors distribution; second order, $g_2$, is the global representation of the norms; third order, $g_3$, is the global representation of the phases; and fourth order, $g_4$, is the global complex representation of the gradient pattern. Considering the sets of $\{r_{i,j}\}$ and $\{\phi_{i,j}\}$ as discrete compact groups, spatially distributed in a lattice at instant t, the gradient moments are equivalent to *Haar-like* measures, $h$, which has the basic property of being, at least, rotational invariant:

$$g_1^{(t)} \equiv h_1(\{(r_{1,1}, \phi_{1,1}), ..., (r_{i,j}, \phi_{i,j}), ..., (r_{\ell,\ell}, \phi_{\ell,\ell})\}_t), \tag{1}$$

$$g_2^{(t)} \equiv h_2(\{(r_{1,1}), ..., (r_{i,j}), ..., (r_{\ell,\ell})\}_t), \tag{2}$$

$$g_3^{(t)} \equiv h_3(\{(\phi_{1,1}), ..., (\phi_{i,j}), ..., (\phi_{\ell,\ell})\}_t), \tag{3}$$

$$g_4^{(t)} \equiv h_4(\{(z_{1,1}), ..., (z_{i,j}), ..., (z_{\ell,\ell})\}_t). \tag{4}$$

From the definition of the gradient moments $g_\zeta$, with $\zeta = 1, ..., 4$, it is possible to represent the gradient field $\mathcal{G}_t = \nabla[\mathcal{M}(x, y)]_t$ as a set of four gradient moments: $\mathcal{G}_t \equiv (g_1, g_2, g_3, g_4)_t$ (see Figure 3).

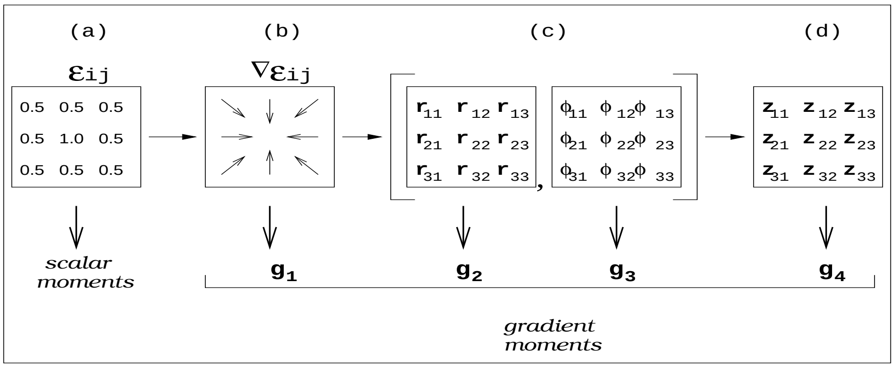


Figure 3. A schematic representation of the Gradient Pattern Analysis of a matricial scalar field:(a) an arbitrary normalized extended scalar field; (b) the corresponding gradient pattern of the amplitude fluctuations; (c) the norm and the phase of the fluctuations; (d) the complex representation of the fluctuations.

## II.2 Computational operations to extract the gradient moments

### II.2.1. The first gradient moment

As we are interested in nonlinear spatio-temporal structures we have introduced a computational operator to estimate the gradient moment $g_1$ based on the asymmetries among the vectors of the gradient field of the scalar fluctuations. A global gradient asymmetry measurement, can be performed by means of the asymmetric amplitude fragmentation (AAF) operator[8,9]. This computational operator measures the symmetry breaking of a given dynamical pattern and has been used in many applications [9-14]. From the $\nabla(\mathcal{M})$ the symmetric pairs of vectors (i.e., the pairs of vectors that have the same modulus but opposite directions) are removed, obtaining the asymmetric field of vectors $\nabla_A(\mathcal{M})$. The measurement of asymmetric spatial fragmentation $g_1^a$ (usually called, the *asymmetric amplitude fragmentation* $F_A$) is defined as:

