Antoni C. Mituś, Rafał Orlik, Alexander Z. Patashinski*

Recognition of fluctuating patterns: from informatics to dynamic structure of two-dimensional liquids

1. Local structure of two-dimensional liquids

Standard methods of pattern recognition, generalized onto the case of a system of fluctuating material points representing atoms or molecules in computer-simulated liquids at non-zero temperatures, has established the concept of locally solid-like ordered instantaneous structure of liquids in two dimensions [13]. Probabilistic method of structural invariants [6–8, 13], briefly presented in the next Section, was applied to Lennard-Jones liquid [8], hard discs liquid [9] and liquid with quantum degrees of freedom [3]. In each case the system close to freezing line (we do not discuss here the challenging question of the order of phase transition – see, e.g. Refs. [5, 18]) developed approximately 50% of solid-like atoms (see below) which together with their 6 nearest neighbours form a part of regular triangular lattice in 2D. Moreover, the SLA atoms show a tendency to form large clusters. The conjecture that the local structure is a slow-relaxing mode in low-temperature equilibrium liquids opens new possibilities in statistical mechanics treatment of classical liquids [15].

Dynamic features of local solid-like structure in 2D liquids were also studied using the same formalism and revealed a non-exponential relaxation of various correlation functions in the two-phase interval [14]. Quite recently, this approach enriched by topological characterization of neighbouring relations revealed that the 2D LJ liquid becomes a complex liquid in a narrow strip of thermodynamic states close to the melting line, characterized by a super-Arrhenius increase of relaxation times, stretched-exponential decay of correlations in time, and a power-law distribution of waiting times for changes in the local order [12].

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* prof. dr hab. inż. Antoni C. Mituś, Dolnośląska Wyższa Szkoła Przedsiębiorczości i Techniki w Polkowicach, Polkowice, Poland, Institute of Physics, University of Technology, Wrocław, Poland, Institute d'Alembert, Ecole Normale Superieure de Cachan, Cachan, France (visiting professor); dr inż. Rafał Orlik, Orlik Software, Wrocław, Poland; prof. Alexander Z. Patashinski, Department of Chemistry, Northwestern University, Evanston, Illinois, United States.

Various structure-based physical processes are related to various spatial scales characterizing the structure. The time of life of those structures in 2D liquids are dependent on the spatial scale. It seems plausible that the time evolution of large clusters of SLA atoms may be governed by very different time scales because of a solid-like environment of a given atom [12]. Those structures or their topological counterparts [12] are natural candidates for long-time structural hydrodynamic modes in liquids, which may manifest themselves in various physical phenomena related to short-time thermodynamics [15].

The aim of the paper is to present first results on time evolution of SLA clusters in 2D LJ liquid.

The paper is organized as follows. Probabilistic pattern recognition approach is briefly presented in the next Section. Some details concerning the molecular dynamics simulation are given in section 3. In Section 4.1 the algorithm for the search of SLA clusters is briefly discussed. Section 4.2 deals with a challenging problem of the definition of the "identity" of a cluster during the time evolution. In section 4.3 the corresponding MD results are shown. Conclusions are presented is section 5.

2. Fluctuating pattern recognition: probabilistic method of structural invariants

2.1. Pattern recognition: object and feature spaces

The canonical pattern recognition task is to classify a given object Γ using as a reference a set of patterns $\Gamma_i, i = 1, \ldots, N$. To this end one introduces a merit function which plays a role of a metric in the space of objects and finds the pattern Γ_i which displays maximal similarity with object Γ.

As a rule, the object has a complicated geometrical structure represented by a set of parameters which span the so-called feature space. The metric becomes a function in feature space and the classification of an unknown object acquires a well-defined mathematical meaning.

The situation gets more complicated when the object Γ can, a priori, represent a kind of "mixture" of basic patterns Γ_i. This is, e.g., the case when the object is a system of geometric points which dynamically undergo fluctuations. In this case the basic patterns Γ_i are fluctuating – and not static – patterns. Moreover, the fluctuations of the pattern should result from the same ensemble of fluctuations as the classified object does. All this makes the recognition procedure more complicated and inevitably increases the degree of arbitrariness, already present in the canonical formulation of the problem due to the arbitrariness of the choice of merit function.

