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LOCAL STRUCTURES IN COMPUTER-GENERATED LIQUID

II. Two-Dimensional Lennard-Jones Liquid

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Local Structures In Computer-Generated Liquid.
II. Two-Dimensional Lennard-Jones Liquid

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Abstract

We study the local structures of 2-d Lennard-Jones liquid of 2500 atoms near the melting line (ρ^*=0.75, T^*=0.47). The determination of types of local structures is done within the framework of the probabilistic formalism of structural invariants. We analyze the local structures of individual configurations, the correlations between the local structures in subsequent configurations and study the time evolution of patterns of "good" matter. We conclude that the model liquid displays two types of local structures: hexagonal and "chaotic". The first one corresponds to the fluctuations of hexagon with r.m.s. fluctuations ξ of atoms equal ξ=0.14-0.16 while the second can be represented by strongly fluctuating (ξ=0.25-0.30) "defect" pattern. We discuss briefly the consequences of the physical picture of liquid as locally ordered two-structure system for methodology of computer simulations and for theories of 2-d melting.

1. Introduction

In this paper we present the preliminary results of the probabilistic analysis of local structures in a two-dimensional (2-d) Lennard-Jones (LJ) liquid. The analysis is carried out within the framework of formalism of structural invariants proposed recently by Mitus and Patashinskii[1]. This formalism provides new methods of description of a "structural identity" of a small group of a few tens of atoms (cluster) in a liquid in the presence of thermal fluctuations. The detailed presentation of the mathematical apparatus was given in the first part of this paper [2] henceforth referred to as I.

The paper is organized as follows. In the next Section we define the local order parameter and structural invariant used for the analysis of local structure and introduce the ideal patterns Γ_i of local structure for 2-d liquid. Section 3 deals with molecular dynamics simulation of 2-d LJ liquid of 2500 atoms. In Section 4 we identify the local structures of individual configurations of atoms. This includes the classification of local structures into two groups with subsequent determination of the parameters describing the classified local structures. Section 5 is devoted to the study of statistical correlations of local structures of subsequent configurations. In Section 6 we study the evolution in time of "macroscopic" patterns corresponding to definite type of local order and discuss the problem of "structural" time scale in our liquid. In Section 7 we discuss the physical picture of liquid as locally ordered two-structure system and some implications for the methodology of computer simulations and for theories of 2-d melting.

2. Structural invariant and patterns of local structure in 2-d liquid

In this paper we restrict ourselves to the study of one "relevant" structural invariant Ψ. The results of the analysis of 3-d close packed clusters show that the main contribution into parameters P_{ij} (see I) at the melting point is given only by a few "relevant" invariants [1]. The rest of the invariants describe the details of the structure and are of interest at lower temperatures, i.e. for solid. We describe the local order of 2-d liquid in the vicinity of an atom located in point $\underline{r}$ by 2-d local version of bond-order parameter of Nelson et all. [2-4]:

$$\hat{Q}_{6m}(\underline{r}) = \frac{1}{N}\sum_i Y_{6m}(0,\phi_i) \qquad (1)$$

where $Y_{6m}(\vartheta,\phi)$ denotes the spherical harmonic function, the sum is over the N neighbours of atom $\underline{r}$ and the pair of azimutal and polar angles (ϑ_i,ϕ_i) fix the direction between the central atom and i-th of its neighbours. The structural invariant $\Psi = Q(\underline{r})$ describing N+1 atom cluster "centered" at point $\underline{r}$ is defined as [2,4]

$$Q^2(\underline{r}) = \frac{4\pi}{13}\sum_{m=-6}^{m=6} |\hat{Q}_{6m}(\underline{r})|^2 \qquad (2)$$

As far as regular polygons are concerned the invariant Q has only three different "eigenvalues": Q_s=0.586 for square, Q_h=0.741 for hexagon and triangle and Q_e=5/16 for all the other polygons). Invariant Q is closly related to the one used for the study of 2-d systems (see, e.g. ref.21). The problem of the choice of the sets of local-order parameters and structural invariants for 2-d systems will be presented elsewhere.

The choice of the static patterns Γ_k (see I) for the analysis of local structure of 2-d LJ liquid follows from the following arguments. The natural choice is hexagon (Γ_h) with N=6. The other 7-atom clusters, the candidates for the description of "bad" matter

correspond to the arrangement of atoms in the vicinity of dislocation. Γ_5 is the cluster centered around 5-coordinate atom (dislocation), Γ_s is the "side" cluster with central atom being the neighbour of dislocation and the pattern Γ_7 is centered around the 7-coordinate atom. The central atoms of clusters are marked in Fig. 1. In the cases of patterns Γ_5 and Γ_7 the choice of sixth atom is not unique: there are left- and right-hand patterns. This, however, creates no problems because Q is invariant under mirror reflection. The coordinates of atoms for "defect" patterns were found from elasticity theory [5]. More strict approach requires the minimization of the potential energy of a configuration with dislocation. The choice of small patterns is dictated by necessity: we do not know a priori what the sizes of domains of "good" matter are.

The ensemble of fluctuations of atoms is chosen to be gaussian. Each atom fluctuates independently with probability density $\rho(\underline{r})=\rho(x)\rho(y)$, where $\rho(x)=\frac{1}{\xi\sqrt{\pi}}\exp\left[-\frac{x^2}{\xi^2}\right]$ and $\underline{r}=(x,y)$ denotes the vector of displacement. The root-mean-square (r.m.s.) displacement of atoms from static configuration of pattern is ξ. The histograms of invariant Q, which approximate the probability density functions $\rho_i(Q;\xi)$ (i=h,5,7,s), see I, were calculated from 2500 configurations representing the fluctuations of static patterns Γ_i. Each of the configurations was obtained by random displacements of all the atoms of the patterns according to the probability density function $\rho(\underline{r})$.

3. The model and simulational method

We have analyzed the local structures of a two-dimensional liquid, interacting via the LJ (12,6) potential

$$u(r)=4\varepsilon\left[(\sigma/r)^{12}-(\sigma/r)^{6}\right] \qquad (3)$$

at $T^*=kT/\varepsilon=0.47$ and $\rho^*=\rho\sigma^2=0.7574$. This state point is located in the

liquid in vicinity of the triple point - c.f. the phase diagram evaluated by Abraham [6].

The constant temperature Molecular Dynamics method used in this work has been quite similar to that described previously [7,8]. The equations of motion were integrated by using a fifth-order predictor-corrector scheme with a time step equal to 0.004. All calculations were carried out by running vectorized programs on CYBER 205 supercomputer. The simulational cell dimensions were $55\sqrt{3}\times2^{1/6}\sigma$ and $55\times2^{1/6}\sigma$. Except for minimum image convention, no additional cut-off of the interaction potential was used in our calculations. No long-range corrections were introduced neither during or after simulations. We have started form the "zero-temperature" crystal built of 50×50 atoms, placed in an ideal hexagonal lattice with the interatomic distance $2^{1/6}\sigma$. Our starting configuration is rather far from equilibrium. The studies of such system would give interesting information about the time evolution of local structures of strongly non-equilibrium systems. In this paper, however, we restrict ourselves to the study of the equilbrium properties only. Taking into acco int the starting configuration we have decided to use long simulation runs (up to 25000 time steps).

The equilibration of the system was controlled by analyzing the behaviour of the averages, as well as subaverages, of the potential energy $E^*=E/\varepsilon$ and of the compressiblity factor $Z=p/\rho kT$. The subaverages were determined after each 1000 time steps. The average equilibrium energy E^* and the compressibility factor were found to be equal to -1.895 and 0.686, respectively. In Fig. 2, however, we have displayed the changes in evaluated subaverages with the time. We conclude that after approximately 6000 time steps the equilibrium was reached.

4. Local structures of individual configurations

We determine the types of local order present in liquid in two ways. First, we extract the components of local order by analyzing only a part of the histogram. In our simulations the MD histograms of invariant Q have two-peak structure. We split the MD histogram into two parts; the splitting line $Q=Q^{(d)}$ passes between the two peaks. Cluster are classified to one of the two groups depending on whether $Q > Q^{(d)}$ or $Q < Q^{(d)}$. The meaning of the classification results from determination of local structures of clusters belonging to these two groups. Alternatively, we decompose the histogram into components corresponding to some assumed types of local structure. More details can be found in I.

4.1 Determination of hexagonal component of local order

A preliminary analysis shows that the right parts of MD histograms could correspond to hexagonal structure characterized by probability density function $\rho_h(Q;\xi)$ for some value $\xi = \xi_h$. ξ_h is determined by an analysis of the significance level $\alpha\left[Q^{(d)};\xi\right]$ as described in I.

The results are as follows. After 500 MD steps the r.h.s. MD peak is determined as corresponding to fluctuations of hexagon for ξ=0.11 at significance level $\alpha\simeq$0.06. The determination is "sharp": the null hypothesis is rejected at $\xi\leq$0.10 and $\xi\geq$0.12 ($\alpha < 10^{-3}$). The significance level increases with increasing number of time steps. Simultaneously, the uniqueness of the determination is lost. The typical case, corresponding to 15000 MD steps is presented in Figs. 3, 4. Fig. 3 displays the MD histogram and the histogram of hexagon at ξ=0.15. The determination is done on basis of Fig. 4. For small values of $Q^{(d)}$, $\alpha\left[Q^{(d)};\xi\right]\simeq 0$, which means that liquid has some non-hexagonal component of local order. We determine the "best" value of ξ by maximizing the merit function $\hat{\alpha}(\xi)= \max \alpha\left[Q^{(d)};\xi\right]$ (see I). We

look for maximum of $\alpha\left[Q^{(d)};\xi\right]$ (as function of $Q^{(d)}$) for $Q^{(d)}<Q_{1/2}(\xi)$. We chose $Q_{1/2}(\xi)$ in such the way that the line $Q=Q_{1/2}(\xi)$ crosses the left part of trial pattern histogram approximately at its half-heigth (Fig. 3). The function $Q_{1/2}(\xi)$ for hexagon is plotted in Fig. 5. In Fig. 6 we show the merit function $\hat{\alpha}(\xi)$. The interval estimation $\Delta\xi_h$ of the parameter ξ_h is given by the solutions of the inequality $\hat{\alpha}(\xi) \geq \alpha_o$, where α_o is some chosen significance level (see I). When, for example, α_o = 0.40 then the determination yields the values ξ_h=0.14, 0.15 and 0.16.

The results of the determination of hexagonal component in our liquid are summarized in Fig. 7, where the plot of the dependence of ξ_h on number of MD steps is displayed. We present only these values of ξ_h for which $\alpha \geq 0.2$ (with the exception of ξ_h=0.14 and 0.15 for a configuration after 6000 time steps, for which α= 0.04 and 0.10, respectively). We put a bar of length 0.01 around each of the points.

4.2 Determination of other components of local order

In an analogous way we have determined the structural component responsible for the left part of MD histogram after 15000 time steps by assuming that it corresponds to fluctuations of pattern Γ_5. We obtained $\alpha\left[Q_{1/2}(0.30);0.30\right]$=0.03. This time the line $Q=Q_{1/2}(\xi)$ crosses the right part of graph of $\rho_5(Q;\xi)$ approximately at its half-heigth. We conclude that at the significance level α=0.03 there is no reason to reject the null hypothesis. The analysis of the case ξ=0.25 yields α=0.01: for $\xi \leq 0.20$ and $\xi \geq 0.35$ $\alpha < 10^{-4}$.

Analogous determinations have been performed for configurations at various values of MD steps and yield the same results: the "best" determinations correspond to $0.25 < \xi < 0.30$. The significance levels are, as a rule, higher than in the case of 15000 MD steps (α=0.4 for ξ=0.25 at 6000 MD steps or α=0.2 for ξ=0.25,0.30 at 25000 MD steps).

For high values of ξ the structure of a fluctuating pattern is no more well-defined; the probability density functions $\rho_i(Q;\xi)$ (i=h,5,7,s) appproach some universal function ρ^* corresponding to "structureless" pattern (compare [1]). In Figs. 8a,b we show the plots of the functions $\rho_i(Q;\xi)$ for ξ = 0.25 (part a) and ξ = 0.30 (part b). In both the cases the quantities P_{ij} are not small; for ξ = 0.30 they are bigger than 0.5. Correspondingly, the non-hexagonal component of local order is "structureless".

4.3 Global determination of the local structures

We assume (see I) that the probabilty density function $\rho(Q,t)$ where t denotes the MD time depends linearly on the probability density functions $\rho_i(Q;\xi)$ for patterns. The "best" determination of the coefficients results from extremizing some merit function [2,9]. The merit function we use is the significance level $\alpha(c_h,c_5,\xi_h,\xi_5)$ ($c_h+c_5=1$, $c_h,c_5 \geq 0$) obtained from χ^2-test verification of null hypothesis for $\rho(Q,t)$ (represented by MD histogram) and linear trial combination ρ_{trial} :

$$\rho_{trial}(Q;c_h,c_5,\xi_h,\xi_5) = \sum_{i=h,5} c_i\ \rho_i(Q;\xi_i) \qquad (4)$$

In Fig. 9 we present the best trial combination (4) for the configuration after 25000 MD steps. We have obtained α=0.12 for c_h=0.46, ξ_h=0.20 and ξ_5=0.25. The reasonable values of α (0.04 to 0.12) correspond to ξ_5=0.25 and $0.17 \leq \xi_h \leq 0.20$ for which $0.40 \leq c_h \leq 0.46$, see Fig. 10. For ξ_h outside this interval $\alpha < 10^{-3}$. For ξ_5<0.25 $\alpha < 10^{-3}$; for $\xi_5 > 0.25$ the best determination corresponds to the above interval for ξ_h and yields $\alpha \simeq 0.01$. The upper bound on ξ_5 is not well-defined because there are very small differences between $\rho_5(Q;0.25)$ and, say, $\rho_5(Q;0.30)$, see end of previous Section. The analysis of other equilibrium configurations yields the same values

for "best" ξ_h, ξ_5 and concentrations c_h. We have also investigated the generalized combination (4) accounting for other patterns (Γ_7,Γ_s) and obtained that c_7, $c_s \ll c_5$.