$$g_1^a \equiv (C - V_A)/V_A \qquad | \qquad C \geq V_A > 0, \tag{5}$$

where $V_A$ is the number of asymmetric vectors and $C$ is the number of correlation bars generated by a Delaunay triangulation having the middle point of the asymmetric vectors as vertices. The Delaunay triangulation $T_D(C, V_A)$ is a fractional field with dimension less than two - the lattice dimension [8]. When there is no asymmetric correlation in the pattern, the total number of asymmetric vectors is zero, and then, by definition, $g_1^a$ is null. For a given $\ell \times \ell$ lattice size, while a random and totally disordered pattern has the highest $g_1^a$ value, a totally ordered and locally symmetric pattern (e.g. an extended Gaussian or Besselian envelope) has $g_1^a$ equals to zero; and complex patterns composed by locally asymmetric structures has specific nonzero values of $g_1^a$.

### II.2.2. The fourth gradient moment

In this paper we are not interested in measurements of the second and third gradient moments because still there are no formal computational operators to calculate them in the literature. However, from a generalization of the concept of degeneracy $W$, given by the multinomial coefficient formula, and normally used to deduce the expression of Shannon's entropy of positive scalar fields, such as numerical lattices, Ramos et al.[9] have introduced a computational operator to estimate the modulus and phase related to the complex form of the fourth gradient moment, $g_4$. Considering the gradient $\nabla(\mathcal{M})$ defined above, $W(z_{1,1}, \ldots, z_{\ell,\ell})$ may be generalized as follows:

$$W(z_{1,1}, \ldots, z_{\ell,\ell}) \equiv \frac{\Gamma(z)}{\Gamma(z_{1,1}) \ldots \Gamma(z_{\ell,\ell})} \ , \quad (6)$$

where $z = \sum_{i,j} z_{i,j}$. Using Stirling's approximation, we immediately have

$$z^{-1} \ln W \longrightarrow S_z = -\sum_{i,j} \frac{z_{i,j}}{z} \ln(\frac{z_{i,j}}{z}) \ . \quad (7)$$

We can easily verify that this complex entropic form (CEF), $S_z \equiv g_4 = |g_4| e^{i\Phi_{g_4}}$, is invariant under rotation and scaling of the gradient field. Extensive applications of CEF in chaotic coupled map lattices [9] and on solutions of the Swift-Hohenberg equation [10] have shown that: (i) the $|g_4|$ measurement is very sensitive to the spatio-temporal relaxation processes preserving the information on nonlinear local amplitude fluctuations and (ii) the $\Phi_{g_4}$ measurement characterizes, by means of phase disorder, the transitions from amplitude to phase dynamics. In the presence of spatio-temporal nonlinear fluctuations, such measures from a gradient field on a lattice is more robust than derivative measures and spatial correlation lengths. Particularly, several calculations on random patterns have shown that, in particular, $g_1$ and $\Phi_{g_4}$ are much more sensitive and precise in characterizing asymmetric structures than the correlation length measures [8,9].

### II.2.3. Gradient scale invariance

Whenever the statistics for the configurations of a complex gradient pattern (composed by $V_A$ asymmetric vectors distributed in a global 2D-scale $R \times R$) has the property that, by scaling the normalized gradient moments $\bar{g}_\zeta$, one can make the analysis for a smaller sub-pattern (local arbitrary scale $r$ - See Fig. 1) exactly matching that of a larger scale, then the *gradient statistics* is said to be scale invariant.

At a possible *gradient critical point*, the two-point correlation function for local *macroscopic* observable (here, the $\bar{g}_\zeta$ gradient moments), $G(r, R) = \langle \bar{g}_\zeta(r) \bar{g}_\zeta(R) \rangle$, tall off as some power of $|r - R|$, that is $\langle \bar{g}_\zeta(r) \bar{g}_\zeta(R) \rangle \sim |r - R|^{-\lambda}$, where the statistical average, indicated by the brackets, is over the fluctuation of norm, phase and symmetry of the gradient field $\nabla[\mathcal{M}(x, y)]_t$. Note that, also a time-dependent correlation function can be defined.

This formalism implies that the fundamental assumption of renormalization group theory can be considered into the context of the gradient pattern analysis. A direct consequence is that in a Landau-Ginzburg approach the gradient moments $\bar{g}_\zeta$ will describe local disorder that are averages over larger and larger scales. As the scales become much larger than a characteristic correlation length, the averages over different domains become statistically independent and the concept of *fixed point* can be considered into the GPA formalism.