Those difficulties are present in the case of computer-simulated liquids in thermal equilibrium, where its constituent atoms, molecules etc. are represented

by geometrical points. In the next Section we present a classification scheme for local structures based on a probabilistic approach.

2.2. How to differentiate between fluctuating patterns: structural invariants

Local structure hypothesis [13] states that the local structure of simple liquids in 2D resembles that of a regular triangular solid. Thus, an object of main interest is a two-dimensional 7-atom cluster. Its structure, which is invariant with respect to 2D translations and rotations, depends on 11 parameters which span the 11-dimensional feature space. Instead of using the whole set of 11 parameters, we take into account only one which describes the orientational relations between the atoms in this cluster. Namely, local order in a 2D system in the neighborhood of an atom located at the point $\vec{r}$ is described by 2D local version of bond-order parameter of Nelson et al. [8, 10, 17]:

$$Q_{6m}(\vec{r}) = \frac{1}{N_0} \sum_{i=1}^{N_0} Y_{6m}(\pi/2, \phi_i), \tag{1}$$

where $Y_{6m}(\theta, \phi)$ $(m = -6, \ldots, 6)$ denotes the spherical harmonic function, the sum is taken over the N_0 nearest-neighbors of the atom located at the point $\vec{r}$ and the pair of polar and azimuthal angles, (θ_i, ϕ_i), describes the direction between the central atom $\vec{r}$ and its i-th nearest neighbor. The structural invariant $Q(\vec{r})$ for $(N_0 + 1)$-atom cluster with central atom at $\vec{r}$ is defined as [8, 17]:

$$Q_6^2(\vec{r}) = \frac{4\pi}{13} \sum_{m=-6}^{6} |Q_{6m}(\vec{r})|^2. \tag{2}$$

Within the probabilistic formalism of structural invariants the local solid-like component in a 2D liquid is calculated using the decomposition of a probability density function $\rho(Q_6)$ (PDF) of invariant Q_6, calculated from computer simulations, into fluctuating patterns of structure $\rho_i(Q_6), i = 1, \ldots, N$. In other words, the feature space is spanned by normalized probability density functions. The reliability of this decomposition is given in terms of standard mathematical statistics parameters like, e.g., significance level α calculated from χ^2 test [16]. Very small values of α (of order of 10^{-6} and smaller) indicate that the decomposition is statistically not reliable [8]. The choice of patterns Γ_i and of ensembles of fluctuations of their constituent atoms is dictated by the physical picture of fluctuating local structure in solids and liquids in 2D. In the case of liquids, satisfactory results were obtained using only two patterns of structure: Γ_6 and Γ_5, in which the atoms fluctuate independently, with gaussian distributions, around their positions in a static pattern. The first of the static patterns is a 7-atom 2D hexagon (part of 2D triangular lattice) and the second – a 7-atom

cluster of atoms close to a dislocation in 2D triangular lattice. They represent, respectively, solid-like and non solid-like local order. The decomposition takes form:

$$\rho(Q_6; T^*, \rho^*) = c_6(T^*, \rho^*)\, \rho_6(Q_6, \xi_6) + c_5(T^*, \rho^*)\, \rho_5(Q_6, \xi_5), \qquad (3)$$

where T^* and ρ^* stand for, respectively, reduced temperature and reduced density, see Section 3. ξ_5 and ξ_6 denote, respectively, the r.m.s displacement of the atoms undergoing gaussian fluctuations in patterns Γ_5 and Γ_6. The distributions are normalized and thus $c_5 + c_6 = 1$. The parameters c_6 and c_5 give, respectively, a concentration of solid-like and non solid-like clusters at given thermodynamic conditions. In the two-phase region an important new effect appears: at the liquidus line a dramatic crossover of an ensemble of fluctuation takes place, from gaussian to a non-gaussian ensemble [5]. This new non-gaussian ensemble has to be used for modelling the fluctuations of the atoms of patterns in order to produce statistically reliable results of the decomposition (3). [4]