4.4 The case of 15000 MD steps

In this Section we analyze the space distribution of hexagonal clusters for various degrees of "hexagonality" $\beta = \beta_5(Q_0,\xi_5)$ of the competing pattern Γ_5 in a configuration after 15000 MD steps. The function $\beta_5(Q_0,\xi_5)$ is defined as follows [2]:

$$\beta_5(Q_0,\xi_5) = \int_{Q>Q_0} \rho_5(Q;\xi_5) \qquad (5)$$

We treat a cluster as hexagonal when $Q > Q_0$; Q_0 is a solution of the equation $\beta_5(Q_0,\xi_5)=\beta$. According to the results of Sections 4.2, 4.3 we put ξ_5=0.25. The function $\beta(Q_0;0.25)$ corresponding to $\rho_5(Q;0.25)$ (c.f. Fig. 11) is shown in Fig. 12. The distributions of hexagonal clusters for β = 0.01, 0.02, 0.04 and 0.08 are presented in Figs. 13a-d, respectively. The squares denote the centers of hexagonal clusters. All the space distributions have one common feature, namely the tendency to form clusters. When β increases, the "nuclei" of clusters shown in Fig. 13a are growing by the process of inclusion of hexagonal clusters lying near their rim. At the same time the structural "identity" of these clusters is being gradually lost. The dependence of the number N_h of hexagonal clusters on β is shown in Fig. 14 and can be approximated by formula $N_h(\beta) = 2100\ \beta^{0.32}$.

The "structureless" clusters contributing to the left part of MD histogram do not show the tendency to form big clusters.

We conclude that our liquid displays two structural components of local order: "defect" structure Γ_5 at ξ_5=0.25 - 0.30 and hexagonal structure Γ_h at ξ_h=0.14 - 0.16 (which correspond to maximal values of α, c.f. Fig. 7). The question of the width of interval of ξ_h is

discussed in Section 7. The approximate functions $\rho_h(Q;0.15)$ and $\rho_5(Q;0.25)$ are shown in Fig. 11. The reliability of the determination depends on the values of parameters P_{ij} , see I. We obtain $P_{5h} \simeq 0.12$ which means that fluctuating pattern Γ_h is still well-defined.

5. Local structures: time-correlations

In this Section we study the time evolution of the local structures in liquid by the time-dependent probability density function $\rho(Q,t)$ and by a time correlation function [2] $C(t_1,t_2)$.

The MD-time evolution of function $\rho(Q,t)$ is depicted in Fig. 15. At t=0 $\rho(Q)$ corresponds to finite 2-d hexagonal crystal at $\xi=0$, i.e. $\rho(Q) \propto \delta(Q-Q_h)+ \ldots$; $Q_h=0.741$. The terms which were not written out explicitely are due to the finite size of the system, have also δ-like form and correspond to the clusters lying at the boundaries. The finite width of MD histogram at t=0 is the result of gridding procedure used for plotting the surface. We conclude that after 5000 - 6000 MD steps the function $\rho(Q,t)$ does not seem to be systematically dependent on t. This qualitative statement can be formulated rigorously in the following way [2]. For two configurations of atoms after t_1 and t_2 we verify the null hypothesis stating that the density probability functions $\rho(Q,t_1)$ and $\rho(Q,t_2)$ are drawn from the same distribution function. Verification is provided by Kolmogorov-Smirnov test [2,9]. The resulting significance level $\alpha_{ks}(t_1,t_2)$ is our time correlation function: $C(t_1,t_2) = \alpha_{ks}(t_1,t_2)$. In Fig. 16 we present this function for t_1=3000 and t_1=5000. In the first case the correlations decay quickly with the increase of $\Delta t = t_2-t_1$. We conclude that after 3000 time steps liquid is not in "structural" equilibrium. Function C(5000,5000+Δt) displays oscillatory character. This means (see I) that the system is in structural equilibrium (see also next Section).

We conclude that the structural equilibrium is achieved after t_{eq}=5000-6000 MD steps, in agreement with results of qulitative analysis of data in Fig. 15 and with thermodynamic results of Section 3. The local structures of configurations after t_{eq} are statistically the same. We stress once again the meaning of this statement: there is no reason to reject the null hypothesis at significance level $\alpha_{ks} \simeq 0.1$.

6. Time evolution of patterns of "good" matter

Figures 13 show that the centers of hexagonal clusters form complicated patterns of "good" matter. In this Section we analyze time evolution and some structural properties of these patterns.

Consider first the problem of time of "life" of patterns. We have analyzed the subsequent configurations with time interval of a few tens of MD steps. Big patterns fluctuate weakly; the fluctuations influence mainly patterns consisting of a few clusters. Noticeable fluctuations of big patterns occur over time intervals of order of 100 MD stps. In Fig. 17a-d we present the configurations after 13100, 13200, 13300 and 13400 MD steps. The squares represent the centers of hexagonal clusters. We treat a cluster as hexagonal when $Q > Q_0$ such that the degree of hexagonality $\beta_5(Q_0;0.25)$ is 0.04. We conclude that the memory about the shape of the pattern is the better the more compact and bigger pattern is.

In last Section we have shown that for $t > t_{eq}$ the functions $\rho(Q,t)$ are not dependent on time (in statistical meaning). This, in particular, means that the number of hexagonal clusters N_h fluctuates around some mean value, as shown in Fig. 18, but says nothing about the shape of patterns of "good" matter.

In Figs. 19a-d we present various stages of the process of the equilibrating of MD system, starting from 500 MD steps up to 25000 MD steps. In the early stages of simulation the change of pattern of

"good" matter is rapid. In order to draw conclusions about the evolution of these patterns for $t > t_{eq}$ we have studied the relative concentrations p_i (with respect to the total number of hexagonal clusters), i=1,..,4, of i-atom patterns such that all its atoms are the centers of hexagonal clusters. As before, we treat a cluster as hexagonal when β=0.04. The parameter p_1 increases until t_{st}=10000 - 13000 MD steps after which it fluctuates around some equilibrium value, as shown in Fig. 20. We conclude that in time interval $t_{eq} < t < t_{st}$ the process of loosing one hexagonal cluster by big patterns is non-equilibrium one. The other quantities p_i behave less regularly; the quantity $p_2+p_3+p_4$ increases monotonously up to 7.000 - 9000 MD steps, see Fig. 20. In Fig. 21 we present the total number of seperate patterns as a function of number of MD steps. The structural equilibrium occurs approximately after $t=t_{st}$.

We conclude that besides the "thermodynamical" time scale t_{eq} model liquid displays the existence of "structural" time scale $t_{st} \simeq 2t_{eq}$.

7. Discussion and conclusions

The results presented in Sections 4-6 can be summarized as follows. Model LJ liquid near the melting line (T^*=0.47, ρ^*=0.75) displays two types of local structure: ordered and disordered. The first one corresponds to the fluctuations of hexagon with r.m.s. fluctuations of atoms ξ_h=0.14 - 0.16, the second can be represented by defect pattern Γ_5 at ξ_5=0.25 - 0.30. The concentrations of 7-atom clusters of first and second type are c_h=0.40-0.46 and c_5=1-c_h. Both types of local structure are relatively well-defined ($P_{h5} \simeq 0.12$). These statements have probabilistic meaning and their reliability is determined by significance levels discussed above.

Let us discuss some methodological aspects of our approach. The width $\Delta\xi$ of the intervals of "best" ξ_h are determined by the degree

of correlations of fluctuations of hexagon at two close values of ξ. Our method gives $\Delta\xi$=0.04, see Sections 4.1 and 4.3. Next, the significance levals α depend noticeably on the small changes of data. To investigate this point we have provided the global identification of local structures after 25000 time steps using two sets of data to represent $\rho_h(Q;0.20)$. The verification of the null hypothesis for these two sets yields high value of α=0.84. The second structure was Γ_5 at ξ_5=0.25. The significance levels obtained in the way explained in Section 4.3 were 0.12 and 0.04; nevertheless the values of c_h were the same in both cases. To "stabilize" the fluctuations of α one would have to use better statistics for fluctuations of patterns. Finally, we believe that the global determination of ξ_h is not as reliable as determination based on the study of right parts of MD histograms. This is the consequence of the crude simulation of fluctuations of patterns, where each atom fluctuates independently. We have analyzed the local order in solid and have concluded that more refined ensemble of fluctuations of patterns is necessary to obtain satisfactory significance levels.

The physical picture of liquid as locally ordered two-structure system has important methodological consequences both for theoretical studies and computer simulations. Hexagonal clusters form complicated patterns of "good" matter with tendency to form compact groups containing up to 50 hexagonal clusters. These groups should be taken into account in an analysis of various properties of liquids. The average parameters over the system have two components corresponding to subaverages over domains of "good" and "bad" matter. In particular, global averaging of parameters describing the correlations of local anisotropies can supress relevant information. Consider the simple analogy: antiferromagnet below Neel point has null average spin but well-defined magnetic substructures exist. The

two-structure picture of liquid offers a new point of view on the problems of entropy of simple liquids and entropy of melting and may be useful in answering the question how and where the entropy arises in going from the solid over liquid to gas. Consider the problem of diffusion in locally ordered liquid. The coefficients in Fokker-Planck equation are some averages over elementary processes of collisions (see e.g. ref.10) and can be different in "good" and "bad" matter. Thus, the studies of diffusion at different temperatures and densities and subsequent comparison with the prediction of the two-structure approach would be of noticeable interest.

Let us discuss briefly some consequences for theory of melting. The description of condensed matter in the vicinity of the melting line has two aspects. The first one is connected with evaluation of the thermodynamic functions and the phase diagram. These problems can be reasonably well solved by using recent versions of the density functional theories [11,12]. The second problem concerns the studies of local properties of liquids and, in particular, the character and distribution of various defects. The local and global structures of condensed matter are results of interplay of two mechanisms. The first one is responsible for type of local arrangement of atoms; the second - for long range correlations between local structures. The standard analysis of melting is done by an effective hamiltonian, which is the functional of some order-parameter fields. As a rule, these fields are chosen to represent various kinds of defects - elastic dipoles (KTNHY theory [13]) or dislocations and disclinations (Chui [14], Kleinert [15]). Our results show that it is neccesary to include an order parameter which describes the local structure. The general formulation of the problem was given by Patashinskii and Shumilo [16]. In such approach the effective hamiltonians for defects can be obtained by integrating Boltzmann factor (with initial

effective hamiltonian) over the local-structure parameters. Although technically difficult, this approach can provide systematic approach to the construction of effective hamiltonians for defects.

Our analysis casts some light onto the problems of time and length scales in computer generated liquids. The patterns of "good" matter are complicated geometrical objects which conserve their form (statistically) in time. The distribution of number of hexagonal clusters in various groups of "good" matter is an equilibrium characteristic in an infinite system. In computer simulations the effect of the boundary conditions can be described by an external field (Steinhardt et all. [4]) acting on orientational degrees of freedom and change this distribution. The study of this problem would require the repetition of our analysis for bigger systems. The repercussions for 3-d systems can be more dramatic. Suppose that the 2-d patterns are not self-similar under the change of the length scale, i.e. the maximal compact groups of hexagonal clusters contain 6×6 or 7×7 atoms. We expect that the picture of local order in 3-d is qualitatively similar as in 2-d, with compact groups of good matter containing 6^3 or 7^3 atoms. Adding the same number of clusters of "bad" matter we conclude that the inherent unit of local order and disorder in 3-d liquid contains approximately 1000 atoms. The study of smaller systems could lead to misleading interpretations of local structure. We believe that reliable results could be obtained from study of liquids of 10^4 or more atoms. The analogous argumentation holds for time scale. We have shown that the liquid which is in equilibrium judging by the time behaviour of thermodynamic functions shows non-equilibrium relaxation as far as some structural characteristics are involved. It is the manifestation of general tendency in relaxation of systems displaying a few length scales (see, e.g. ref.17). The relaxation time increases as the size of the

system increases. In particular, the big patterns of "good" matter relax more slowly than thermodynamical functions determined by pair correlations. We conclude that the repetition of our analysis for bigger systems (10.000 and more atoms) could give answers to the open question of self-similarity of physical picture of liquid as of locally ordered two-structure system.

Finally, let us discuss briefly the problem of character of oscillatory movements of atoms in liquid. First of all, the concept of r.m.s. displacement ξ of atom in equilibrium liquid has to be defined. A straightforward generalization of ξ which measures the r.m.s. displacement of the atoms in the solid from ideal lattice configuration onto the case of liquid was proposed recently by LaViolette and Stillinger [18] in the formalism of inherent structures (Stillinger and Weber [19]). The r.m.s. return distance [19] gives the average ξ in the sense discussed above. Our approach defines this quantity separately for "good" and "bad" matter, as parameter of an ensemble of fluctuations of ideal patterns which approximate in the "best" way the MD density probability functions of structural invariant. We believe that the combination of the method of "inherent" structures with our formalism of structural invariants would provide a powerfull tool for the study of the problem.

The analysis of local structures of liquid presented in this paper is the first step towards the understanding of local and global structures of simple liquids. The full information about the type of local arrangement of atoms is contained in the set of relevant invariants. The treatment of this information will require the use of methods of multi-variate statistical analysis. Next, we have studied one point in ρ^*-T^* plane. The more complete picture will emerge when a few points, say at constant ρ^*, are analyzed and the results compared with each other. This problem is in progress now.