## III Results and interpretation

Next we show the characterization of extended relaxation regimes by means of $\mathcal{G}_t(g_1^a, |g_4|$ and $\Phi_{g_4})$. We applied the CEF and AAF operators on the spatio-temporal series, partially illustrated in Fig. 1. For a proper application of the operators [8,9], the relaxation process is described by a sequence of many lattices (here, 20 frames), each of which consists of a $64 \times 64$ matrix of real values, representing the sectional state of the system at a given instant. In Figure 4 is shows, for the time-step 15, the asymmetric gradient field and its correpondent triangulation field, from where,by means of CEF and AAF computational operators, it is possible to determine the gradient moments $g_1$, $|g_4|$ and $\Phi_{g_4}$.

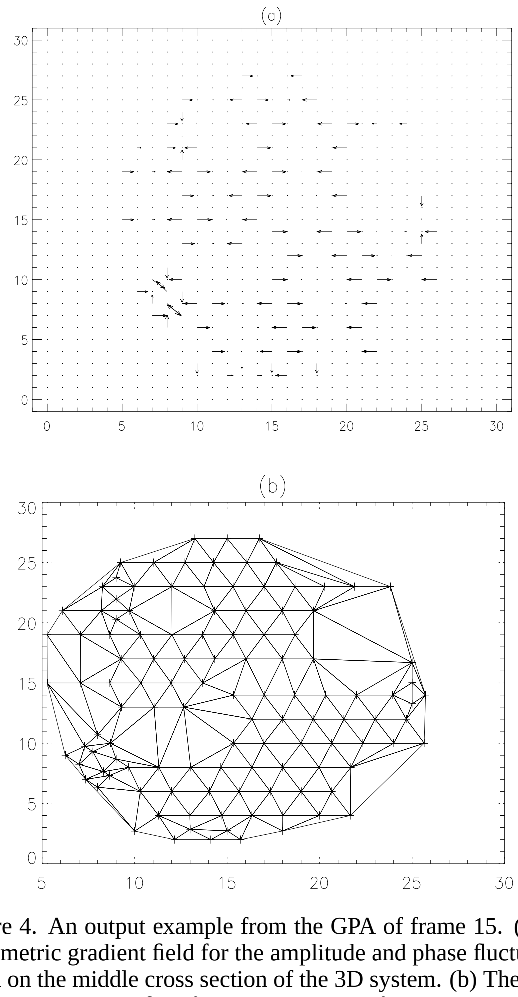


Figure 4. An output example from the GPA of frame 15. (a) The asymmetric gradient field for the amplitude and phase fluctuations taken on the middle cross section of the 3D system. (b) The asymmetric triangulation field for the calculation of the gradient moment $g_1$.

The global relaxation process may or not be dominated by the amplitude dynamics and also by the influence of the boundary on the local pattern equilibrium. For local abnormal relaxation there are many small sub-relaxation regimes which affect the global pattern equilibrium (characterized when the time derivative of the gradient moments ($g_\zeta$) is null). An useful description of the relaxation process is given by: (i) the temporal variation of $|g_4|$ shows the influence of the amplitude dynamics on the STR evolution; (ii) the equilibrium pattern (local and global) is characterized by the dynamics in the plane $g_1 \times \Phi_{g_4}$.