Fig.1 summarizes the most important features of the fluctuating patterns discussed above. Dotted and dashed lines correspond to typical non solid-like and solid-like patterns close to the liquidus line, calculated using gaussian fluctuations with $\xi_5 \simeq 0.30$ and $\xi_6 \simeq 0.15$. Solid line shows the PDF calculated from a 2D solid at $T^* = 0.7$, $\rho^* = 0.9$, i.e. close to the solidus line ($\rho^* \simeq 0.88$ [4]). The r.m.s. fluctuation is approximately equal to 0.15, as in the case of gaussian fluctuations of hexagonal pattern. Clearly, the two PDFs for local solid-like structure are different, which proves that the ensembles differ from each other. On the other hand, all PDFs intersect approximately at the same value of $Q_6^{(0)}$.
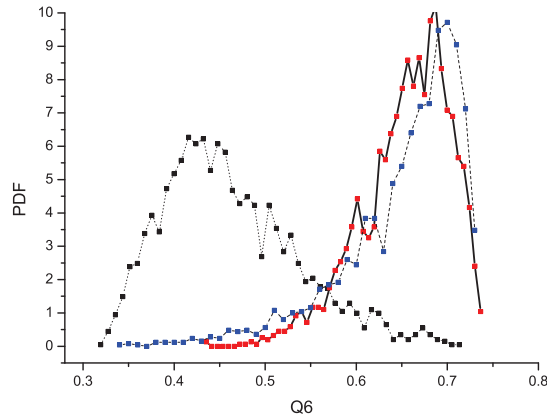

Fig. 1. PDFs for patterns: non solid-like (dotted), gaussian hexagonal (dashed) and non-gaussian hexagonal (solid), see text for more details.

2.3. Maximal Probability Decision Rule

The method presented in the last Section has a "global" character and does not provide any means for a discrimination of a single cluster as a solid- or non solid-like. To this end we use the Maximum Probability Decision Rule (MPDR) [2,8]. It states that the instantaneous cluster belongs to this fluctuating pattern for which the corresponding PDF has a larger value. In our case, 7-atom cluster is recognized as solid-like when the invariant Q_6 takes large values:

$$Q_6 > Q_6^{(0)}. \tag{4}$$

Obviously, the point $Q_6^{(0)}$ corresponds to the intersection of PDFs: $\rho_6(Q_6^{(0)}, \xi_6) = \rho_5(Q_6^{(0)}, \xi_5)$. In the liquid close to the liquidus line $Q_6^{(0)} = 0.555 - -0.56$. Small variations of this value lead to small variations in the estimated concentrations of solid-like clusters.

An important question appears: what is the relation between the concentrations c_6 calculated from the decomposition, formula (3), and from $Q_6^{(0)}-$ criterion, formula (4). Close to the liquidus line the two distributions are well separated, the numbers of clusters which are erroneously classified according to the $Q_6^{(0)}-$ criterion are small and, what is more important, approximately equal for both structures. For this reason the concentrations of local solid-like structures calculated using both approaches are approximately equal.

In what follows we refer to the central atoms of solid-like clusters as solid-like atoms (SLA); the central atoms of remaining clusters are referred to as liquid-like atoms (LLA).

The MPDR-based classification has a probabilistic character. The total probability of a false classification: a fluctuation of pattern Γ_5 as a fluctuation of pattern Γ_6 and vice versa is given by the overlap of the corresponding PDFs:

$$E(\xi_5, \xi_6) = \int min \ [\rho_5(Q, \xi_5), \rho_6(Q, \xi_6)] \ dQ. \tag{5}$$

$E(\xi_5, \xi_6)$ defines a measure of structural identity of two fluctuating patterns and introduces the metric in the feature space [2]. When the overlap is small then the probability of a false classification is also small and fluctuating structures preserve their structural identity. With increasing fluctuation level the overlap of the PDFs increases and the structural identity of fluctuating patterns is gradually lost.