A compact report of our study will appear elsewhere [21].

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Figure captions

Fig. 1.

Atom-atom nearest-neigbour network in the vicinity of dislocation. The symbols 5, 7 and s denote the central atoms of static patterns Γ_5, Γ_7 and Γ_s, respectively.

Fig. 2.

The dependence of subaverages of the total internal energy $E^*=E/\varepsilon$ and of the compressiblility factor Z on the number of time steps. The subaverages were calculated after each 1000 time steps.

Fig. 3.

Probability density function $\rho(Q)$ evaluated from MD simulations after 15000 time steps (circles) and the probability density function $\rho_h(Q;0.15)$ for hexagon at $\xi=0.15$ (asterisks). The parameter $Q_{1/2}$ is defined in the text. The solid lines are the 4-th rank polynomial best fits to the data.

Fig. 4.

Plot of the significance level $\alpha\left[Q^{(d)};\xi\right]$ versus $Q^{(d)}$ (after 15000 time steps). The different markers correspond to different values of ξ displayed in the figure.

Fig. 5.

The dependence of $Q_{1/2}$ on ξ for hexagon.

Fig. 6.

Plot of the merit function $\hat{\alpha}(\xi)$ for a configuration after 15000 time steps. The solid line is the 4-th rank polynomial best fits to the data (asterisks).

Fig. 7.

The dependence of ξ_h on number of time steps. The small horizontal bars denote the values of ξ_h for which the significance levels α are the biggest.

Fig. 8.

Plots of the probability density functions $\rho_i(Q;\xi)$ for patterns for ξ = 0.25 (part a) and ξ = 0.30 (part b). The solid and dashed lines correspond to different values of ξ displayed in the figure and are the 4-th rank polynomial best fits to the data.

Fig. 9.

MD histogram of Q after 25000 time steps (asterisks) and the "best" trial combination (4) of histograms for patterns (circles). The coefficients of the trial combination are given in the text. The solid and dashed lines are the 4-th rank polynomial best fits to MD and trial combination data.

Fig. 10.

Plots of the merit functions $\alpha(c_h,1-c_h,\xi_h,\xi_5)$ for a configuration after 25000 time steps for ξ_5 = 0.25 and for a few values of ξ_h displayed in the figure.

Fig. 11.

Probability density functions $\rho_h(Q;0.15)$ (for hexagon at $\xi=0.15$ - circles) and $\rho_5(Q;0.25)$ (for the pattern Γ_5 at $\xi=0.25$ - asterisks). The solid lines are the 4-th rank polynomial best fits.

Fig. 12.

The dependence of "degree of hexagonality" $\beta_5(Q_0;\xi_5)$ on Q_0 (eq.(5)) for pattern Γ_5 at ξ_5 = 0.25.

Fig. 13.

Configuration of atoms (points) and centers of hexagonal clusters (squares) after 15000 time steps for selected values of β: β=0.01, N_h=473 (part a); β=0.02, N_h=596 (part b); β=0.04, N_h=764 (part c) and β=0.08, N_h=911 (part d).

Fig. 14

Plot of the dependence of the number N_h of hexagonal clusters on degree of hexagonality β of pattern Γ_5 in a configuration after 15000

time steps.

Fig. 15

Plot of the probability density function $\rho(Q,t)$.

Fig. 16.

The dependence of the time correlation function $C(t_1,t_2)$ upon the number of MD time steps t_2 for t_1 = 3000 (asterisks) and t_1 = 5000 (circles).

Fig. 17.

Configuration of atoms (points) and centers of hexagonal clusters (squares) for β=0.04 after 13100 time steps (part a), 13200 time steps (part b), 13300 time steps (part c) and 13400 time steps (part d). The numbers of hexagonal clusters were equal to N_h=749, 800, 783 and 755, respectively.

Fig. 18.

Plot of the number N_h of hexagonal clusters (β_5 = 0.04) versus number of time steps.

Fig. 19.

Configurations of atoms (points) and centers of hexagonal clusters (squares) for β=0.04 after 500 time steps (part (a), N_h=1990) and in an equilibrium regime after: 6000 time steps (part b, N_h=849), 20000 time steps (part c, N_h=813) and after 25000 time steps (part d, N_h=806).

Fig. 20.

The time dependence of relative concentrations p_i of i-atom clusters of "good" matter: p_1 (solid line) and $p_2+p_3+p_4$ (dashed line).

Fig. 21.

Total number of clusters of "good" matter versus number of MD time steps (β=0.04).

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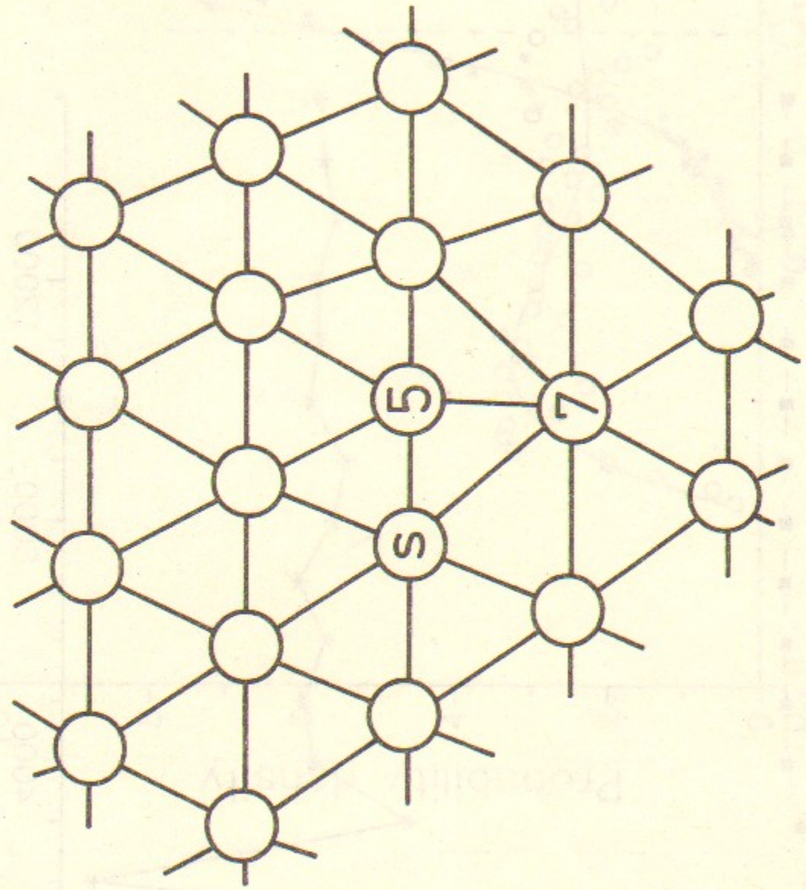

Fig. 1

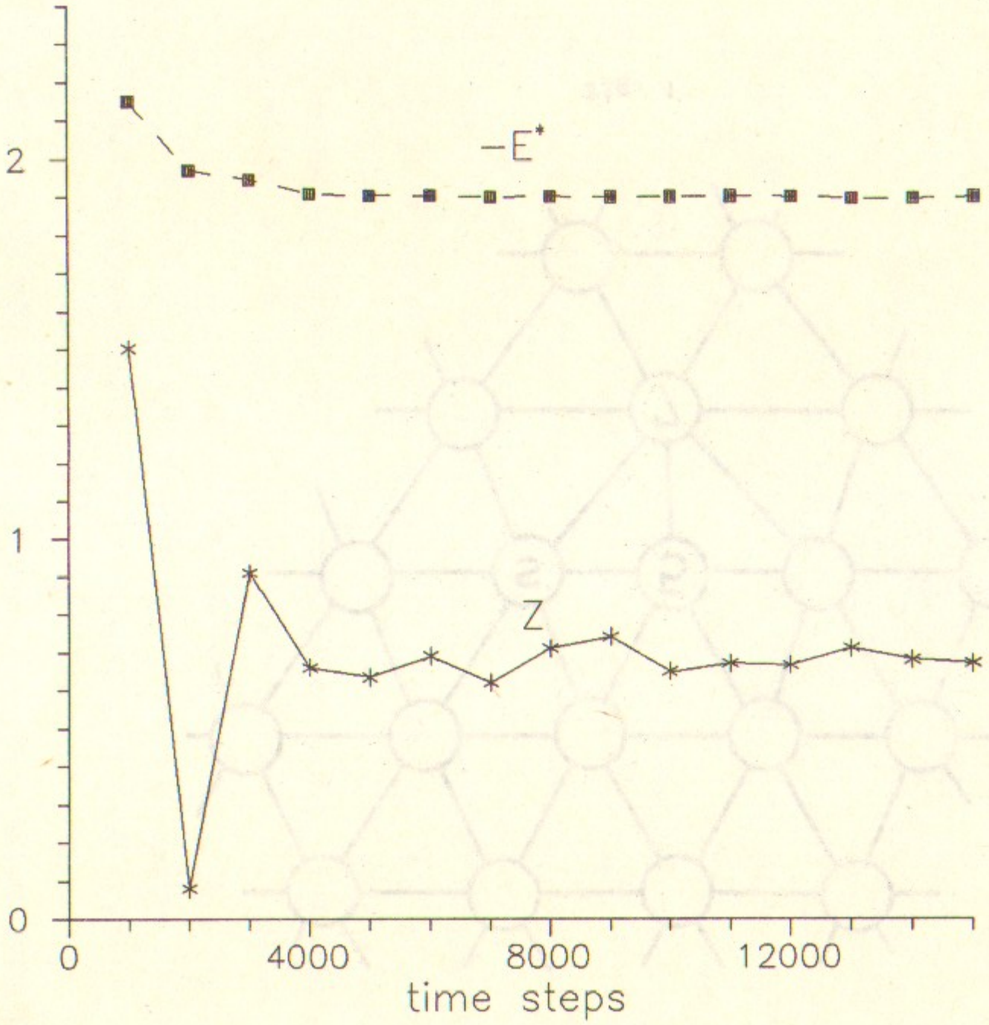
2
1
0
$-E^*$
Z
0
4000
8000
12000
time steps

Fig.2

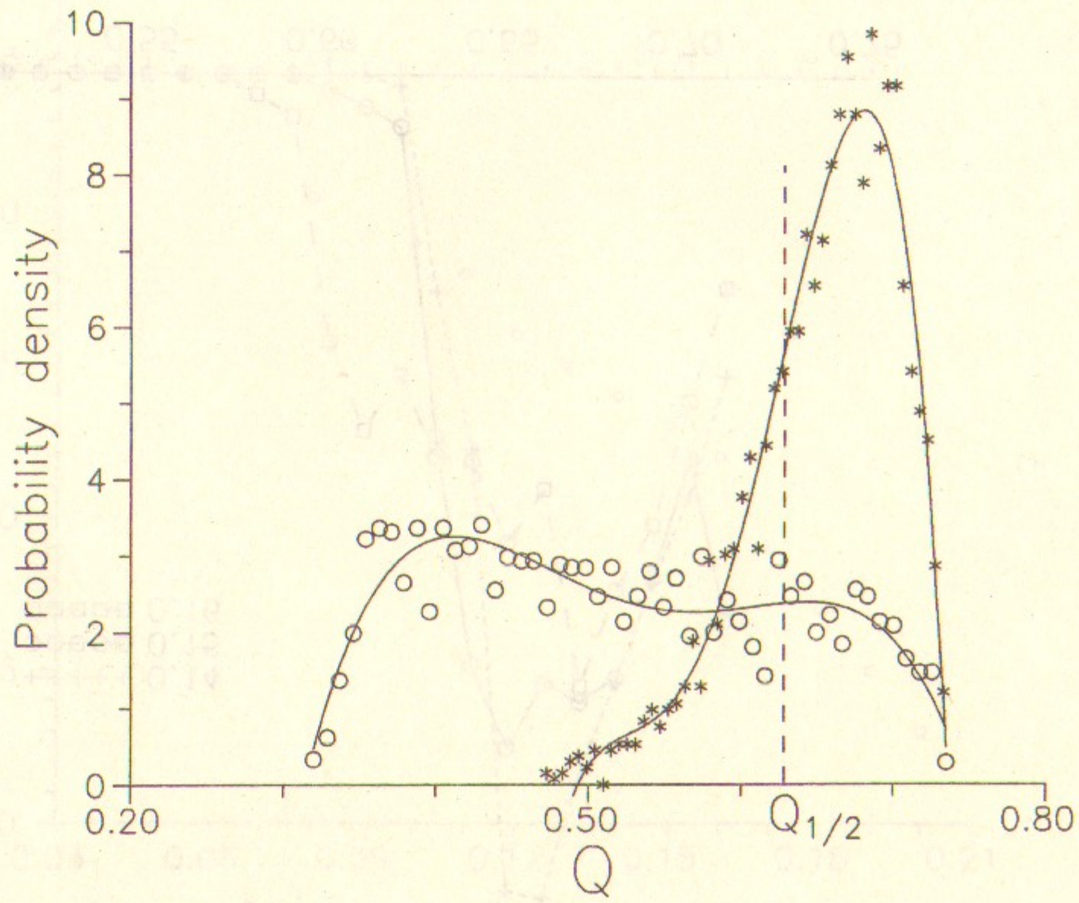
10
8
6
4
2
0
Probability density
0.20
0.50
$Q_{1/2}$
0.80
Q