The short chain-molecule system quickly evolves from a totally disordered state to a state exhibiting several domains of oriented structures with quasi-regular hexagonal boundary. The molecular oscillons interact slowly until only one domain with the same orientation and typical aspect ratio is resulted. Figures 5a-b illustrate the results of gradient pattern analysis applied to these data. In Figures 5a, we plot the values of $|g_4|$ for each frame in the series. The molecular x-y layer starts with disordered oscillatory amplitude moving to quasi-ordered oscillatory amplitudes. During the first integration steps, there is a variation in the maximum amplitude of the oscillons, while the system nucleates to cellular structures. This situation is accurately characterized by the time evolution of the gradient moment $|g_4|$, as shown in Fig.5a. After some random *accomodation* (into the interval 1 ps $\leq t \leq 5 \times 10^2$ ps) of the system, due to the spatio-temporal potential arrangement, the effective relaxation starts and reaches the *relaxation straight line* showed in Fig. 5a, characterized by $|g_4| = 0.945 \pm 0.009$. Figure 5b shows that the global pattern becames approximately stable around a fixed point in the $g_1 \times \Phi_{g_4}$ space. From previous application of GPA on chaotic coupled map lattices and amplitude equations [9,10] it means that for the molecular oscillons analysed here there is a meta-stable amplitude dynamics represented in the $g_1 \times \Phi_{g_4}$ space (Fig. 5b). From the temporal behaviour of $|g_4|$ we found the transition from the dominant norm regime to the dominant phase regime well characterized in the meta-stable $g_1 \times \Phi_{g_4}$ space dynamics. During the relaxation the phase correlations become stronger and the averaged equilibrium pattern shows, approximately, a characteristic local geometric scale invariance responsable for the global pattern symmetry.

# IV Concluding remarks

The spatio-temporal relaxation into a stable state takes place when the system is instantaneously changed into a nonequilibrium state, and this universal regime is often observed in many physically different systems [e.g., 1-15]. Therefore when a extended system is driven far from equilibrium, it will evolve to a minimum energy state in a stepwise relaxation and, generically, this self-organized behaviour is independent of the types of oscillons and the nature of their interactions.

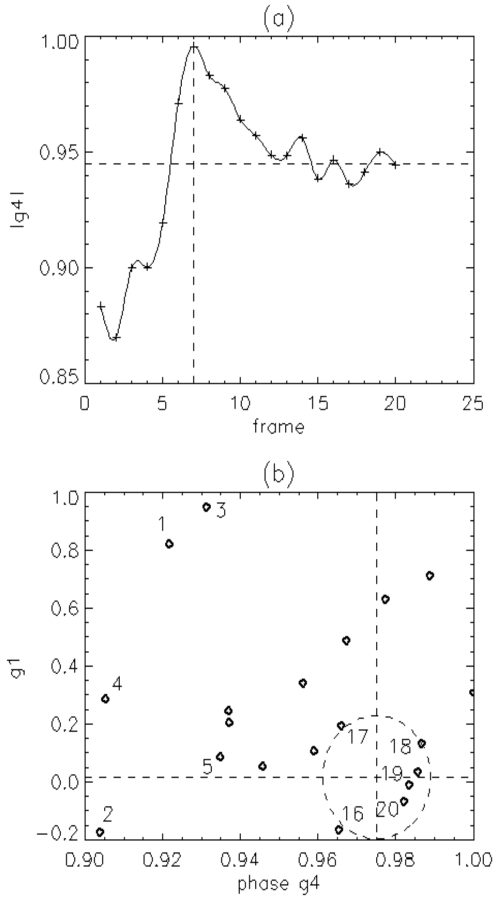


Figure 5. Dynamical behaviour of the gradient moments calculated for the cross sections of the data shown in Figure 1. (a) Time evolution of the gradient moment $|g_4|$, showing the transition (vertical dashed line) from the amplitude dynamics to the normal STR regime; (b) The pattern equilibrium dynamics in the plane $g_1 \times \Phi_{g_4}$, where are shown the values $(g_1, \Phi_{g_4})$ for the first and the last five time-steps (the last three are in the circle).

In short, the gradient pattern analysis specifies quantitatively the relative fluctuations and scaling coherence at a dynamical numerical lattice and this is a proper measure of the global pattern variability due to small fluctuations in the lattice gradient field. The gradient pattern analysis is still under detailed investigation in order to make more precise the concept of characterizing spatio-temporal disorder (nonlinear pattern equilibria, topological intermittency, entropy and chaos) in extended systems. In this sense such gradient moments and their characteristic two-point correlation functions can be considered as a plus to other spatio-temporal measures (e.g. disorder functions [15]). A natural way of extending the GPA application would be analysing magnetization patterns on a two-dimensional Ising lattice characterizing the rate of spatial variation (the gradient) of the magnetization. This new phenomenological approach is also in progress and will be communicated later.

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