3. Molecular Dynamics simulation

We have simulated a 2D system of 2500 atoms interacting via Lennard – Jones potential $v_{\mathrm{LJ}}(r)$

$$v_{\mathrm{LJ}}(r) = 4\,\epsilon \ \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \tag{6}$$

at $T^* \equiv k_B T / \epsilon = 0.7$. Here k_B stands for Boltzmann constant and T for temperature. A standard NVT molecular dynamics (MD) method [1] with velocity Verlet algorithm was used. The time step was $\Delta t = 0.0064 \, \tau_0$. In the case of argon $\Delta t = 2 \times 10^{-15} s$. Runs of various lengths were used; the maximal time interval from which data were sampled was 2×10^{-9} s $\simeq 1800 \tau_{\mathrm{LJ}}$, where τ_{LJ} denotes the period of oscillations in a harmonic regime of LJ potential. The equilibrium characteristics were sampled after 5×10^4 equilibration steps. The liquidus line was located via local structure analysis [5] at reduced density $\rho^* \equiv \rho \sigma^2 \approx 0.82$ (ρ denotes density). The critical temperature reads approximately $T^* \approx 0.55$. More details can be found in Ref. [5].

4. Evolution of clusters of SLA atoms in time

4.1. Search for SLA clusters

Below, we present shortly an algorithm for an isolation of a cluster of SLA atoms in an instantaneous configuration. By the definition, two SLA atoms belong to the same cluster it they are metrical nearest neighbours (nn). We point out that in low-density systems, e.g. gases, it is possible than atom 1 is a nn of atom 2 while atom 2 is not a nn of atom 1. The possibility of such an event in dense systems is very small.

The search for SLA clusters is done as follows. For each atom its 6 metrically defined neighbours are found; for the resulting 7-atom cluster the invariant Q_6 is calculated. Recall that if $Q_6 > 0.555$ then the central atom is classified as SLA. In this way all SLA atoms are found. As the next step we start from a chosen SLA atom which constitutes a one-atom cluster. Then, its 6 metrically defined neighbours are found and those of them which have $Q_6 > 0.555$ are the new members of the cluster. In the next step a sweep over all the members of the current cluster is made to find their SLA neighbours in the same way as for the initial atom. The search stops when in a sweep no new members are found. A search of clusters can be conveniently implemented using the concept of a binary tree search.

4.2. SLA cluster-parent and SLA cluster-child relation

Let us briefly formulate the problem. We have two consecutive configurations K and K', separated by a time interval $T_n = n \, \Delta t$. In the former one we pick up a cluster S of SLA atoms. The question is: how to find the SLA cluster S' in K' for which S is an ancestor? Once this relation is defined one can study time evolution and time scales related to SLA clusters.

In this paper we use the following definition. Some of the atoms from cluster S continue to be SLA in configuration K' and, as such, belong to various SLA clusters $S'_i, i = 1, \ldots$ in configuration K'. By the definition, S' is this of clusters

S_i' which contains the largest number of atoms from cluster S in K. The atoms of S may dominate in S', i.e., constitute more than 50% its atoms. We introduce a binary variable P which determines the degree of "parental" similarity of S' with S: if the atoms from S dominate in S' then $P_{S,S'} = 1$, else $P_{S,S'} = 0$. After the cluster S' was identified, the above procedure is continued with S' acting as the parental cluster. As long as the product $\Pi = \prod_i P_{S_i,S_i'}$ is non-zero, the current cluster S_i traces its origin back to cluster S_1 through a sequence of clusters $S_i, S_{i-1}, \ldots, S_1$. We use the notation $S_{i+1} \equiv S_i'$. In liquids after elapsed time t_0 Π becomes zero: $\Pi(t_0) = 0$. Time t_0 has the meaning of the First-Passage-Time and is a random variable, defined by moments (if they exist) and probability density function. The statistics of time t_0, which depends on the size of a parental cluster, provides an information about one of time scales for clusters of SLA atoms. After elapsed time t_0 the subsequent clusters trace their origin back to the cluster $S_i(t_0)$ and, finally, after some time t_1, the parental continuity is again lost: $\Pi(t_1) = 0$. The binary time series $B(t) = 1$ for $t = t_i$, $B(t) = 0$ for $t \neq t_i$, provides the information about this time scale in a different way.