Fig. 3

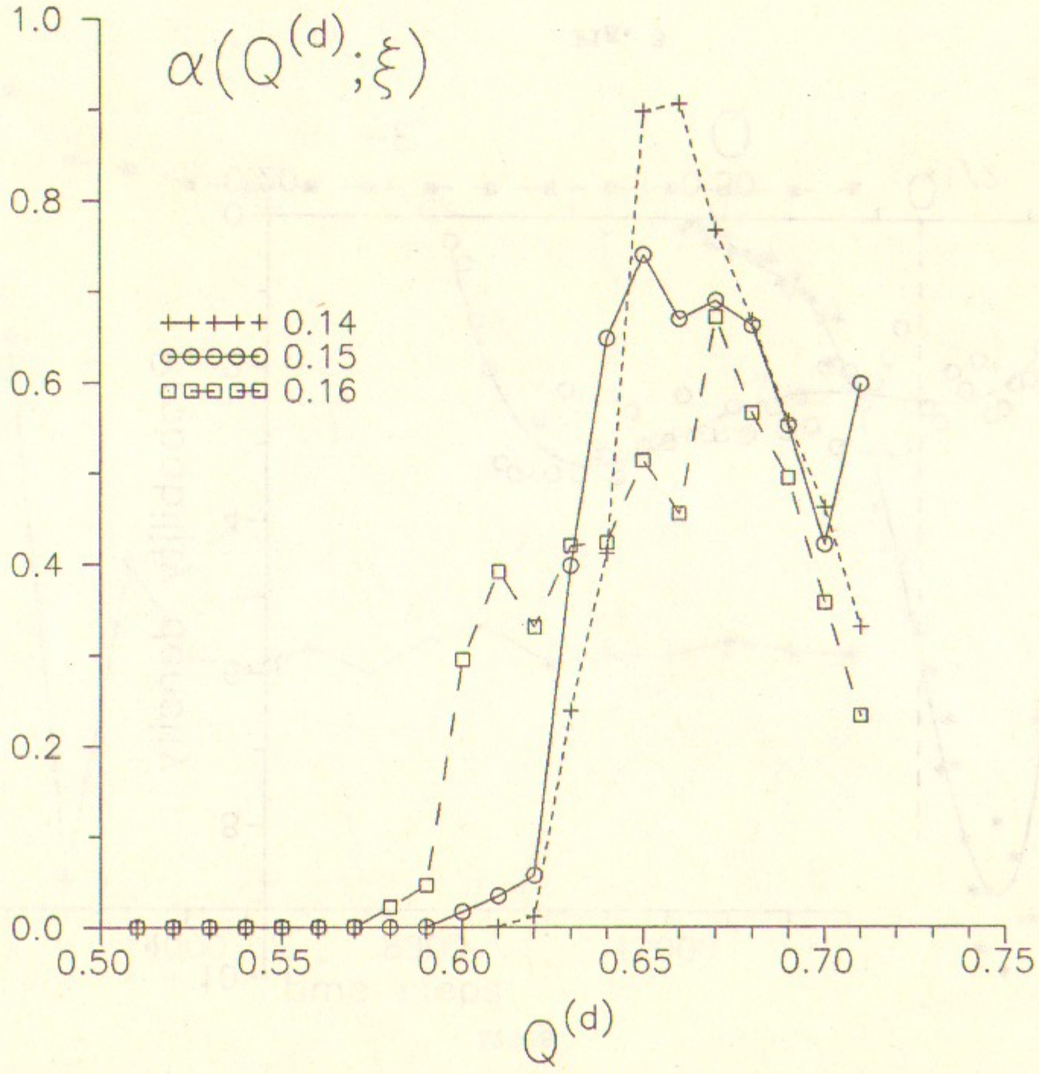
1.0
0.8
0.6
0.4
0.2
0.0
$\alpha(Q^{(d)};\xi)$
0.14
0.15
0.16
0.50
0.55
0.60
0.65
0.70
0.75
$Q^{(d)}$

Fig. 4

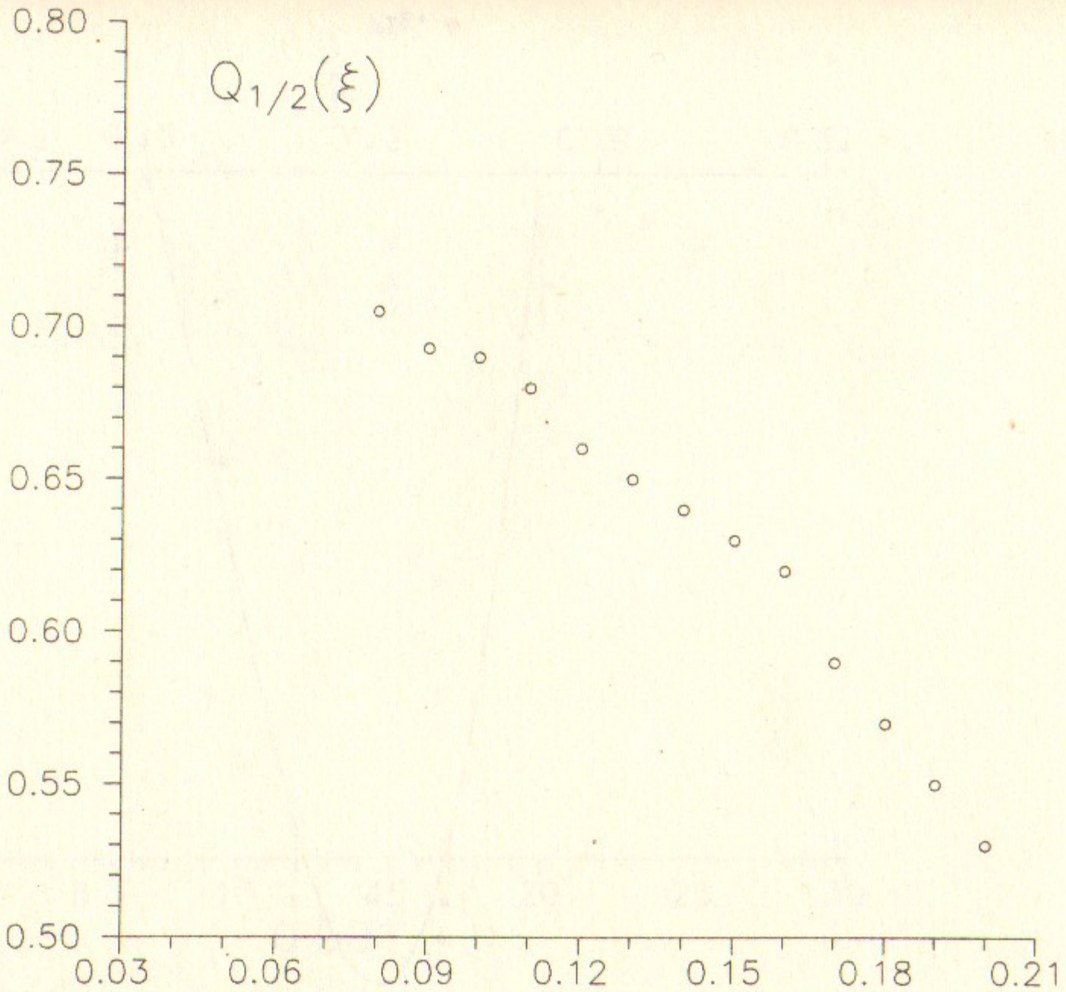
0.80
0.75
0.70
0.65
0.60
0.55
0.50
$Q_{1/2}(\xi)$
0.03
0.06
0.09
0.12
0.15
0.18
0.21
ξ

Fig. 5

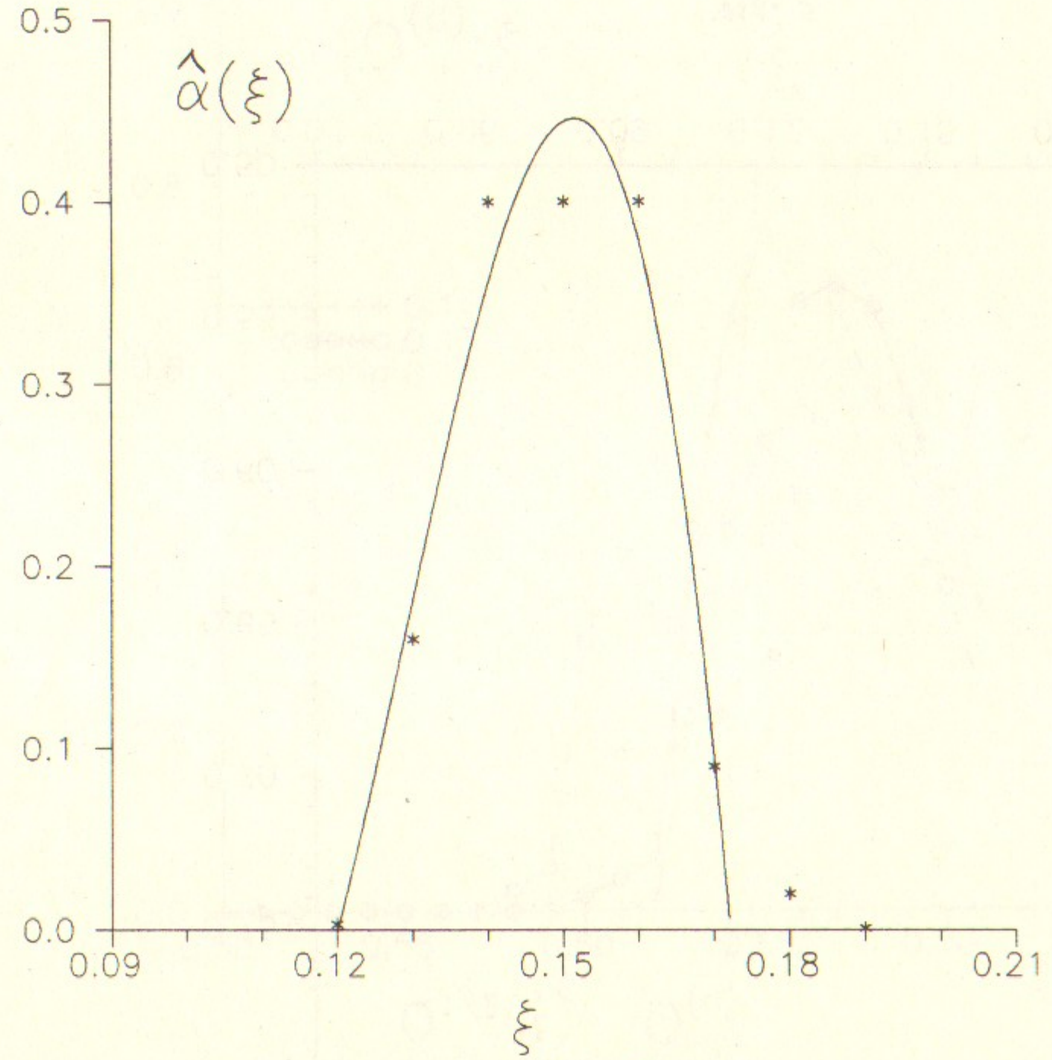
0.5
0.4
0.3
0.2
0.1
0.0
$\hat{\alpha}(\xi)$
0.09
0.12
0.15
0.18
0.21
ξ

Fig. 6

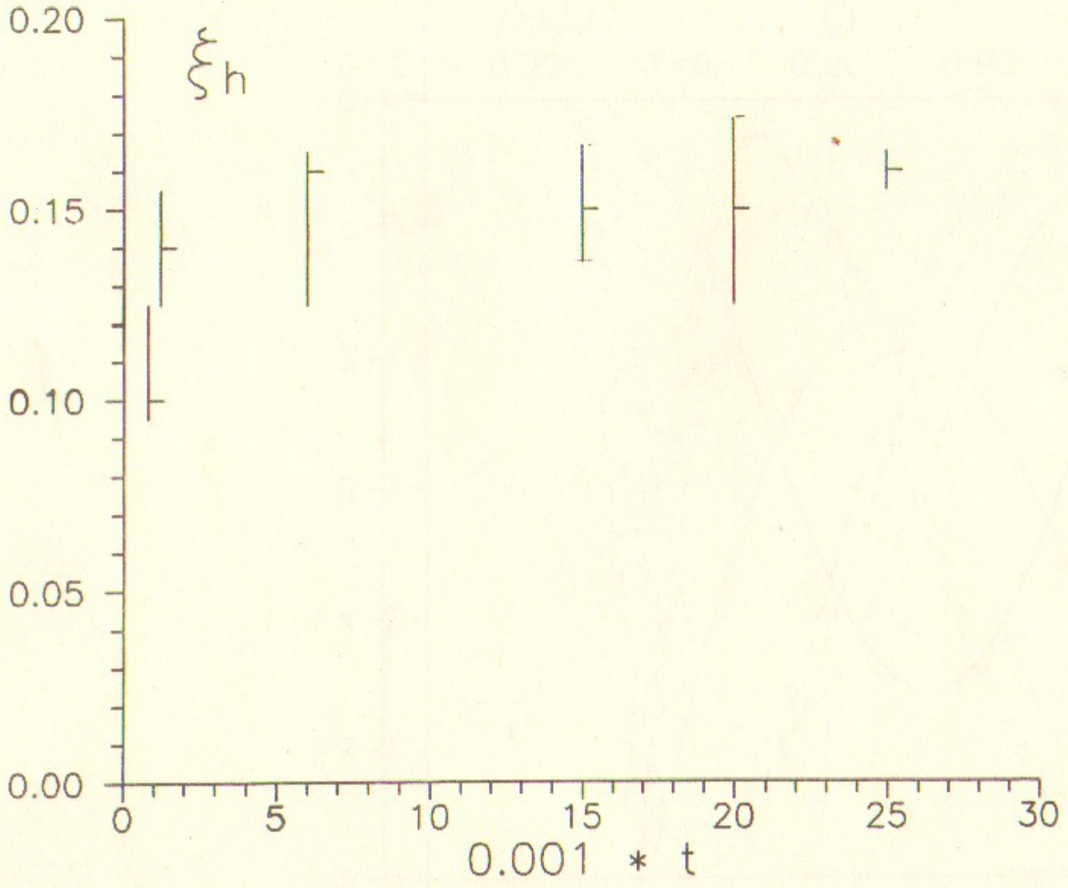
0.20
0.15
0.10
0.05
0.00
ξ_h
0
5
10
15
20
25
30
0.001 * t

