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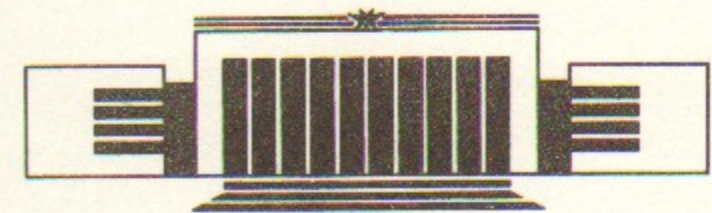
I. General Theory

Local Structures In Computer-Generated Liquid.
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Abstract

We propose a mathematical framework for an analysis of local spatial structures in computer-generated (molecular dynamics and Monte-Carlo) liquids represented by an ensemble of configurations of atoms. We use the methods of the earlier developed probabilistic formalism of structural invariants. The basic concepts of a statistical identification (classification and determination) of types of local structures are discussed. We present the detailed algorithms for an analysis of local spatial structures in individual configurations of atoms and of the statistical correlations between the local structures in subsequent configurations.

1. Local structures of liquid - status of the problem.

A description of the properties of condensed matter (crystals and liquids) in a vicinity of the melting line has two aspects. The first one is the evaluation of the thermodynamic functions and the phase diagram. These problems can be reasonably well solved using the density functional theories, see e.g. ref.1 and 2. The second problem concerns the studies of local and global structures of liquid and, in particular, the character and distribution of defects. Recently, some progress in the theoretical description of the melting of crystals with simple structure (Mitus and Patashinskii[3]) and of local structures of supercooled liquids (Steinhardt et all.[4]) was achieved by the use of the hypothesis of local order in liquid state. This hypothesis (see next Section) bases on the concept of well-defined type of local structure in small volumes of liquid. As a consequence, solids and liquids in some temperature interval above the melting point T_m can be treated from the same point of view, as different states of locally ordered matter. Solid is a locally ordered matter with long-range correlations of local anisotropies of physical parameters; in liquid these correlations are short-ranged. The p-T (pressure and temperature) phase diagram of one-component system, see Fig.1, can be divided into two parts (Mitus and Patashinskii[5]) corresponding to condensed matter (shaded) and to gas. By the definition, condensed matter is characterized by well-defined type of local order.

The direct observation of the local structures of liquids and the verification of the hypothesis of local order remains a challenge to an experiment. The results of X-ray, electron and neutron structural experiments show that, as a rule, the local structure of melt (liquid near T_m) in volumes corresponding to at least two first coordination shells resembles that of the parent crystal[6]. The difficulties of the interpretation of the data result from an indirect character of an information about the instantaneous positions of atoms: the fluctuating crystal structure is characterized by the radial distribution function.

A detailed study of the structure of liquid can be made by the computer simulations (molecular dynamics or Monte-Carlo methods) which provide a sequence of instantaneous configurations of atoms of liquid. The ensemble of these configurations contains a detailed information about local and global structures of liquid. The analysis of this information consists of two parts. The first one includes an introduction of a concept of local structure and requires a definition of a degree of similarity of two structures undergoing thermal fluctuations. These topics were studied in our papers[5]. The second part of the analysis is an identification of the types of local structures in computer-generated configurations of atoms. The aim of this paper is to provide a mathematical apparatus for this purpose. In the second part of this paper[7] we apply our method in order to analyze the local structures of a two-dimensional Lennard-Jones liquid.

The paper is organized as follows. In the next Section we discuss the physical picture of liquid as of locally ordered matter. In Section 3 we review briefly the main concepts of the description of fluctuating patterns of local structures and define the corresponding parameters. The basic concepts of the statistical analysis of local structures in computer-generated liquids are presented in Section 4. The detailed algorithms for the classification, determination and the study of time-correlations of local structures in subsequent configurations are given in Sections 5, 6 and 7, respectively.

2. Local structures of liquid - physical concepts.

In this paper we study a local order in liquids - a characteristic of an arrangement of atoms in a small neighbourhood of an atom. A group of atoms (cluster) mentally picked out of condensed matter can be treated as a geometrical figure characterized by the coordinates x_i of centers of atoms. Such the detailed description is superfluous in the study of structure of real physical systems. Note that the concept of the structure includes the possibility of any motion preserving the interatomic distances. Small fluctuations of atoms' positions lead to various "geometrical" (instantaneous) figures corresponding to one "physical" structure. Thus, one configuration can be selected to represent this infinite set of figures; it displays usually some point-symmetry and can be chosen as the ideal (static) structure pattern Γ. Suppose that the set of patterns Γ_i is known. Then, by the definition, the structure of a trial cluster is determined as that of pattern Γ_i which provides a maximal coincidence of both structures. Mathematical formulation of this criterion is given in Section 3 (see also ref. 5). Such the prescription is of no value when a few patterns approximate the trial cluster equally well. In particular, this is so when the temperature is sufficiently high [5]. Consequently, the set of the patterns should consist only of structures as different from each other as it is possible. The patterns Γ_i are chosen on the basis of symmetry arguments and of the requirement of minimum of potential energy.

In general, a large variety of types of local order (i.e. of patterns Γ_i) can be studied, both with crystallographic and non-crystallographic point- symmetries. In the latter case different crystallographic elements are required to build 3-d quasi-periodic lattice [8]. Frank [9] considered the possibility of the existence of small icosahedrical domains in supercooled liquids.

We assume that for simple melts the local crystal-order hypothesis holds. According to this hypothesis, the statistical picture of ordering of atoms in small volumes of melt resembles that of the parent crystal. The concept of local and global structures is associated with the so called tangent figures. By the definition [10] the tangent position of an ideal structure to physical system minimizes the degree of non-coincidence of atoms and their supposed pre-images (i.e. the sites of tangent figure). The choice of tangent figure is dictated by physical arguments. For example, the local crystal-order hypothesis implies the choice of some crystal lattice as tangent figure. The corresponding local order-parameters were introduced by Hess [11] and in our paper [3]. Another example is the choice of a tangent figure for the study of the structure of metallic glass. The local order is supposed to be icosahedrical, with five slightly distorted tetrahedra sharing an edge. The local topology is the same as in $\{3,3,5\}$ polytope which plays the role of the tangent figure. The local order-parameters were introduced by Sethna [12] and Nelson and Toner [13].

The concept of tangent figure provides the possibility of a consistent analysis of the configurations of atoms of condensed matter. Each of them can be splitted into domains of "good" and "bad" matter. The former one corresponds to slow rotation of the tangent figure in the space; the local structures of the latter are different from that of the tangent figure. For example, the domains of "bad" matter corresponding to the local crystal-order hypothesis are locally equivalent to dislocations [10] while for metallic glasses they correspond to disclinations of Frank-Kasper phase [14].

So far the structure patterns Γ_i were supposed to be à priori

known. In general case it is not clear whether a configuration of atoms displays any type of local structure and, if so, which set of patterns Γ_i is the "proper" one. In this paper we study some topics related to such the formulation of the problem of the identification of local structures in liquid.

In general, one can study three types of local structures in liquid which are associated with different time scales (Fischer [15]). The instantaneous (I) structure is described by the set of coordinates of atoms at some fixed moment of time. The vibrational (V) structure is the averaged structure of an atom's neighbourhood over the period of time less than time of "settled" life. Finally, the diffusional (D) structure arises when the defects are free to move. This paper is devoted to the study of I-structures.

3. Fluctuations of local structures of condensed matter. Structural invariants.

The physical picture presented above uses the concept of well-defined type of local order in small volumes of liquid. This quantity can be introduced in a formalism of probabilistic determination of types of local structures of small clusters of atoms in the presence of fluctuations. The detailed presentation of the formalism is given in our papers [5]. Here, we review briefly the main concepts and definitions.