It should be stressed that the results are dependent on the interval $T_n = n \Delta t$ separating the configurations. Thus, it is necessary to analyze the time evolution using the shortest time T_1 and then to use larger intervals. The use of the later introduces an element of an averaging over time which can result in an artificially induced chaotic behaviour of the time series. We point out that if this scenario occurs, than the crossover from a non-chaotic to chaotic behaviour yields another time scale for a liquid.

4.3. Results

In this Section we present first results on time evolution of largest SLA clusters at reduced density $\rho^* = 0.79$. The data were sampled from last 2000 configurations separated from each other by $T_1 \equiv \Delta t$; those configurations span the time interval $4 \times 10^{-12}s \simeq 3\,\tau_{\mathrm{LJ}}$.
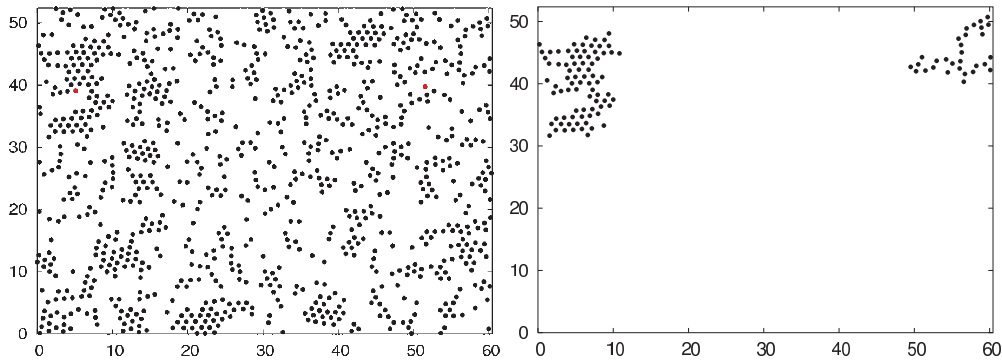

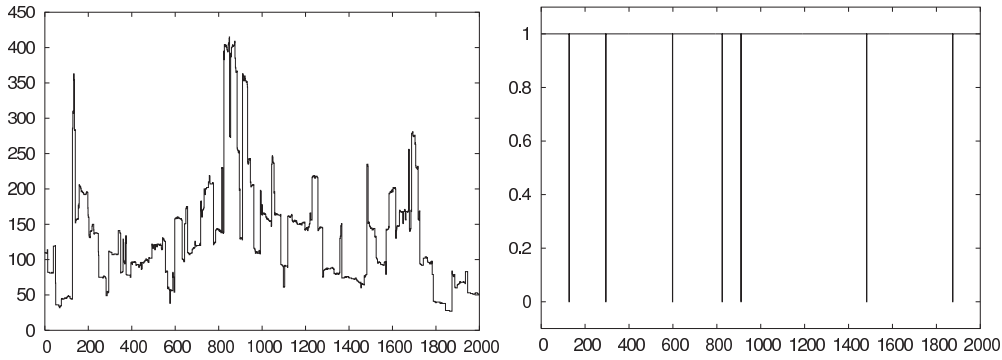**Fig. 2.** $\rho^* = 0.79$: 951 SLA atoms (left) and largest cluster (109 SLA) (right).