Fig. 7

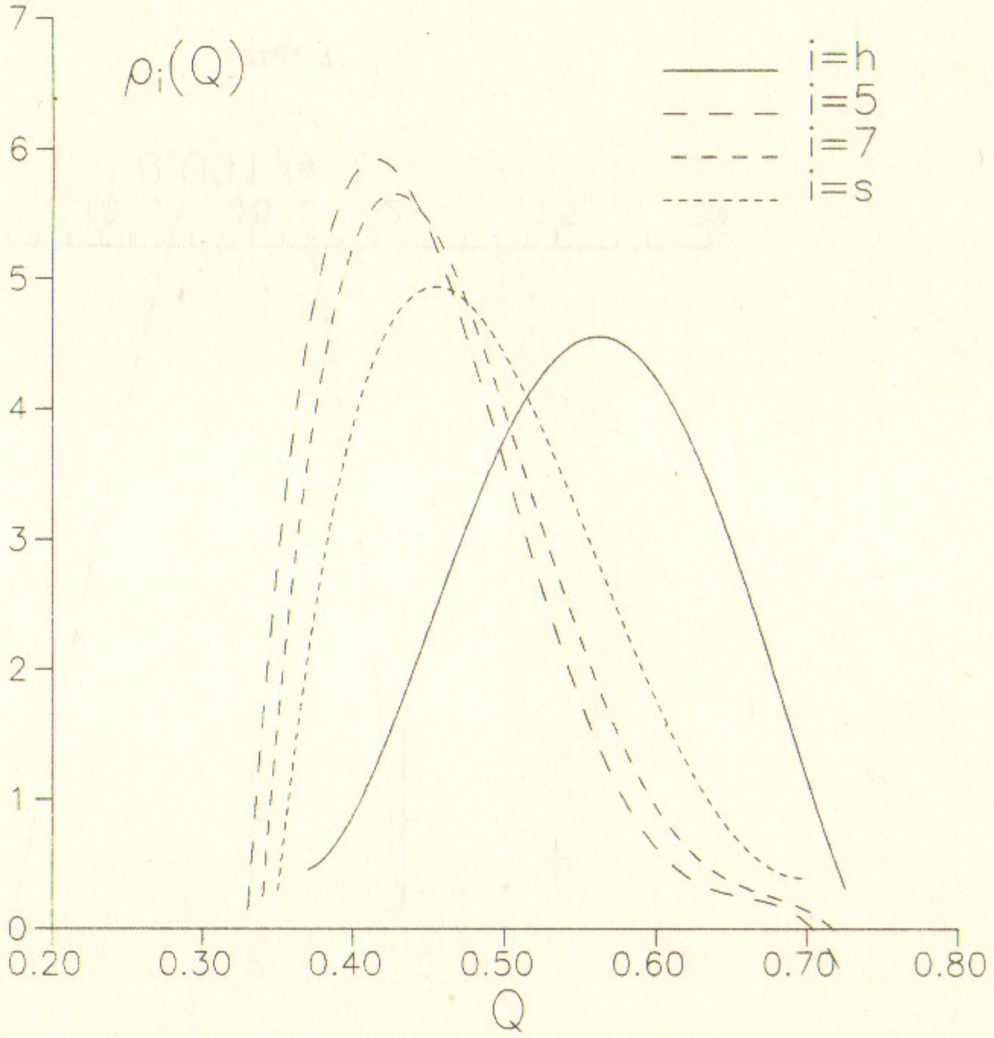
$\rho_i(Q)$
i=h
i=5
i=7
i=s
0
1
2
3
4
5
6
7
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Q

Fig. 8a

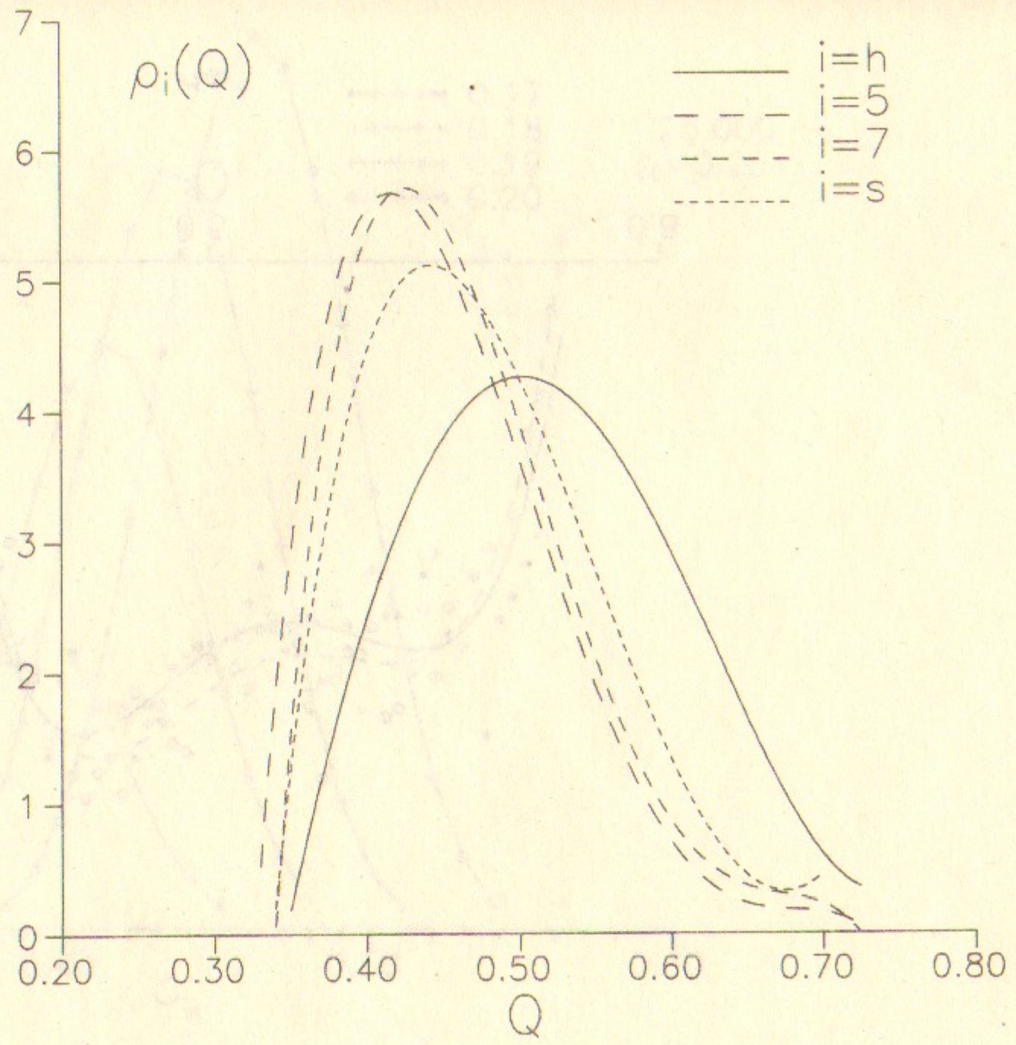
$\rho_i(Q)$
i=h
i=5
i=7
i=s
0
1
2
3
4
5
6
7
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Q

Fig. 8b

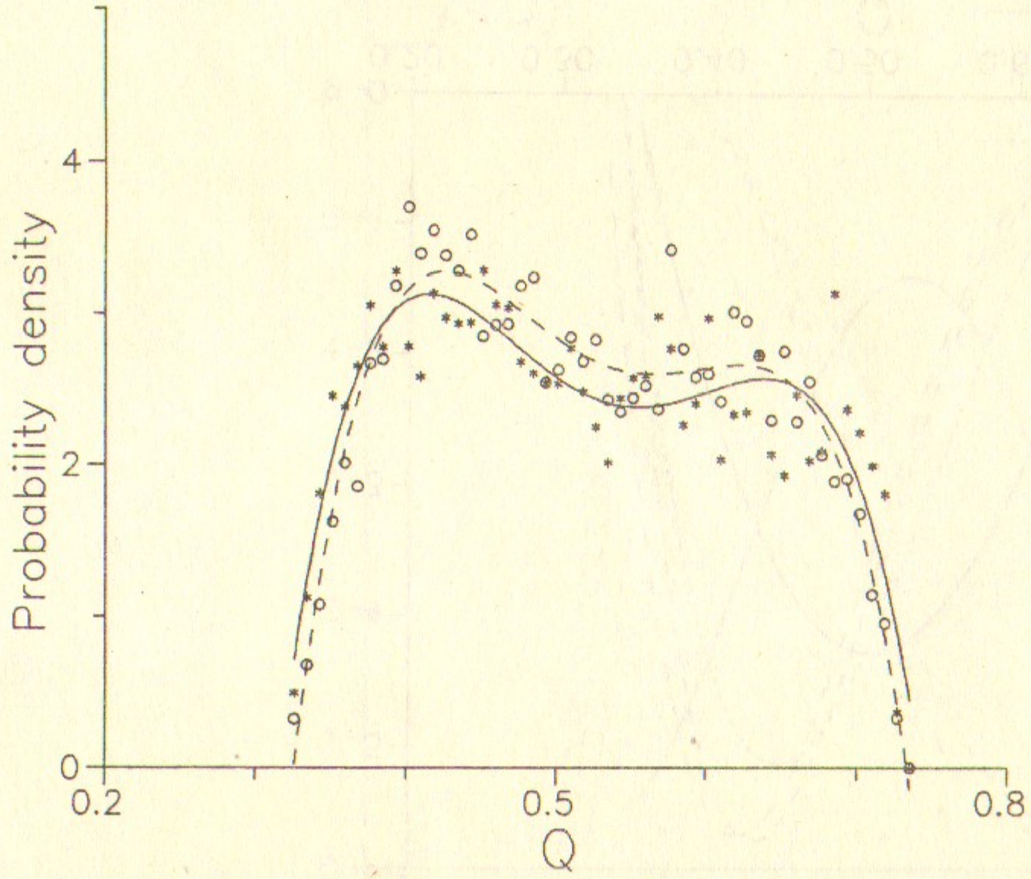
Probability density
4
2
0
0.2
0.5
0.8
Q

Fig.9

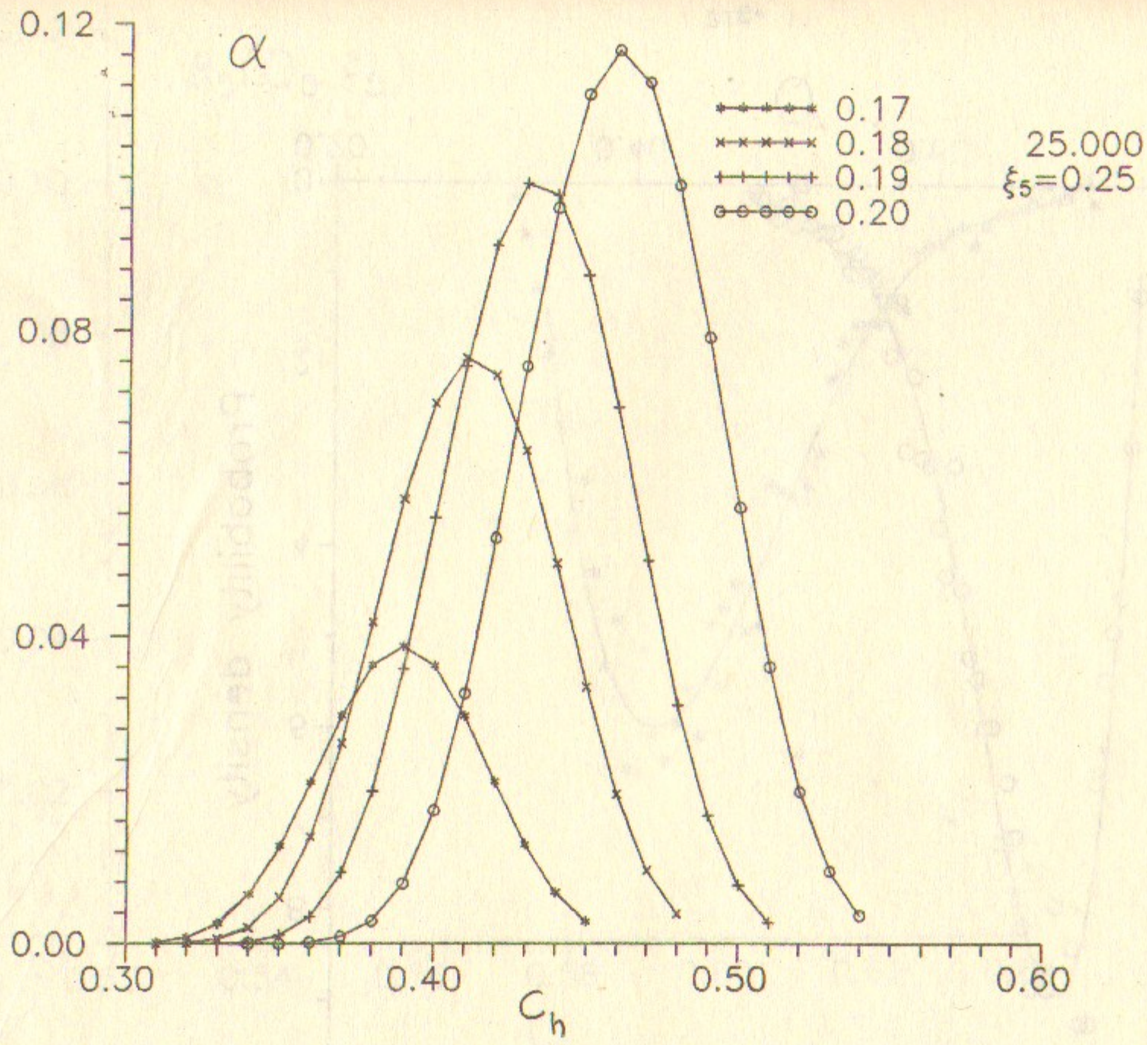
α
0.12
0.08
0.04
0.00
0.17
0.18
0.19
0.20
25.000
ξ5=0.25
0.30
0.40
0.50
0.60
Ch