Consider a trial cluster of N atoms. We assume that it can be treated as a fluctuation of any of the N-atom ideal (i.e. static) patterns Γ_i of structure. Each set of N points in d-dimensional space is uniquely described by the set of d×N coordinates. Instead, one can use some other set of d×N independent characteristics. They determine the structure of the cluster (e.g. slightly deformed cube) and its

orientation in the space (e.g. via Euler angles). The latter information is of interest in the study of a global spatial ordering of atoms in locally ordered condensed matter [3,4,10]. On the contrary, it is not essential for the description of the structure of a cluster because the structure is independent on the choice of a coordinate frame. The characteristics of the structure have to be rotationally and translationally invariant. We call them structural invariants and denote by Ψ_n; they span the so called feature space. The structural invariants $\underline{\Psi} = \left[\Psi_n \right]$ can be defined in a large variety of ways (see, e.g. refs. 4,5). Each of them should, however, meet some requirements (Mitus and Patashinskii [16]), of which the most important is the quantitative definition of a degree of similarity (metric) of two fluctuating structures. A simple metric which meets this requirement has probabilistic meaning. Namely, to each N-atom cluster there corresponds a point in the feature space. Any of the fluctuating patterns Γ_n is represented by a probability density function $\rho_n(\underline{\Psi})$ (which depends on the ensemble of fluctuations). The feature space is divided into domains corresponding to the fluctuations of ideal structure patterns. In general these domains overlap which results in a probabilistic character of recognition. The similarity of fluctuating patterns Γ_i, Γ_j is defined by degree P_{ij} of an overlap of the corresponding probability density functions:

$$P_{ij} = \int \min\left[\rho_i(\underline{\Psi}), \rho_j(\underline{\Psi})\right] d\underline{\Psi} \qquad (1)$$

where the integration is carried over all feature space. The structure of a trial cluster represented by point $\underline{\Psi}^{(0)}$ is determined by the maximal probability decision rule as that of fluctuating pattern Γ_n if $\rho_n(\underline{\Psi}^{(0)}) > \rho_k(\underline{\Psi}^{(0)})$ for each $k \neq n$. The reliability of the determination depends on values of parameters P_{nk}: structure of

trial cluster is well-defined only when $P_{nk} \ll 1$.

Parameters P_{ij} characterize the reliability of the determination of components of local structures in liquid (Section 6) as being the fluctuations of patterns Γ_i and Γ_j. When $P_{ij} \ll 1$ then the "structural identity" of both fluctuating structures is well-defined. On the contrary, when P_{ij} is not small (say, bigger than 0.5) then the determination of two structures is non-physical. The structural identity of fluctuating patterns is lost and one deals with a "structureless" pattern resulting from a fluctuational merging of patterns Γ_i and Γ_j.

The overlapping of the probability density functions $\rho_i(\underline{\Psi})$ determines a degree of the uncertainty of the structural identity of a chosen group of clusters in liquid. Let us define a domain $\underline{\Omega}_k$ in $\underline{\Psi}$ space by the requirement that $\rho_k(\underline{\Psi}) > \rho_0$ for $\underline{\Psi} \in \underline{\Omega}_k$, where ρ_0 is a constant. The N-atom clusters for which $\underline{\Psi} \in \underline{\Omega}_k$ can be treated either as fluctuations of pattern Γ_k or of any other pattern Γ_i. Consider the physically interesting case when P_{ik} is small. The quantity

$$\beta_i \left[\underline{\Omega}_k \right] = \int\limits_{\underline{\Psi} \, \in \, \underline{\Omega}_k} \rho_i(\underline{\Psi}) \, d\underline{\Psi} \qquad (2)$$

which is an error of first kind for structure Γ_i (see ref. 5) we call a degree of presence of pattern Γ_k in the fluctuations of pattern Γ_i, for the given domain $\underline{\Omega}_k$. If this degree is small then the clusters in liquid, for which $\underline{\Psi} \in \underline{\Omega}_k$, have well-defined structures corresponding to the fluctuations of pattern Γ_k. For example, if we study a large number n_0 of the fluctuations of pattern Γ_i, then approximately $\beta_i \left[\underline{\Omega}_k \right] n_0$ of them will be determined as being the fluctuations of pattern Γ_k.

4. Basic concepts of statistical analysis of local structures in computer-generated liquids

In this Section we present the basic concepts of the statistical identification of local structures in liquids represented by an ensemble of semimacroscopic (10^2-10^4 atoms) I-configurations. We propose two approaches. In the first one the identification of local structures consists of a classification and determination. According to the terminology of Kendall and Stuart [17], a classification is a division of local structures of N-atom clusters in an I-configuration into groups consisting of similar structures. A priori the types of local structures are not known. Thus, the aim of the classification is to extract the statistically uniform domains (i.e. groups of clusters) in an I-configuration. Here, a statistical uniformity means a statistical equality of some parameters (e.g. one of the structural invariants or its moments) characterizing the clusters in this domain. The choice of these parameters is dictated by the behaviour of structural invariants in the presence of the fluctuations and, in turn, determines how detailed the classification will be. The hypothesis of local crystal-order states that the results of the classification are the same ones (in statistical sense) for each of the I-configurations. In the second stage of the identification the classified structures are compared with ideal patterns of structure (determination). We look for a pattern Γ_k and for an ensemble of the fluctuations for its atoms which approximate in the "best" way the classified structures. The meaning of the "best" approximation is explained below.

In an alternative approach we assume that a few types of local structures represented by some set of patterns Γ_k exist in liquid. The aim of the identification is to find an ensemble of fluctuations

of atoms of pattern Γ_k and to estimate the concentrations c_k of clusters displaying Γ_k-th type of structure.

The next topic in a study of the local structures of liquid is a comparison of the results of identification for subsequent configurations. The positive verification of the hypothesis that these results are statistically time-independent means that the classified structures are inherent local structures of liquid and that the liquid itself is a locally ordered matter. A detailed discussion of the algorithms for the identification is given in the next Sections.

The mathematical objects we are dealing with are the probability density functions $\rho_n(\underline{\Psi})$ introduced in previous Section and the probability density function $\rho(\underline{\Psi},t)$ which characterizes the fluctuations of local structures in liquid. Here, t denotes a time, e.g. the number of time steps in molecular dynamics or number of steps in Monte-Carlo simulations. Function $\rho(\underline{\Psi},t)$ is constructed as follows. For each atom from the configuration at time t, located at point $\underline{x}'$ we find its N nearest neighbours. The invariants $\underline{\Psi}$ calculated for this N+1 atom cluster define a vector field $\underline{\Psi}(\underline{x})$ at the point $\underline{x}=\underline{x}'$. The field $\underline{\Psi}(\underline{x})$ characterizes the local structures of the I-configuration and fluctuates in space. The statistics of these fluctuations is described by the probability density function $\rho(\underline{\Psi},t)$ which is approximated by the histogram of random variable $\underline{\Psi}$. Analogously, the functions $\rho_n(\underline{\Psi})$ are approximated by the histograms of invariant $\underline{\Psi}$ calculated from fluctuations of pattern Γ_n. The ensemble of the fluctuations of the atoms can be parametrized, e.g., by the root-mean-square (r.m.s.) displacement ξ of atoms from the static configuration of pattern Γ_n. Thus, we denote the probability density functions for patterns by $\rho_n(\underline{\Psi};\xi)$.