Fig. 3. $\rho^* = 0.79$: $\mathbf{N(t)}$ **(left) and** $\mathbf{\Pi(t)}$ **(right) for an initial cluster from Fig. 2 (right). Horizontal axis: time counted in units of** Δt**.**
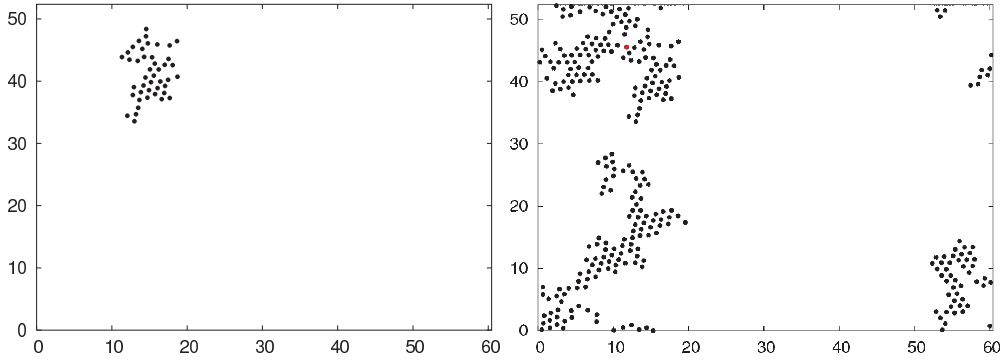

Fig. 4. $\rho^* = 0.79$: **cluster at t=127 (left) and t=128 (right)**

The 951 SLA atoms in the first of 2000 configurations are shown in Fig. 2 (left). The concentration of SLA reads approximately 0.38. The largest cluster in this configuration consists of 109 SLA (Fig. 2 (right)). The number of SLA atoms $N(t)$ in its clusters-descendants oscillates strongly as a function of time, from few tens to four hundred atoms, see Fig. 3 (left). In the studied period of time the cluster lost a few times the relation to its ancestor (in the sense discussed above), see Fig. 3 (right) which shows the plot of the function $\Pi(t)$ – its zeros t_0 indicate the corresponding moments of time. We have found that the spikes in $N(t)$ often correspond to times t_0. For example, the first spike appears at $t_0 = 128\,\Delta t$. The cluster under consideration consists at time $t = 127\,\Delta t$ of 44 SLA, while $N(128) = 284$. A closer inspection of this cluster (Fig. 4) reveals a typical mechanism of the lost of memory about the parental cluster. Namely, because of the very specific spatial distribution of SLA atoms (Fig. 2 (left)), in particular of an abundance of narrow bridge-like structure joining more compact parts of a cluster, appearance or disappearance of a single SLA within a bridge may easily lead to a fission or fusion process. This is exactly what happens in Fig. 4, where a single new SLA atom connects two separate large clusters. To

avoid misunderstanding we point out that periodic boundary conditions were used and the seemingly separate clusters actually form a single one. Similar mechanism occurs at time $t_0 = 911\,\Delta t$, where a cluster with $N(910) = 128$ undergoes a fusion with a larger one, giving rise to a $N(911) = 362$.

Those observations explain an origin of strongly developed fluctuations of $N(t)$. They are due rather to one-atom processes caused by a formal restrictive definition of a SLA state than to real physical processes. As the result, the dynamics of large SLA cluster has a short time character and does not provide quantitative measures of physically meaningful time scales exceeding the time τ_{LJ}.

5. Conclusions

We have used the probabilistic formalism of structural invariants to characterize temporal evolution of clusters of solid-like atoms in two-dimensional Lennard-Jones liquid. We have proposed a method to identify the child SLA cluster originating from a parent SLA cluster in a preceding configuration. We have found that the time interval in which the current cluster preserves memory about its ancestors is small, about the oscillation time τ_{LJ} in a harmonic regime of LJ potential. We have shown that it is the result of easily breakable one dimensional bridge-like connections between parts of the cluster.

Our study is related to metrical features of clusters. We believe that one remedy for avoiding the artificial effects discussed above is to use dressed clusters [11]. In this context, a topological approach is also of an interest, because the topological characterization of local order yields much longer time scales [12]. Study of those topics goes beyond the scope of this paper.