Fig.10

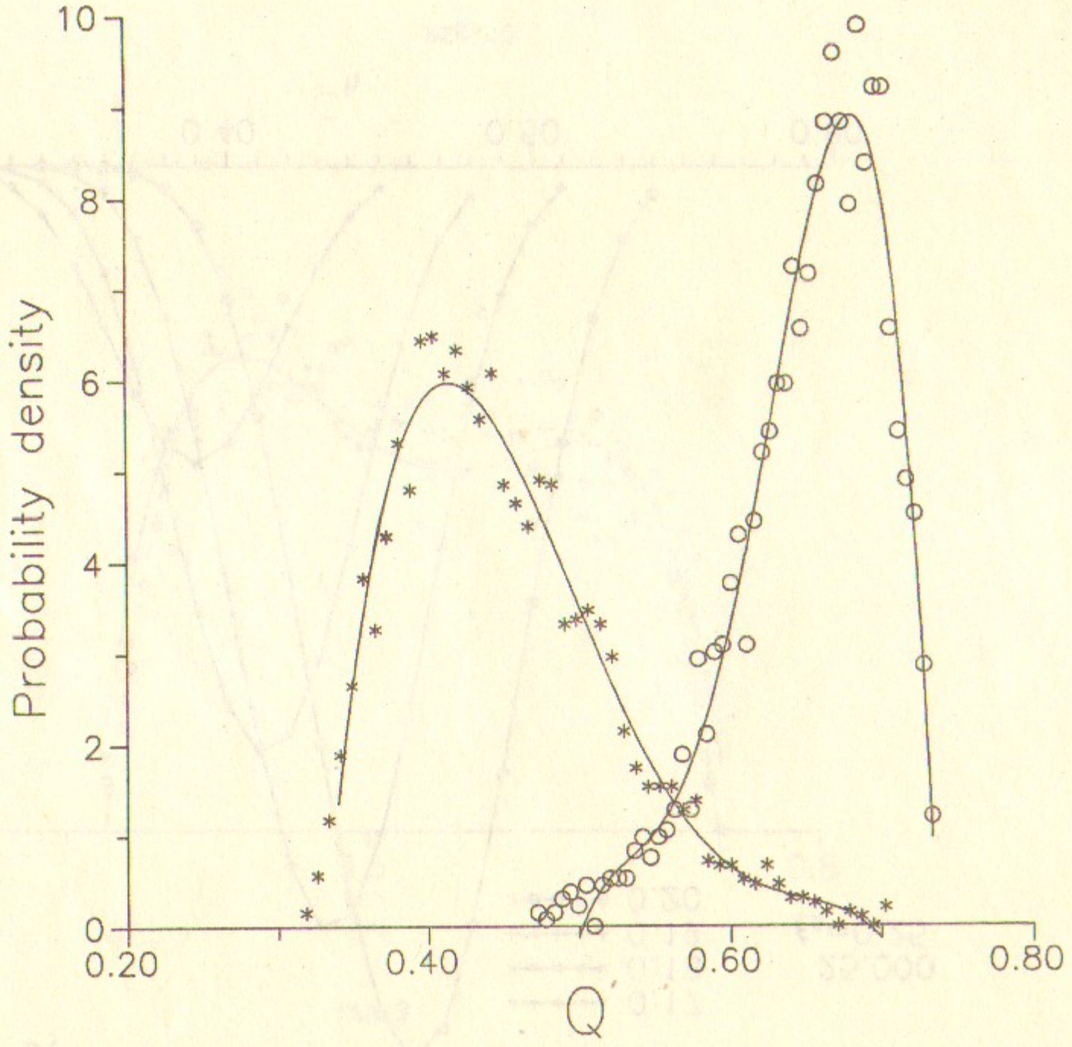
10
8
6
4
2
0
Probability density
0.20
0.40
0.60
0.80
Q

Fig. 11

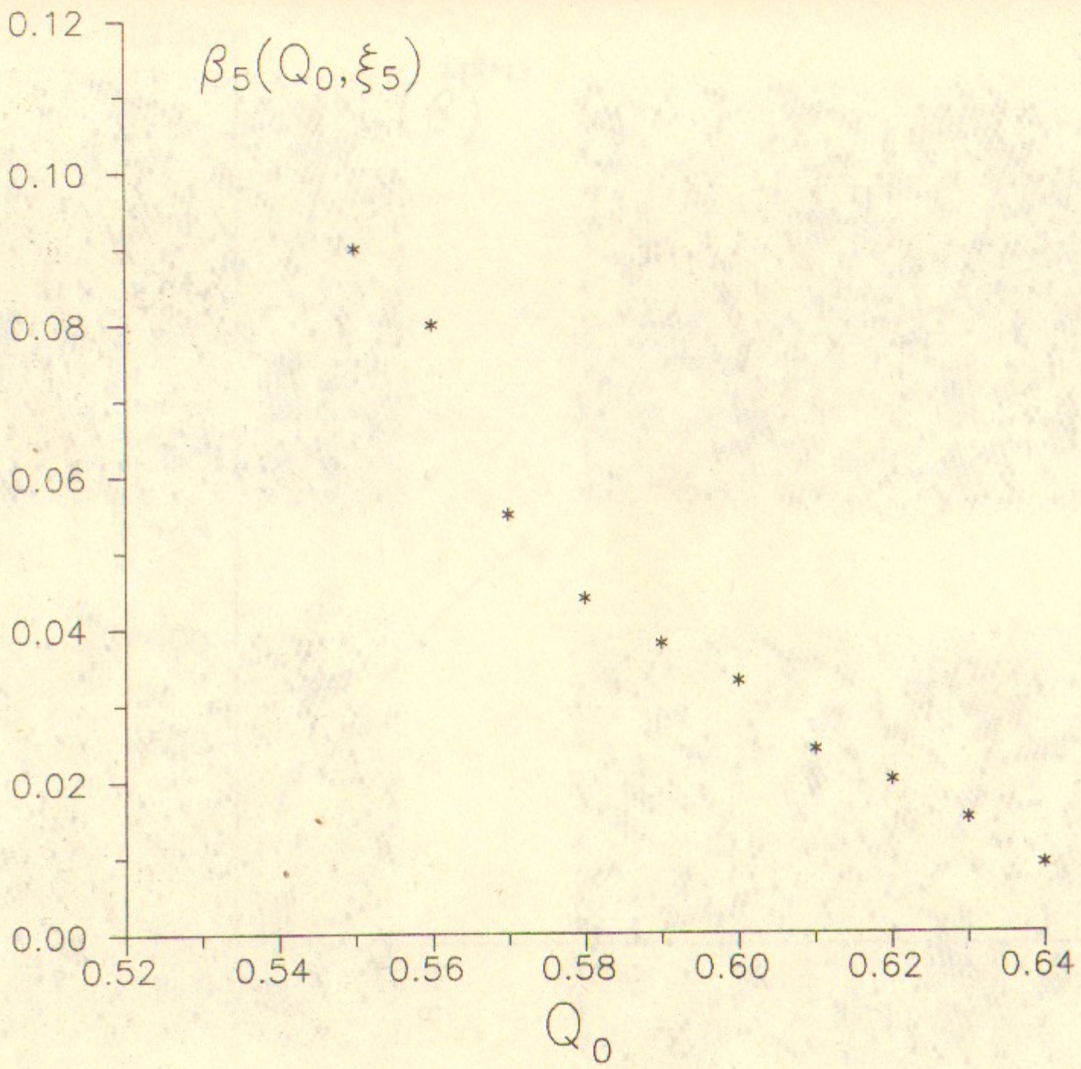
0.12
0.10
0.08
0.06
0.04
0.02
0.00
$\beta_5(Q_0, \xi_5)$
0.52
0.54
0.56
0.58
0.60
0.62
0.64
Q_0