The identification of the local structures of liquid is done by the methods of mathematical statistics and includes the verification of the hypotheses about functions $\rho(\underline{\Psi},t)$ and $\rho_n(\underline{\Psi};\xi)$. Below we provide the brief resume of the concepts, definitions and methods following the book of Press at all. [18]. In our approach the identification reduces to the estimation of some parameters $\mu=\left[\mu_i\right]$, e.g. the r.m.s. ξ_k or the concentrations c_k of clusters determined as being the fluctuations of pattern Γ_k. These parameters are obtained by a maximization of a merit function and are called the best-fit-parameters. The merit function characterizes the differences between the computer data and model data calculated on the basis of a trial hypothesis. The merit function we use is defined in the following way. For the two set of data (MD and model) we verify the null hypothesis stating that both the sets are drawn from the same distribution function. In this way we evaluate a significance level $\alpha(\mu)$ at which there is no reason to reject the null hypothesis. The significance level $\alpha(\mu)$ is our merit function; we say that the parameters μ^* which extremize $\alpha(\mu)$ provide a "best" agreement between computer data and the model.

Up to this point, the best estimation $\underline{\mu}^*$ of parameters $\underline{\mu}$ is quite formal. Its reliability is determined by a statistical measure of goodness-of-fit suggesting whether or not the model is likely to match the computer data. This is provided, e.g. by the quantity $\alpha(\mu^*)$ - its small value indicates a significant difference between the distributions and leads to the conclusion that the model is probably incorrect. If the model is not rejected then there appears a problem of an estimation of the uncertainties (errors) of the best-fit-parameters μ^*. We solve it in the following way. We choose an "acceptable" significance level α_o (say, 0.01 or 0.1) and find the

solutions of the inequality

$$\alpha(\underline{\mu}) \geq \alpha_0 \qquad (3)$$

The parameters $\underline{\mu}$ which satisfy (3) (in particular $\underline{\mu}^*$) provide the interval estimation of the unknown parameters of the model (for the given value of α_0). The uncertainties of the best-fit-parameters $\underline{\mu}^*$ are given by the quantities $\delta\underline{\mu} = \underline{\mu}_b - \underline{\mu}^*$, where $\underline{\mu}_b$ satisfies the equation $\alpha(\underline{\mu}_b) = \alpha_0$ (Fig. 2).

In this paper we present the methods of an identification of local structures described by only one structural invariant. We believe that if the hypothesis of local crystal-order holds then the simplest one-dimensional analysis should display the presence of the dominant types of local structures. The multi-variate analysis can be used as the next step. An algorithm for a multi-variate classification will be presented elsewhere.

5. Classification

In the case of one structural invariant Ψ a simplest classification is done by splitting the MD histogram into two parts by the line $\Psi = \Psi^{(d)}$. Clusters are classified to one of the two groups depending on whether $\Psi > \Psi^{(d)}$ or $\Psi < \Psi^{(d)}$. The choice of the value of $\Psi^{(d)}$ is dictated by physical arguments concerning the expected types of local structures. In what follows we discuss some standard cases which may be of practical interest. In Figs. 3a-d we present the probability density functions $\rho(\Psi)$ corresponding to the simplest concepts of local structures of liquids. The case (a) corresponds to an existence of two types Γ_1 and Γ_2 of local order; in case (b) one type is dominant while in case (d) no definite type of local order exists. In case (a) the splitting is done in a "natural" way. Clusters with

$\Psi > \Psi^{(d)}$ are declared as fluctuations of pattern Γ_1. The uncertainty of this classification is given by the function $\beta_2(\Omega_1)$, c.f.(2), for the competing pattern Γ_2. Here, Ω_1 denotes the interval $(\Psi^{(d)}, \infty)$. For some purposes it may be necessary to deal with clusters for which this uncertainty is smaller - then the splitting has to correspond to higher values of $\Psi^{(d)}$. In the case (b) the structure of the clusters with $\Psi > \Psi^{(d)}$ could be determined (Section 6) as that of some fluctuating pattern Γ_i. If not, then it is worthwhile to change $\Psi^{(d)}$ in the hope that the experimental function $\rho(\Psi)$ (solid line in Fig. 3c) is a sum of two structural components Γ_i and Γ_k (dashed lines in Fig. 3c) for which the parameter P_{ik} is not small.

An algorithm for a multi-variate classification will be presented elsewhere.

6. Determination

6.1 Determination of structural identity of classified structures

We consider a hypothesis stating that the structure of the clusters belonging to one of the earlier classified groups corresponds to the fluctuations of pattern Γ_k, described by the probability density function $\rho_k(\Psi;\xi)$ for some value of $\xi = \xi_k$. Let the classified group consists of the clusters for which $\Psi > \Psi^{(d)}$. The value of the parameter ξ_k is determined in the following way. We introduce a function $\Psi_{1/2}^{(k)}(\xi)$; by a definition the line $\Psi = \Psi_{1/2}^{(k)}(\xi)$ crosses the left part of the plot of function $\rho_k(\Psi;\xi)$ at its half-height (see Fig. 4). The r.h.s. part (i.e. for $\Psi > \Psi^{(d)}$, where $\Psi^{(d)} < \Psi_{1/2}^{(k)}(\xi)$) of the plot of $\rho_k(\Psi;\xi)$ contains a well-defined peak. The r.h.s. parts of of MD histogram and of the trial function $\rho_k(\Psi;\xi)$ are normalized to unity and compared by χ^2-test [18]. We find in this way a significance level $\alpha\left[\Psi^{(d)};\xi\right]$ for which there is no reason to reject the null hypothesis stating that the two sets of data are drawn from the same distribution function. A

small value of α indicates a significant difference between the distributions [18]. When the liquid has two types of local structures (c.f. Fig. 3a) then for small values of $\Psi^{(d)}$ $\alpha\left[\Psi^{(d)};\xi\right]\approx0$; with the increase of value of $\Psi^{(d)}$ the significance level α increases. The typical behaviour of the function $\alpha\left[\Psi^{(d)};\xi\right]$ in this case is shown in Fig. 5. The best-fit-parameter ξ_k is estimated by the maximization of the merit function

$$\hat{\alpha}(\xi) = \max \alpha\left[\Psi^{(d)};\xi\right] \qquad (4)$$

The maximization in formula (4) is done with respect to $\Psi^{(d)}$ with the constraint $\Psi^{(d)} < \Psi_{1/2}^{(k)}(\xi)$. When the function $\hat{\alpha}(\xi)$ has a sharp maximum at $\xi=\xi_k$ (Fig. 6a) then we interpret that the local structure corresponds "in a best way" to pattern Γ_k fluctuating at $\xi=\xi_k$. When the plot of $\hat{\alpha}(\xi)$ has a plateau (Fig. 6b) then the determination yields an interval $\Delta\xi_k$ of "the best" parameters ξ_k. The uncertainties for the estimated parameter ξ_k are given, as discussed above, by the solution of the inequality $\hat{\alpha}(\xi) > \alpha_0$, where α_0 is some chosen significance level.

In an analogous way one can study the other classified groups of clusters.

6.2 Global determination of the local structures

We assume (see Section 4) that the probabilty density function $\rho(\Psi,t)$ is a linear combination of the probability density functions $\rho_i(\Psi;\xi)$ for the patterns:

$$\rho(\Psi,t) = \sum_{i=1}^{N} c_i(t)\rho_i(\Psi;\xi_i) \qquad (5a)$$

We determine the coefficients in (5a) by extremizing a merit function $\alpha(\underline{c},\underline{\xi})$ (where $\underline{c}=(c_1,\ldots c_N)$, $\underline{\xi}=(\xi_1,\ldots\xi_N)$, $\sum c_i=1$ and $c_i \geq 0$), which is

the significance level obtained from the verification of null hypothesis for $\rho(\Psi,t)$ (represented by MD histogram of invariant Ψ) and a trial linear combination ρ_{trial}:

$$\rho_{trial}(\underline{\Psi};\underline{c},\underline{\xi}) = \sum_{i=1}^{N} c_i\rho_i(\underline{\Psi};\xi_i) \qquad (5b)$$

The uncertainties for the estimated parameters c_i^* are given by the solutions of the inequality $\alpha(\underline{c},\underline{\xi}) > \alpha_0$, where α_0 is some chosen significance level.