Summary

Recognition of fluctuating patterns: from informatics to dynamic structure of two-dimensional liquids

We use the probabilistic formalism of structural invariants for structure recognition of fluctuating patterns consisting of geometrical points to discuss some concepts related to time evolution of large clusters of solid-like atoms (SLA) in two-dimensional (2D) Lennard-Jones (LJ) liquid simulated using standard NVT molecular dynamics method. The relation between parental and child SLA clusters in consecutive configurations is

proposed and quantified. The time of life of a cluster is close to the oscillation time τ_{LJ} in a harmonic regime of LJ potential. This small value is due to a fractal-like spatial distribution of SLA atoms in a cluster which results in an appearance of easily breakable one dimensional bridge-like connections between more compact parts of the cluster.

Streszczenie

Rozpoznawanie fluktuujących wzorców struktury: od informatyki do dynamicznej struktury dwuwymiarowych cieczy.

Używając probabilistycznego formalizmu strukturalnych inwariantów do rozpoznawania struktury fluktuujących wzorców utworzonych z układu punktów materialnych, badane są wybrane aspekty związane z ewolucją w czasie dużych klasterów składających się z atomów typu SLA w dwuwymiarowej (2D) cieczy Lennarda-Jonesa (LJ), symulowanej za pomocą standardowej metody dynamiki molekularnej w zespole NVT. Zaproponowano i skwantyfikowano relację pomiędzy klasterami SLA i ich następcami – klasterami SLA w kolejnych konfiguracjach. Czas życia klastera jest bliski czasowi drgań w harmonicznym potencjale przybliżającym potencjał LJ. Ta mała wartość wynika z przypominającego fraktalny rozkładu przestrzennego atomów SLA w klasterze, w którym pojawiają się łatwo ulegające zniszczeniu wąskie połączenia pomiędzy zwartymi częściami klastera.

References

[1] Allen M., Tildesley D., *Computer Simulations of Liquids*, Oxford, 1987.

[2] Gades H., Mitus A., Physica A, vol. 176, 1991, p. 297.

[3] Mitus A., Marx D., Sengupta S., Nielaba P., Patashinski A., Hahn H., J. Phys.: Condens. Matter, vol. 5, 1993, p. 8509.

[4] Mitus A., Orlik R., Patashinski A., Patrykiejew A., Sokolowski S., Riefert O., Acta Phys. Pol. B, vol. 34, 2003, p. 3751.

[5] Mitus A., Patashinski A., Patrykiejew A., Sokolowski S., Phys. Rev. B, vol. 66, 18, 2002, p. 184202.

[6] Mitus A., Patashinski A., Physica A, vol. 150, 2, 1988, p. 371.

[7] Mitus A., Patashinski A., Physica A, vol. 150, 2, 1988, p. 383.

[8] Mitus A., Patashinski A., Sokolowski S., Physica A, vol. 174, 1991, p. 244.

[9] Mitus A., Weber H., Marx D., Phys. Rev. E, vol. 55, 1997, p. 6855.

[10] Nelson D., Toner J., Phys. Rev. B, vol. 24, 1981, p. 363.

[11] Orlik R., Phd thesis, University of Technology, Wrocław, Poland, 2007.

[12] Patashinski A., Grzybowski B., Ratner M., Mitus A., J. Phys. Chem. Lett., vol. 3, 17, 2012, p. 2431.

[13] Patashinski A., Mitus A., Ratner M., Physics Reports, vol. 288, 1977, p. 409.

[14] Patashinski A., Orlik R., Mitus A., Grzybowski B., Ratner M., J. Phys. Chem. C, vol. 114, 2010, p. 20749.

[15] Patashinski A., Ratner M., J. Chem. Phys., vol. 120, 6, p. 2814.

[16] Press W., Flannery B., Teukolsky S., Vetterling W., *Numerical Recipes*, Cambridge University Press, Cambridge, 1986.

[17] Steinhardt J., Nelson D., Ronchetti M., Phys. Rev. B, vol. 28, 2, 1983, p. 784.

[18] Strandburg K., Rev. Mod. Phys., vol. 60, 1988, p. 161.