Fig. 12

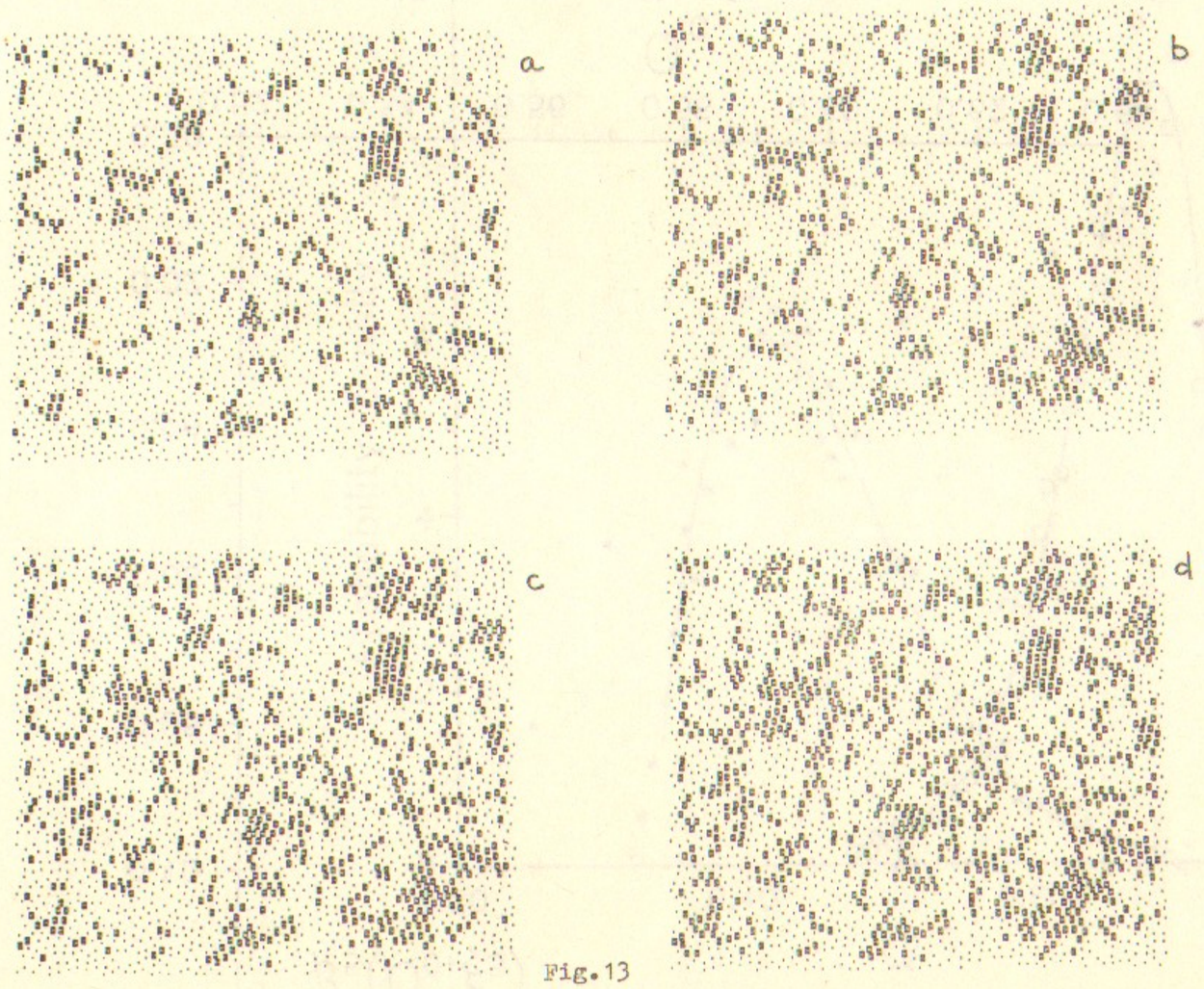
a
b
c
d

Fig.13

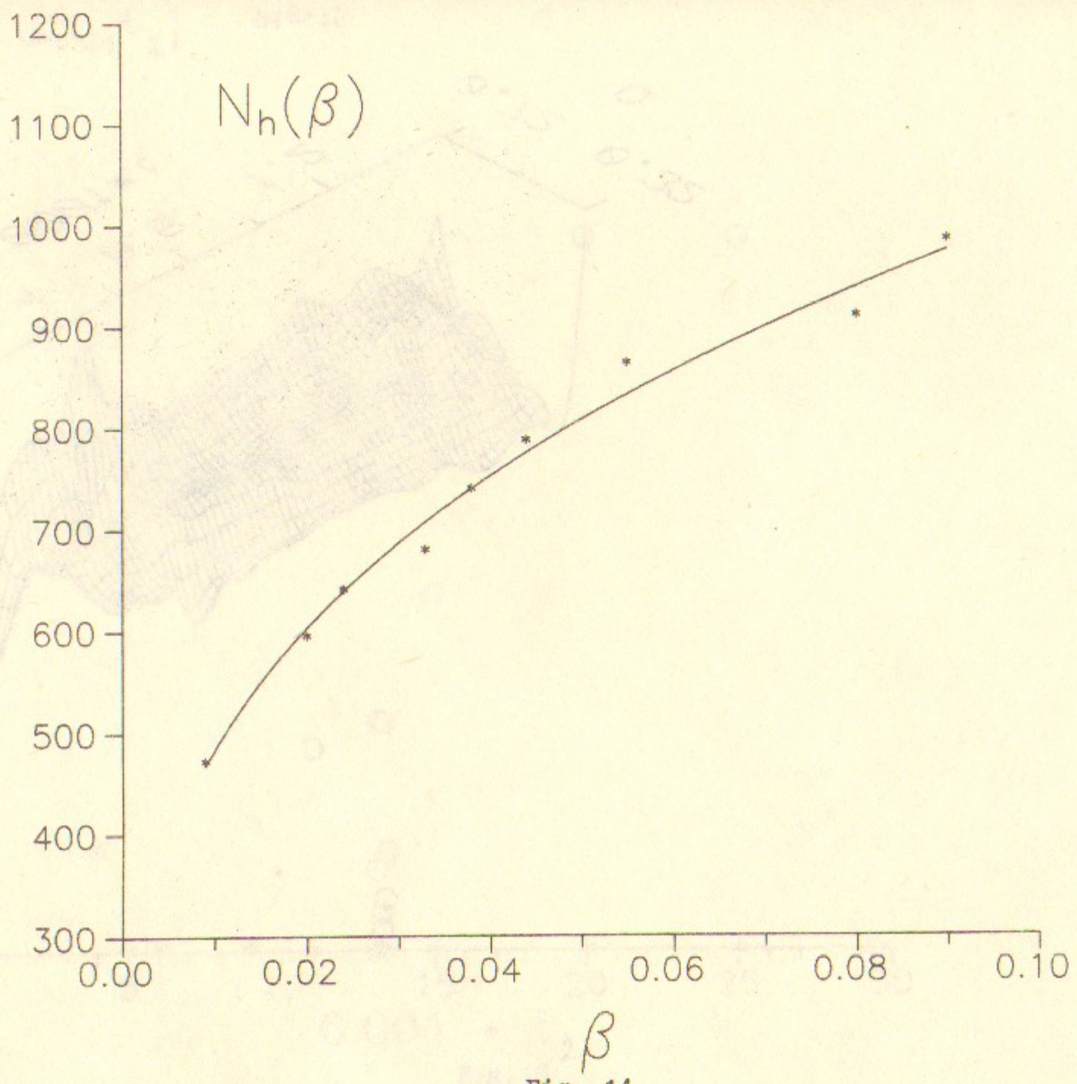
$N_h(\beta)$
1200
1100
1000
900
800
700
600
500
400
300
0.00
0.02
0.04
0.06
0.08
0.10
β

Fig. 14

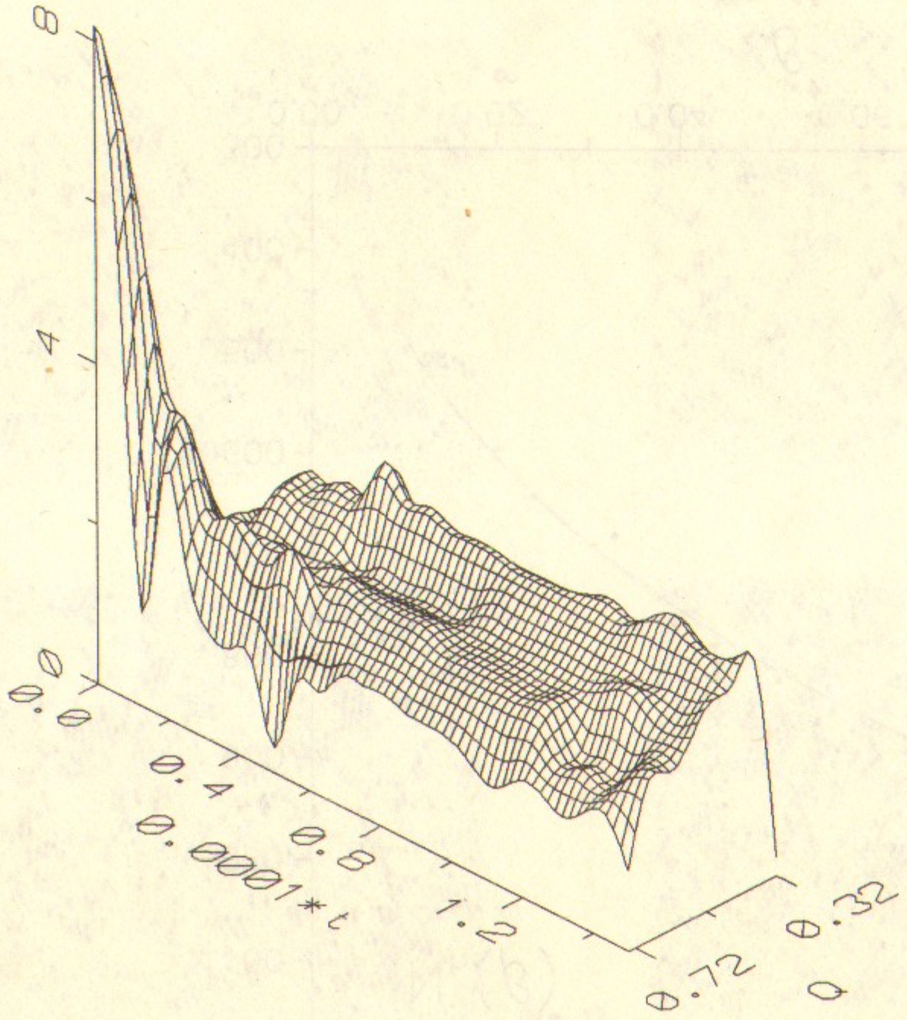
8
4
0
0.0
0.4
0.8
1.2
0.0001*t
0.72
0.32
0

Fig.15

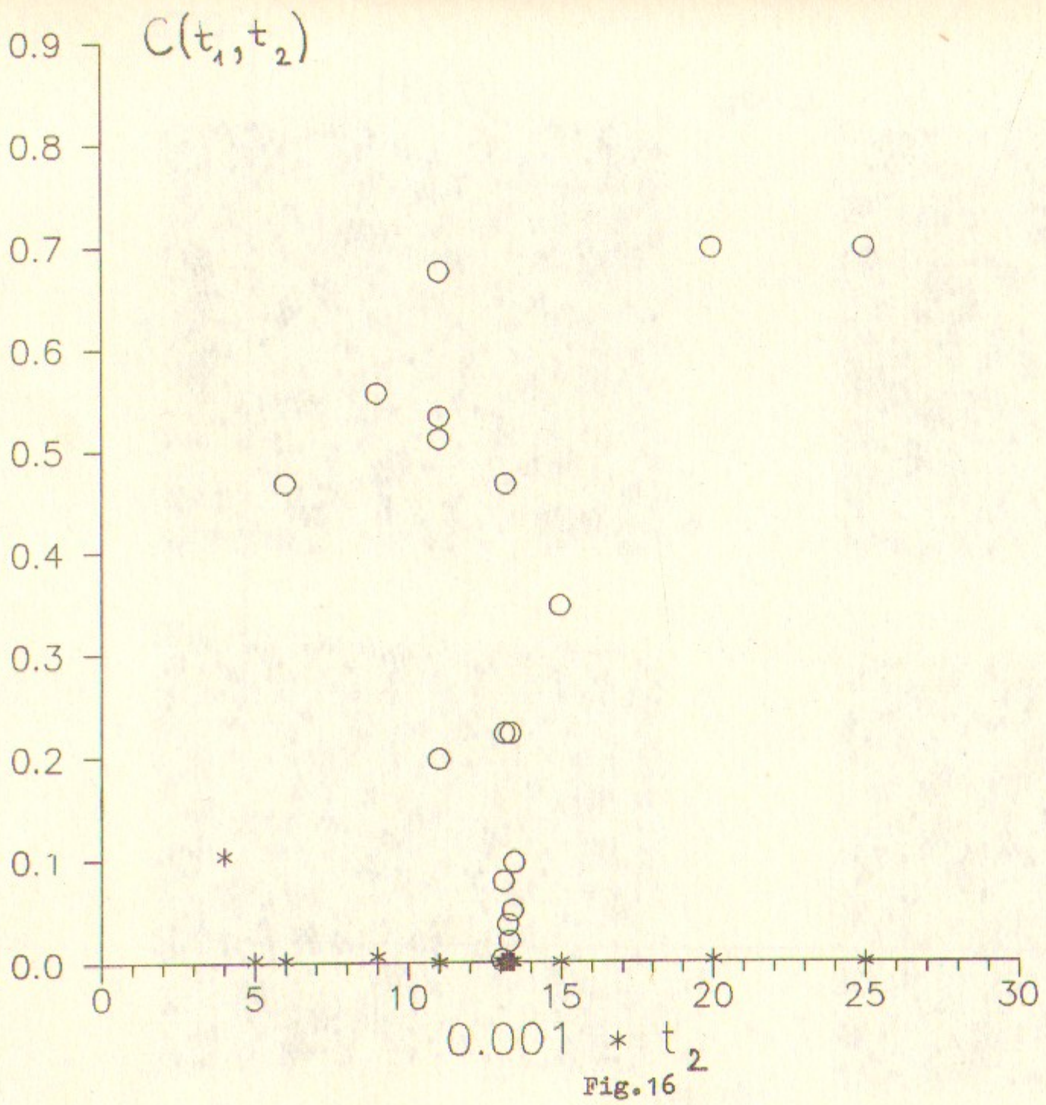
C(t1,t2)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5
10
15
20
25
30
0.001 * t2