When the determination of one of the components of local structure yields high value of ξ_k ($\xi \geq 0.3$ for 3-d close-packed clusters [5]) then this component can be called "structureless". This is the consequence of the fact that for high values of ξ a structure of the fluctuating pattern Γ_k is no more well-defined because the probability density function $\rho_k(\Psi;\xi)$ appproaches some universal function $\rho^*(\Psi)$ corresponding to "structureless" pattern (compare ref. 5) and all the quantities P_{ij} are close to unity. In this case there is no way to obtain reliable upper boundaries for ξ_k.

7. Time-correlations of local structures

The time evolution of the local structures of the liquid is characterized, e.g., by the probability density function $\rho(\Psi,t)$. This function yields information about the onset of equilibrium regime and provides quantitative characteristics for the memory about local structures in subsequent configurations of atoms.

Let $\underline{\Omega}$ denote some chosen domain in the feature space $\underline{\Psi}$. We define the time correlation function $C(\underline{\Omega},t_1,t_2)$ of the local structures in the following way. We consider two configurations after times t_1 and t_2 and verify the null hypothesis for the normalized probability density functions $\rho(\underline{\Psi},t_1)$ and $\rho(\Psi,t_2)$ restricted to domain $\underline{\Omega}$: $\underline{\Psi} \in \underline{\Omega}$.

We find a significance level $\alpha(t_1,t_2)$ for which there is no reason to reject the null hypothesis. The function $\alpha(t_1,t_2)$ has the following properties. When the system is in equilibrium and when the hypothesis of local crystal-order holds than there is no reason to reject the null hypothesis. In other words, the significance level obtained from the verification is not small. On the contrary, when liquid is not in equilibrium then the local structures undergo noticeable changes and the memory about types of local structures is short. When the time interval $\Delta t = t_2 - t_1$ is sufficiently big then the null hypothesis has to be rejected and $\alpha(t_1,t_2) \simeq 0$. The function $\alpha(t_1,t_2)$ is noticeably non-zero only for $t_2 \simeq t_1$. These properties of function $\alpha(t_1,t_2)$ allow us to treat it as a time correlation function of local structures in liquid:

$$C(\underline{\Omega},t_1,t_2) = \alpha(t_1,t_2) \tag{6}$$

It characterizes the time evolution of local structures with structural identity determined by functions $\beta_i(\underline{\Omega})$, c.f.(2). In particular, we define the correlation function $C(t_1,t_2) = C(\underline{\Omega},t_1,t_2)$ where $\underline{\Omega}$ coincides with the full range of variable $\underline{\Psi}$. In non-equilibrium regime function $C(\underline{\Omega},t_1,t_2)$ is quickly decaying with the increase of the time interval Δt. In equilibrium regime it takes non-zero values but can oscillate noticeably. This is the result of the finitness of the model liquid and of the sensitivity of numerical values of significance levels to the details of the arrangement of the atoms when the statistics of the data is not too good. Both types of behaviour are presented in Fig. 7.

8. Conclusions

The hypothesis of local (crystal) order in liquids has two aspects. The first one is connected with the type of local structure (or of a tangent lattice), the second - with the short- ranged correlations of the spatial orientations of local tangent lattices. In this paper we have presented the mathematical tools for the study of the former problem for computer-generated liquids represented by an ensemble of configurations of atoms. An equilibrium liquid has to be characterized by a set of parameters like thermodynamic functions, kinetic coeficients and structural parameters. As the candidates for the latter we propose the parameters P_{ij}, c.f.(1), concentrations c_i and r.m.s. ξ_i (corresponding to pattern Γ_i), c.f.(5) and time correlation functions $C(\underline{\Omega},t_1,t_2)$, c.f.(6). Equally important are functions $\beta_i\left[\underline{\Omega}_k\right]$, c.f.(2), which characterize the structural identity of a chosen group of clusters. In the second part of this paper[7] we apply our method to the analysis of local structures of 2-d Lennard-Jones liquid.

Figure captions

Fig. 1

Qualitative p-T phase diagram of one-component system.

Fig.2

The determination of the uncertainty of the best-fit-parameters $\underline{\mu}^*$ via formula (3).

Fig. 3

The probability density functions $\rho(\Psi)$ corresponding to various concepts of local structures in liquids.

Fig. 4

Graphical representation of the quantity $\Psi_{1/2}^{(k)}(\xi)$.

Fig. 5

The typical behaviour of the function $\alpha\left[\Psi^{(d)};\xi\right]$ when a liquid has two distinct types of a local structures.

Fig. 6

The determination of the best-fit-parameter ξ_k (part a) and of an interval $\Delta\xi_k$ of the "best" parameters ξ_k (part b) on the basis of the merit function $\hat{\alpha}(\xi)$, c.f. formula (4).

Fig. 7

The qualitative behaviour of the time correlation function $C(\underline{\Omega},t_1,t_2)$ c.f. (6), in non-equilibrium (dashed line) and equilibrium (solid line) regimes.

References

[1] P. Tarazona, Molec. Phys. 52 (1984) 81.

[2] B.B. Laird, J.D. McCoy and A.D.J. Haymet, J. Chem. Phys. 87 (1987) 5449.

[3] A.C. Mitus and A.Z. Patashinskii, Sov. Phys. JETP 53 (1981) 798; Phys. Lett. A 87 (1982) 79; R.Lyzwa, A.C.Mitus and A.Z. Patashinskii, Sov. Phys. JETP 54 (1981) 1168.

[4] P.J. Steinhardt, D.R. Nelson and M. Ronchetti, Phys. Rev. B 28 (1983) 784.

[5] A.C. Mitus and A.Z. Patashinskii, Physica A 150 (1988) 371,383; J.Michalski, A.C. Mitus and A.Z. Patashinskii, Phys. Lett. A 123 (1987) 293.

[6] L.I. Tatarinova, The structure of Solid, Amorphous and Liquid Matter (Nauka, Moscow, 1983) (in Russian).

[7] A.C. Mitus, A.Z. Patashinskii and S.Sokolowski, submitted to Physica A.

[8] A.L. Mackay, Kristallografiya 26 (1981) 910; Physica A 114 (1982) 609; P. Kramer and R.Neri, Acta Crystallogr. A 40 (1984) 580.

[9] F.C. Frank, Proc. R. Soc. London, Ser. A 215 (1952) 43.

[10] A.Z. Patashinskii and B.I. Shumilo, Sov. Phys. JETP 62 (1985) 177.

[11] S.Hess, Z. Naturforsch. A 35 (1980) 69.

[12] J.P. Sethna, Phys. Rev. Lett. 451 (1983) 2198; Phys. Rev. B 31 (1985) 6278.

[13] D.R. Nelson and J. Toner, Phys. Rev. B 24 (1981) 363.

[14] F.C. Frank and J.S. Kasper, Acta Crystallogr. 11 (1958) 184; 12 (1959) 483.

[15] I.Z. Fischer, Statistical Theory of Liquids (Moscow, 1961) (in

Russian).

[16] A.C. Mitus and A.Z. Patashinskii, proceedings of NATO School
"Patterns, Defects and Materials Instabilities", Cargese,
1989 (in print).

[17] M.G. Kendall and A.S. Stuart, The Advanced Theory of Statistics,
vol.3 (Charles Griffin Company Limited, London, 1968).