Fig.16

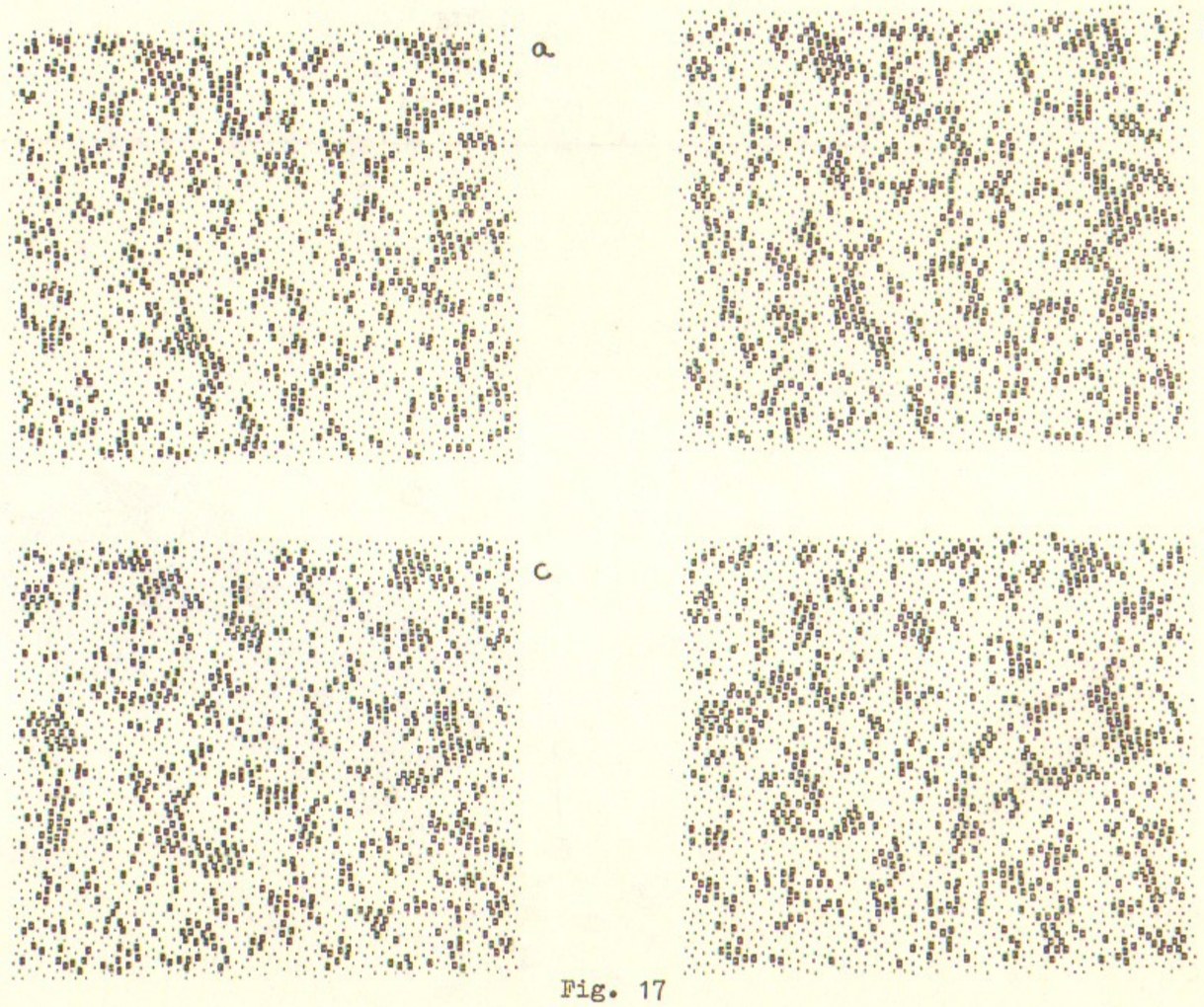

Fig. 17

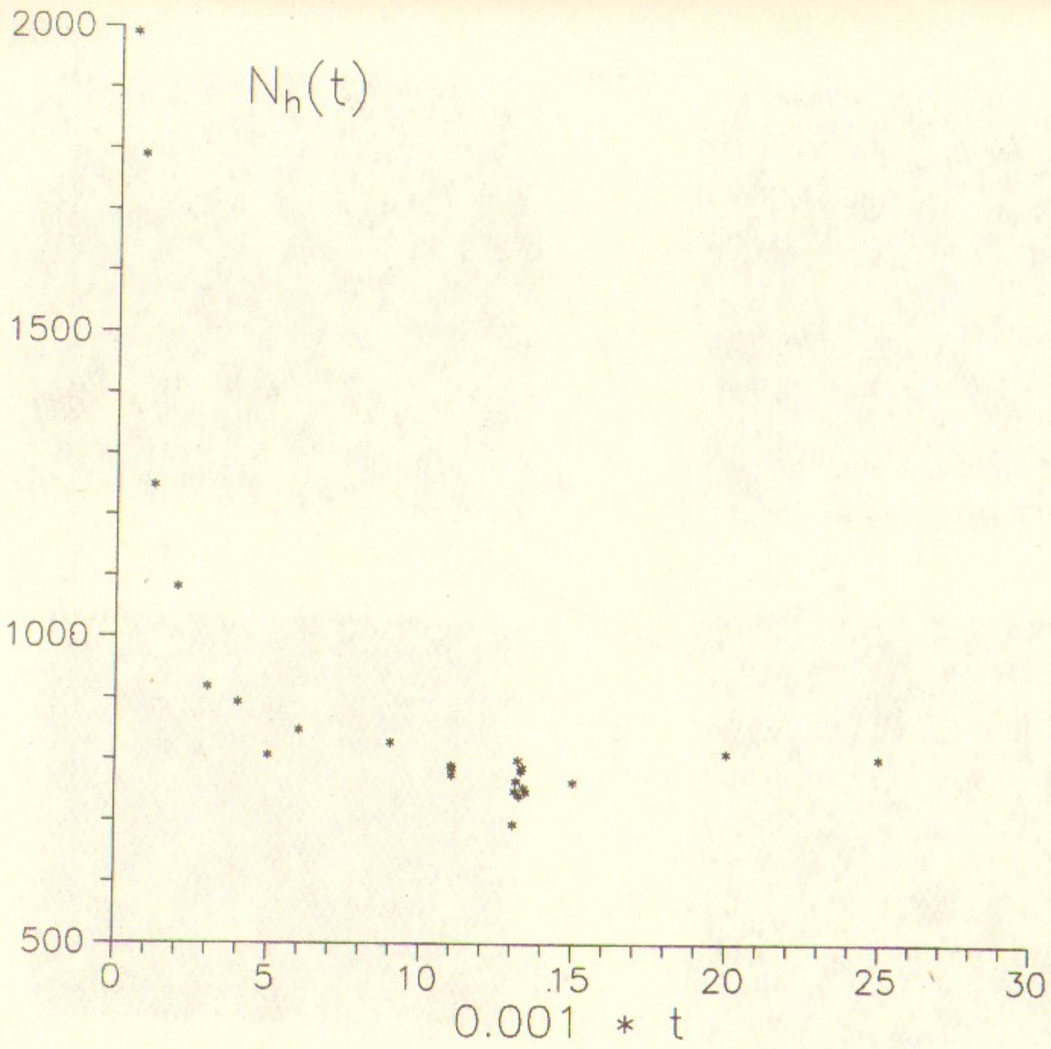

Fig.18

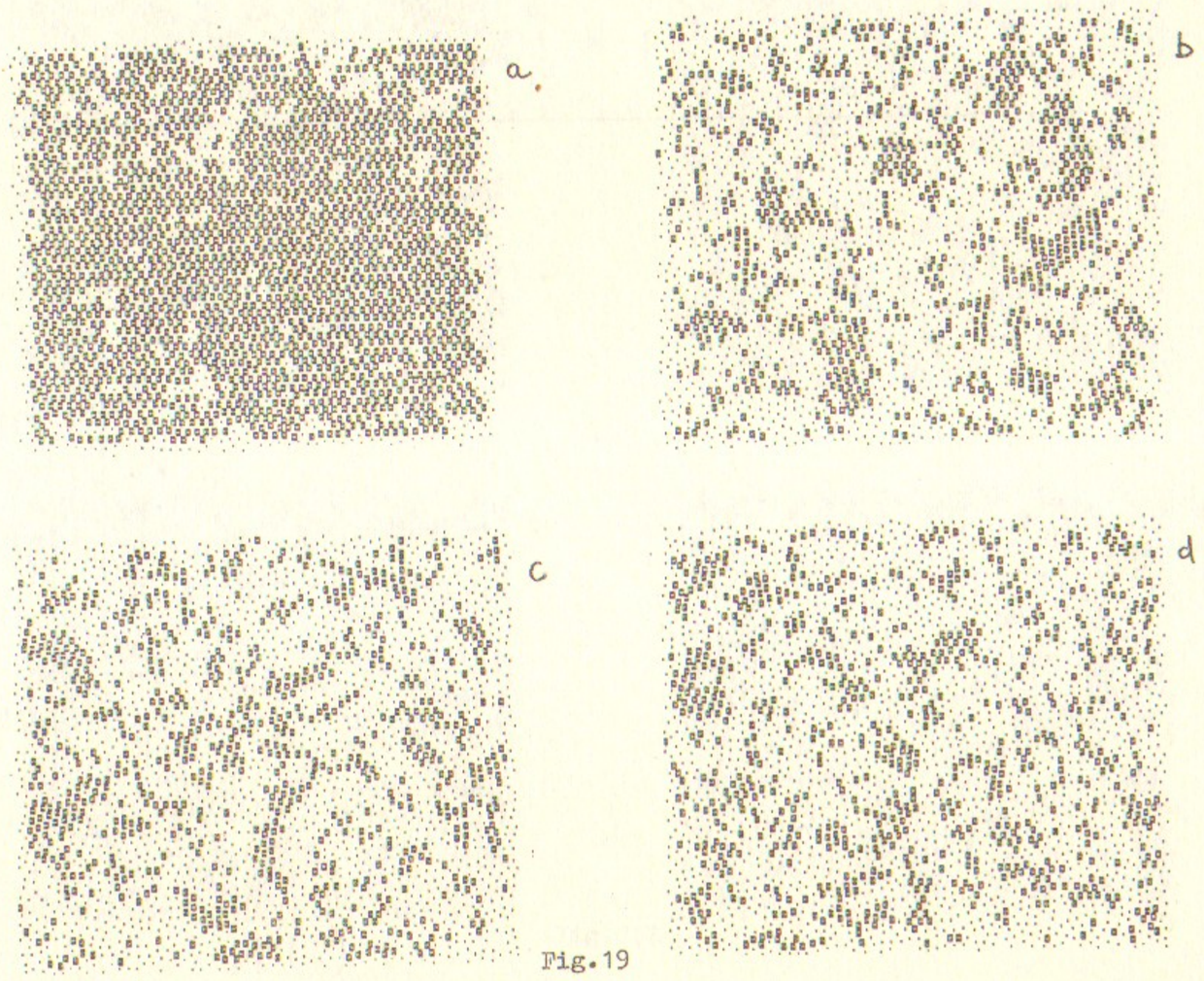

Fig.19

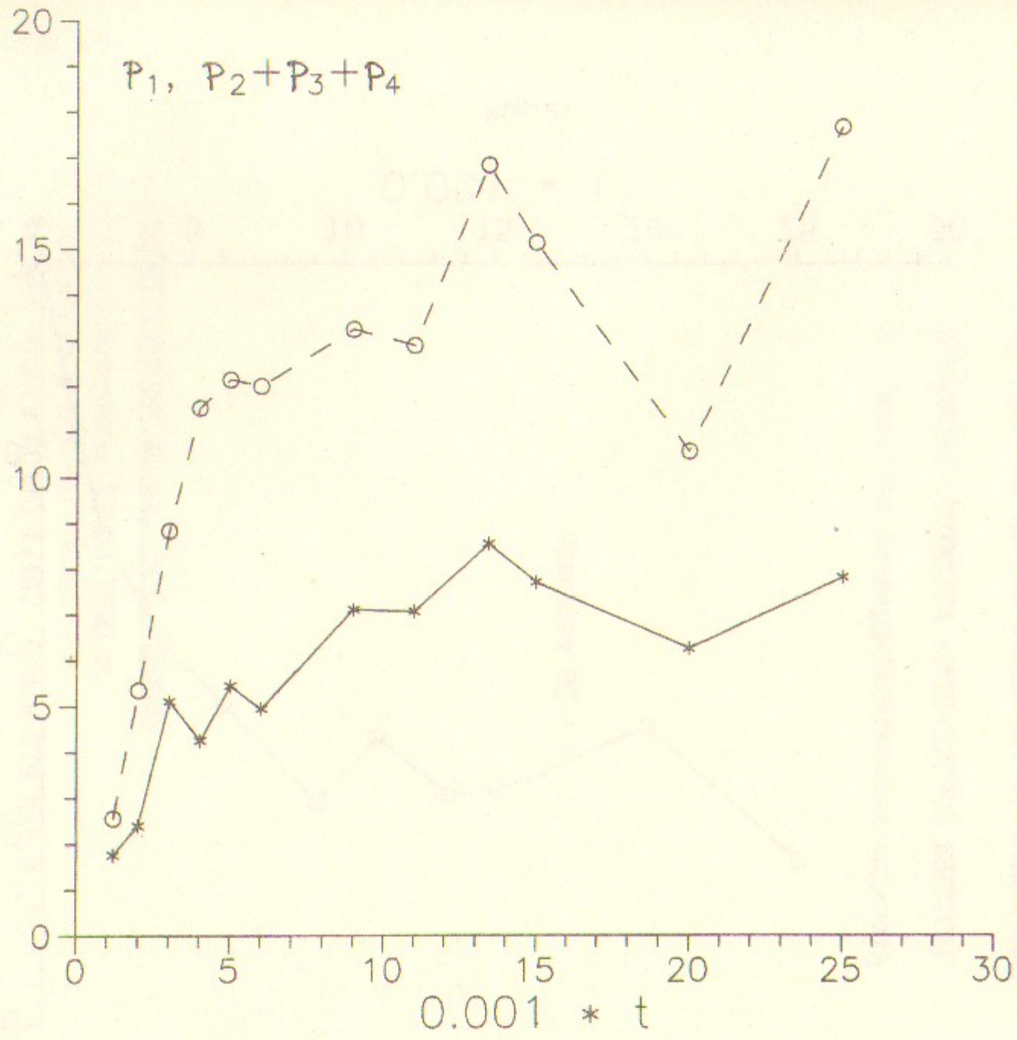

Fig. 20

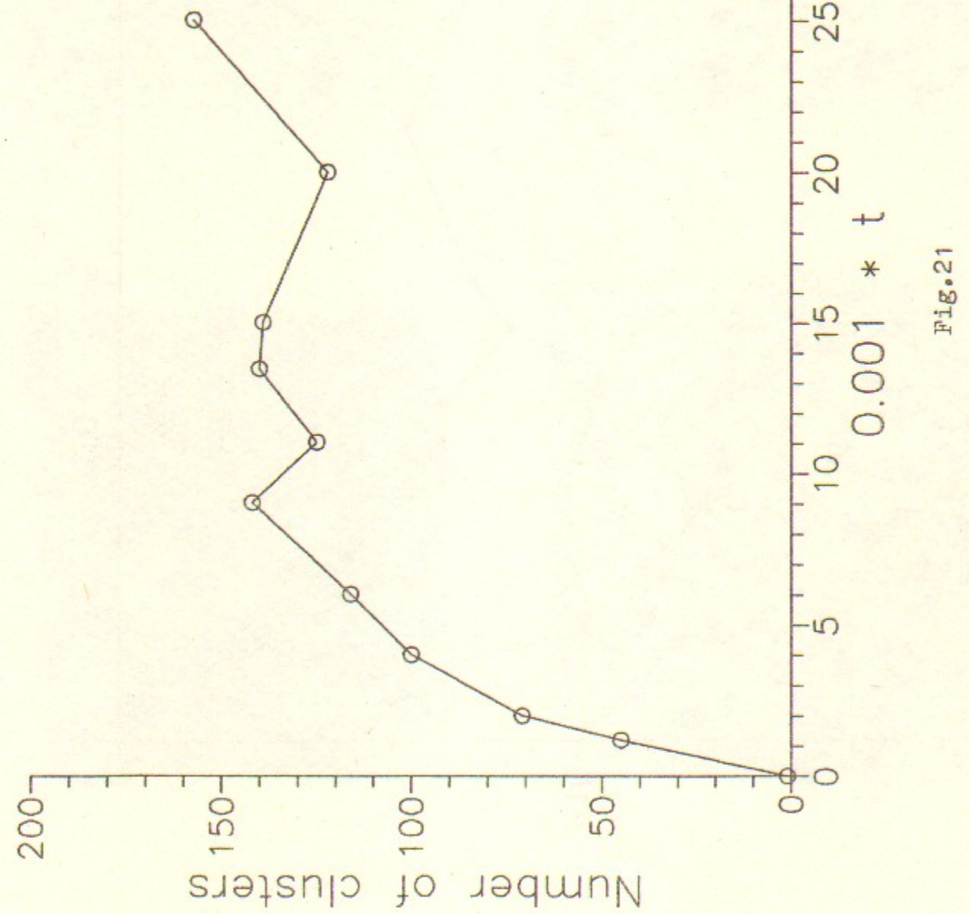

Fig.21

А.С.Митусь, А.З,Паташинский, С.Соколовский

ЛОКАЛЬНАЯ СТРУКТУРА КОМПЬЮТЕРНОЙ ЖИДКОСТИ

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