[18] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling,
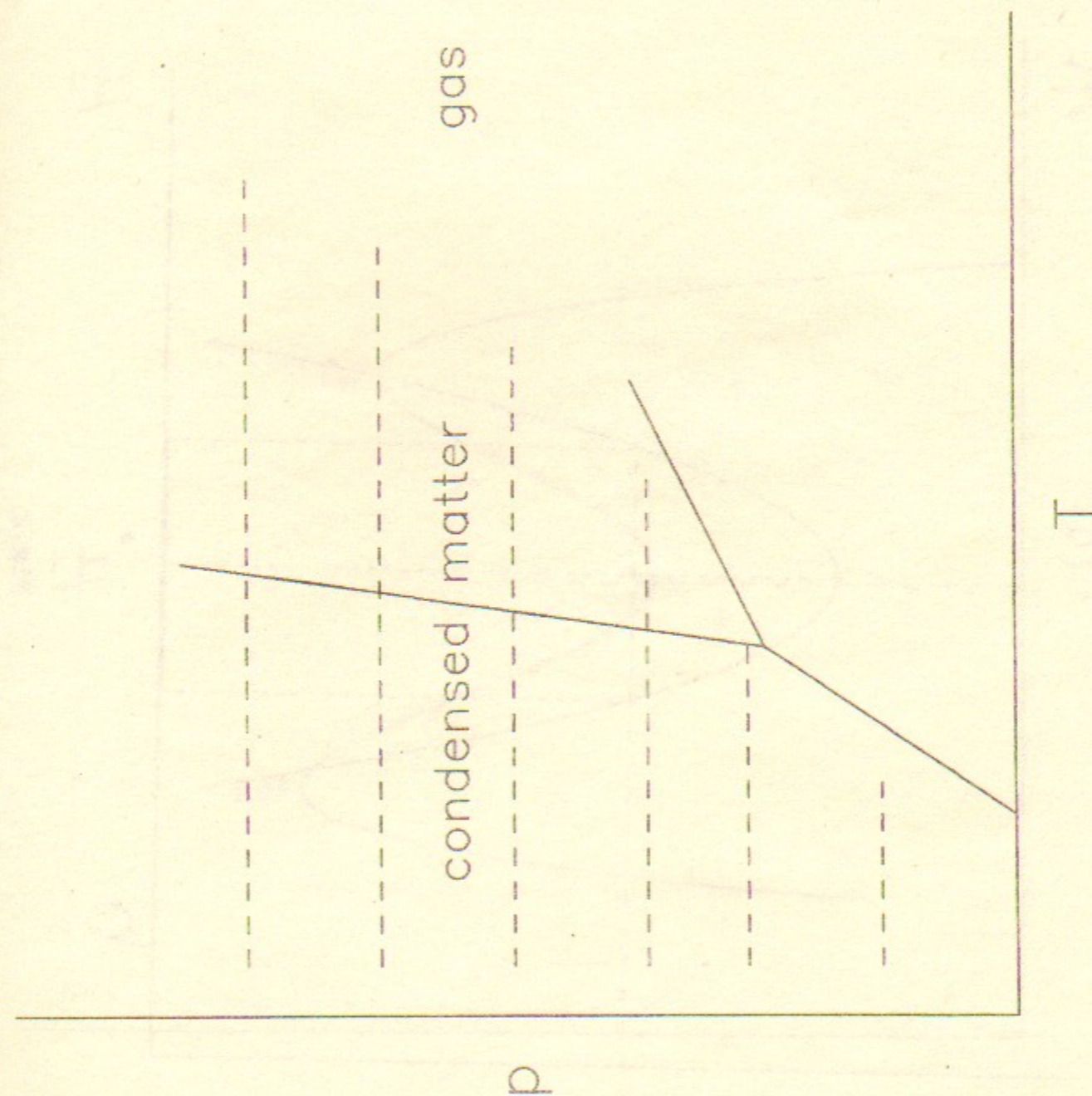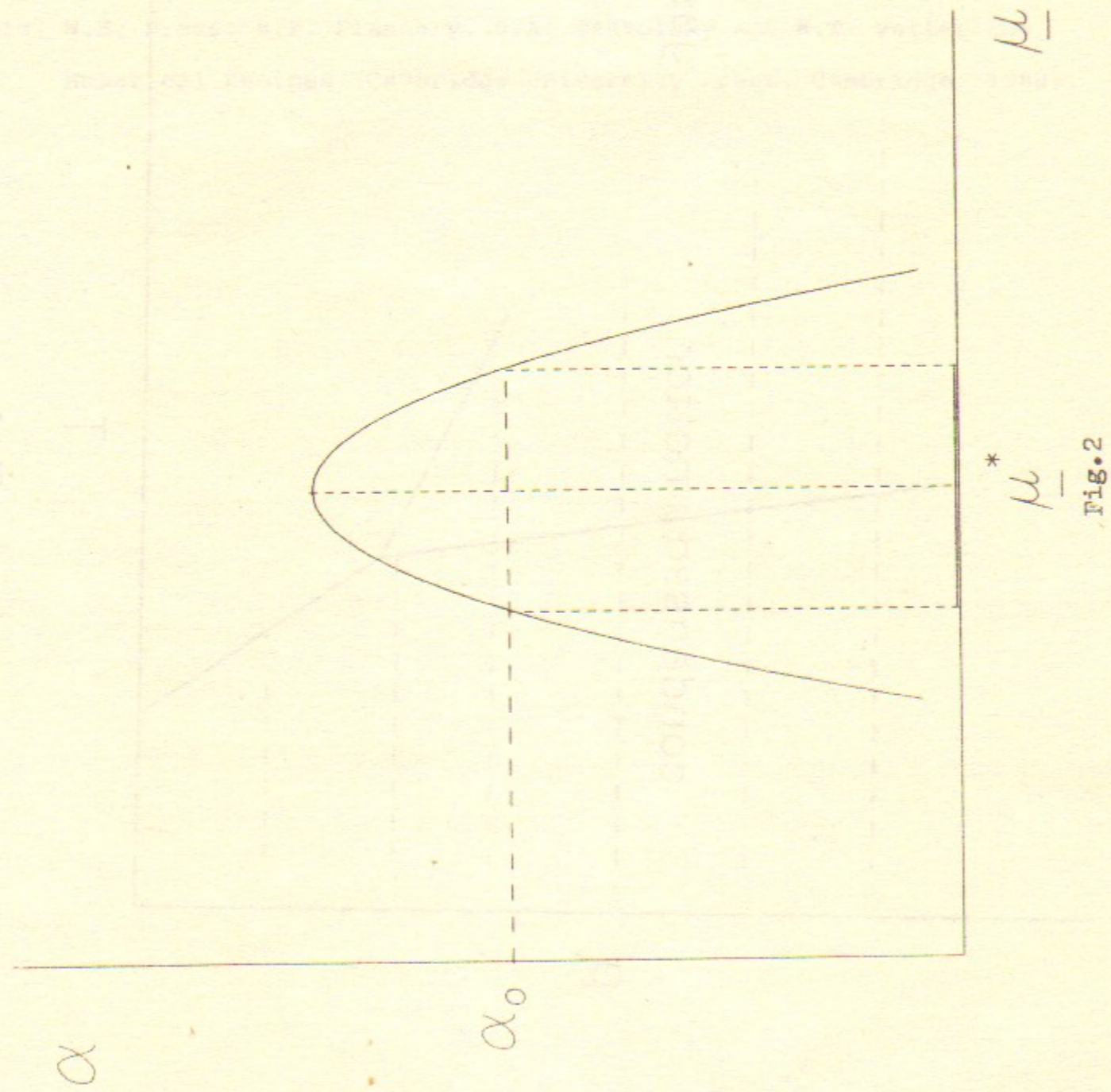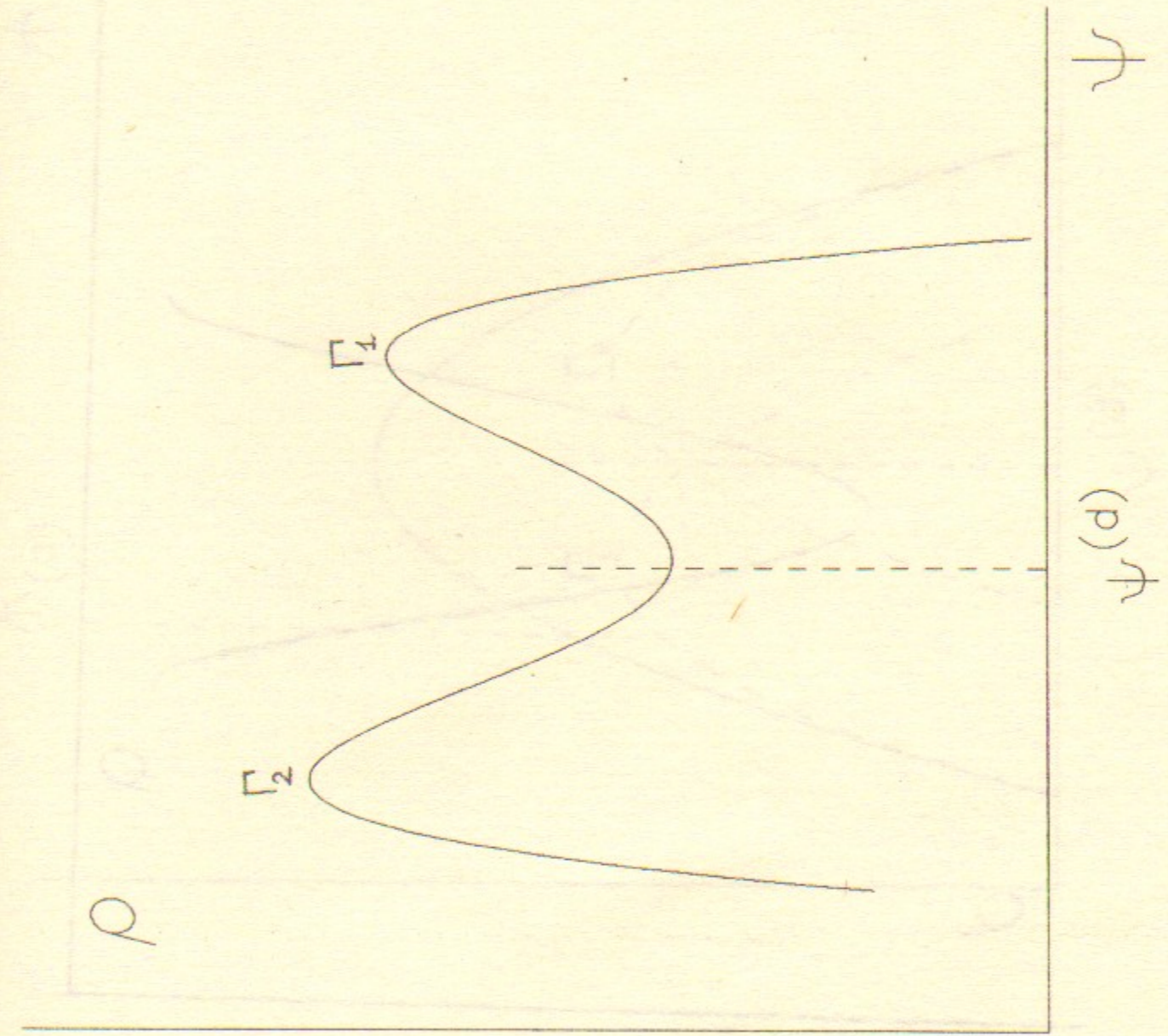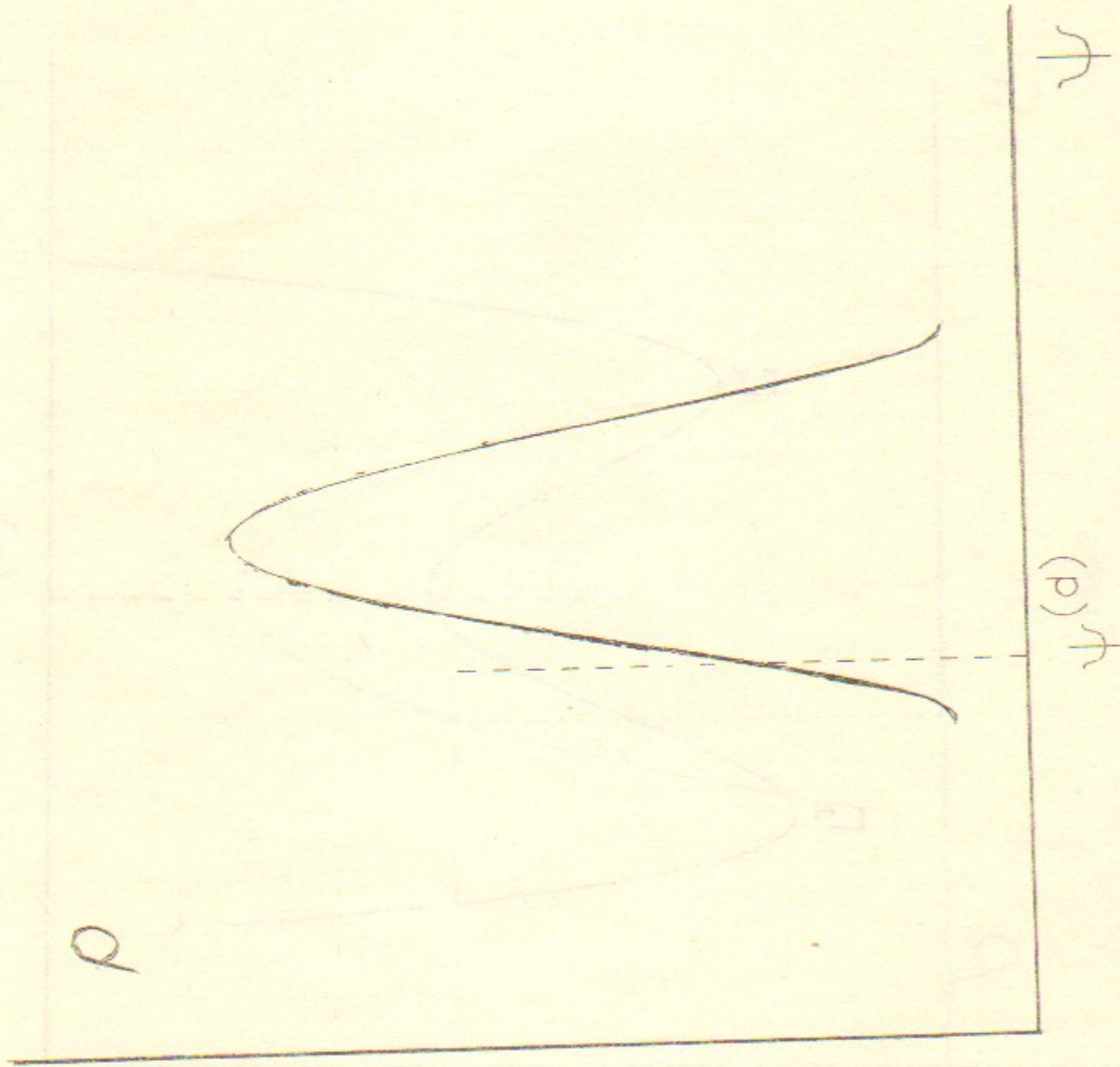Numerical Recipes (Cambridge University Press, Cambridge, 1988).

Fig.1

References

[14] A.C. Offord and A.G. Pakhomenko... Proceedings of NATO Conf...

[15] M.G. Kendall and A. Stuart, The Advanced Theory of Statistics...

[16] M.S. ...

Fig. 2

Fig. 3a

ρ

$\psi(d)$

Fig. 3b

ρ

Π_K

Π_i

$\psi(d)$

Fig. 3c

ρ

ψ

Fig. 3d

$\rho_k(\psi;\xi)$

$\psi^{(k)}_{1/2}(\xi)$

ψ

Fig. 4

$\alpha(\psi^{(d)};\xi)$

$\psi^{(d)}$

Fig. 5

$\alpha(\xi)$

α_0

ξ_k

a

b

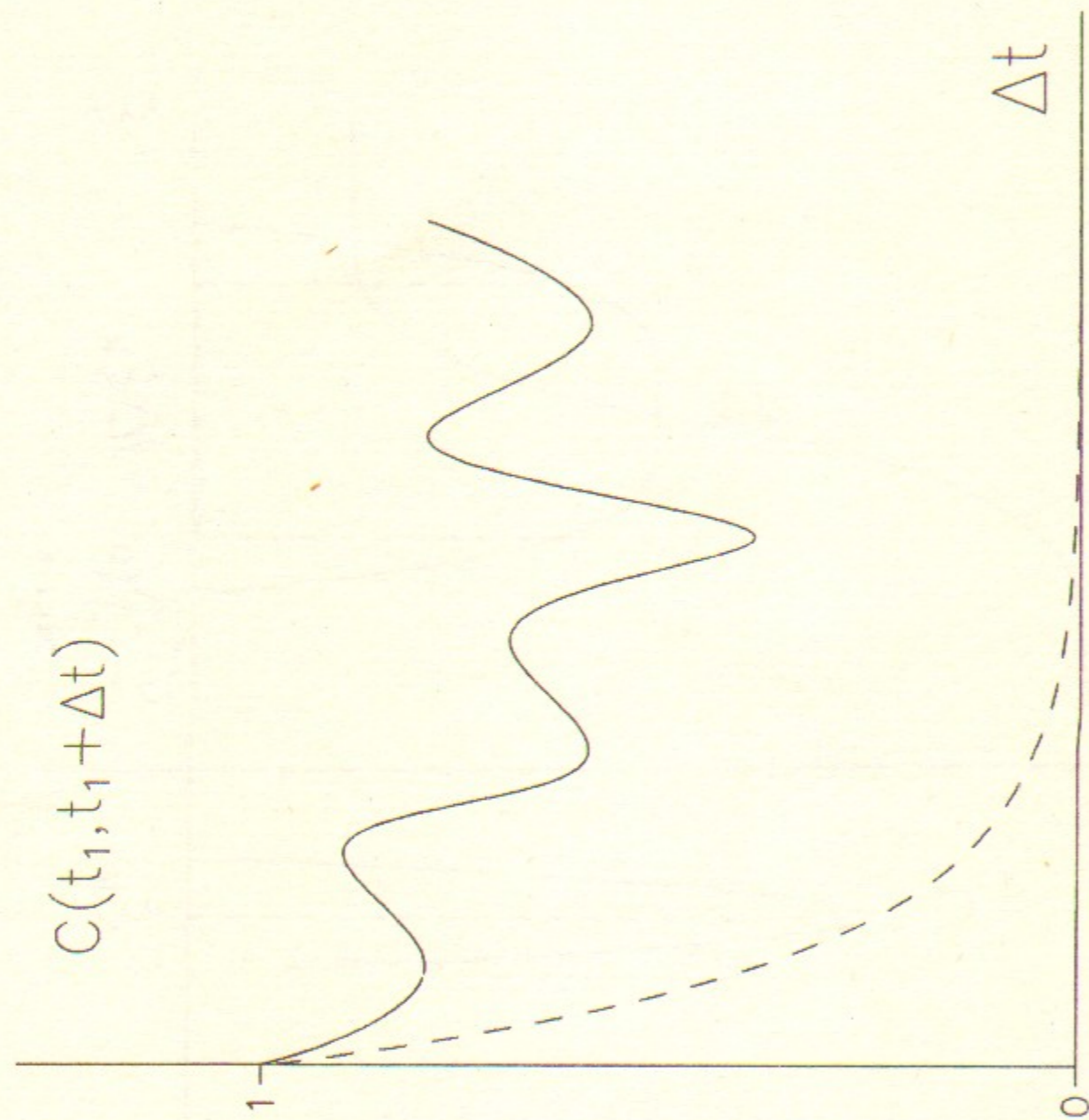$\Delta\xi_k$

ξ
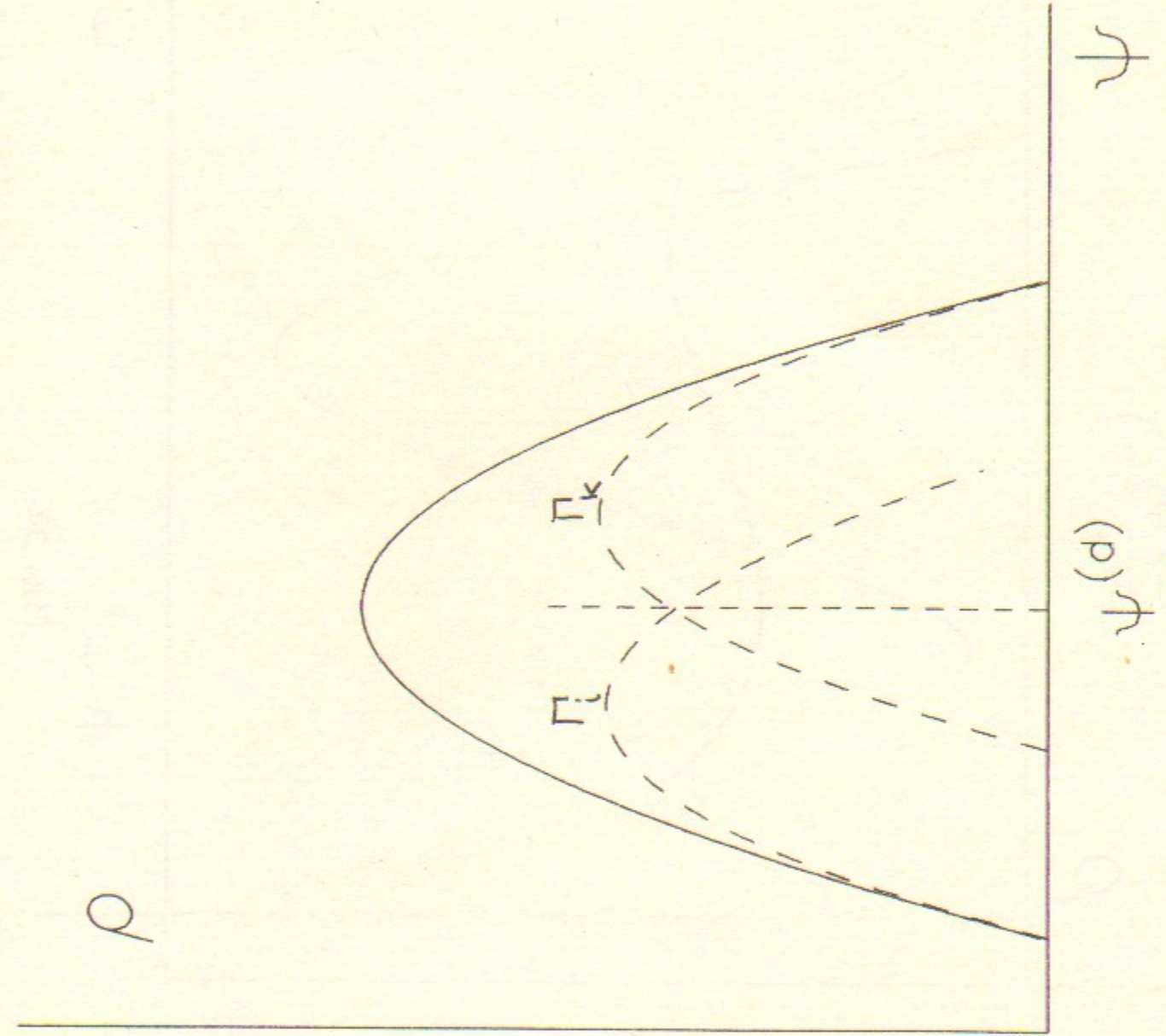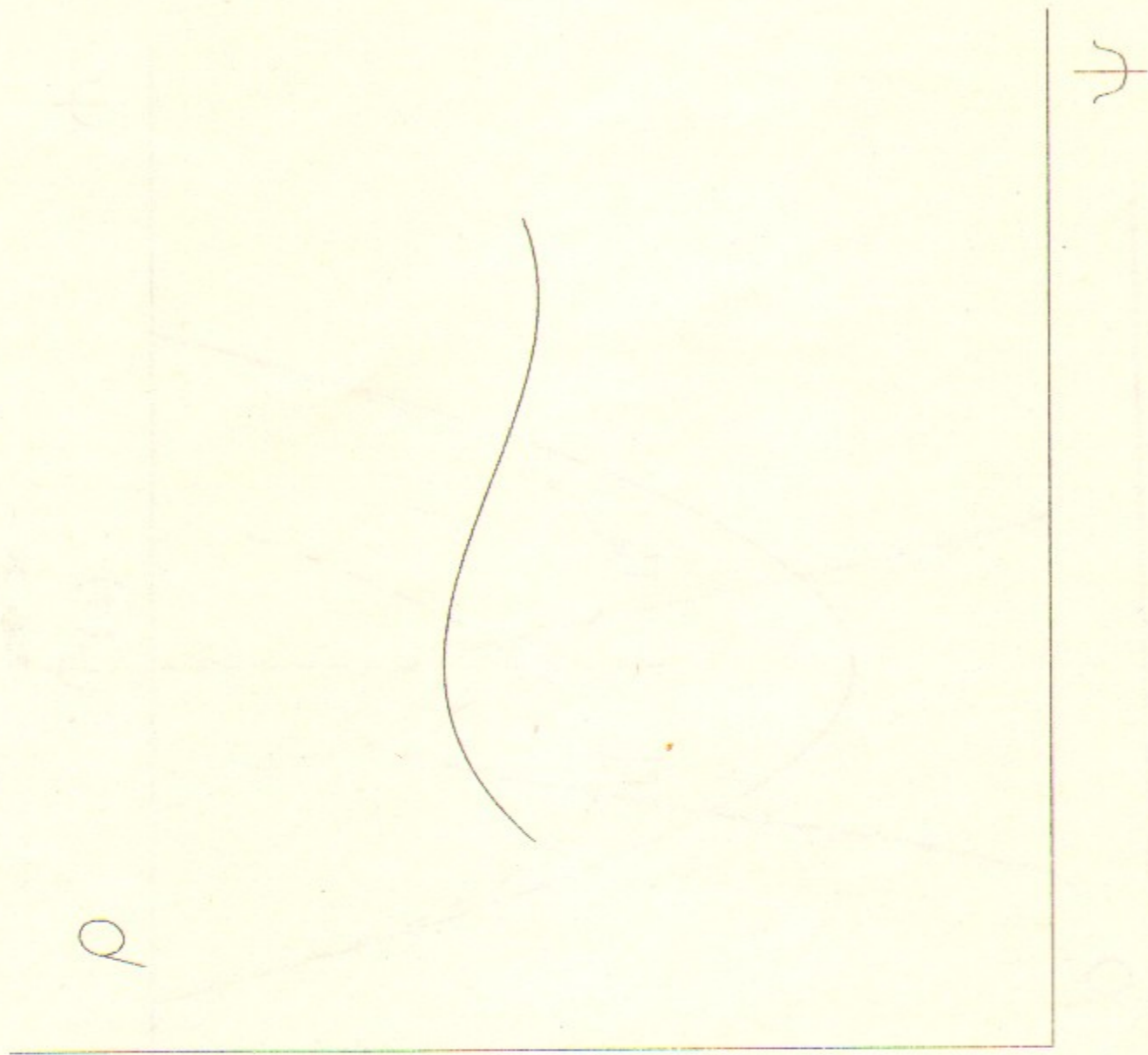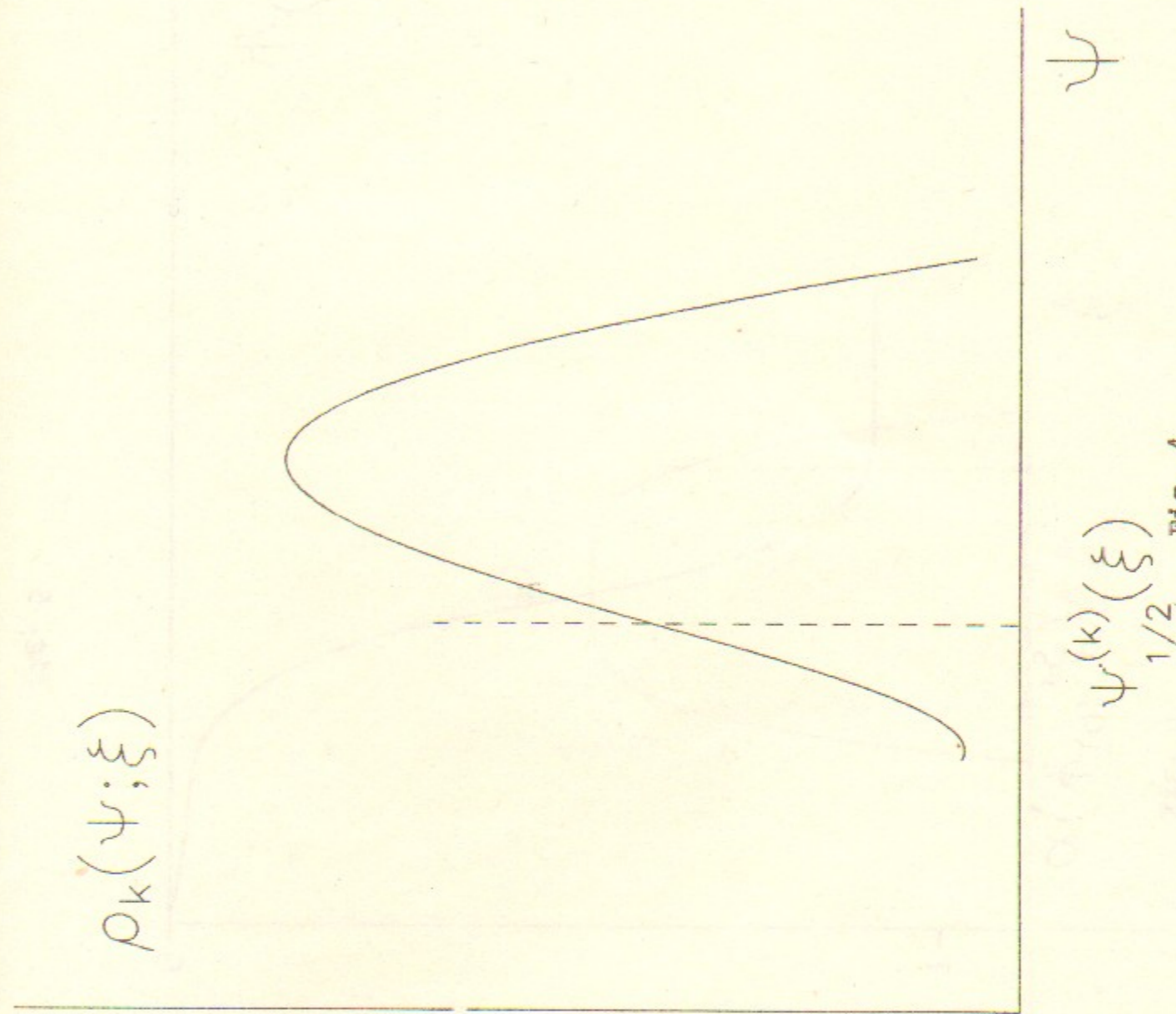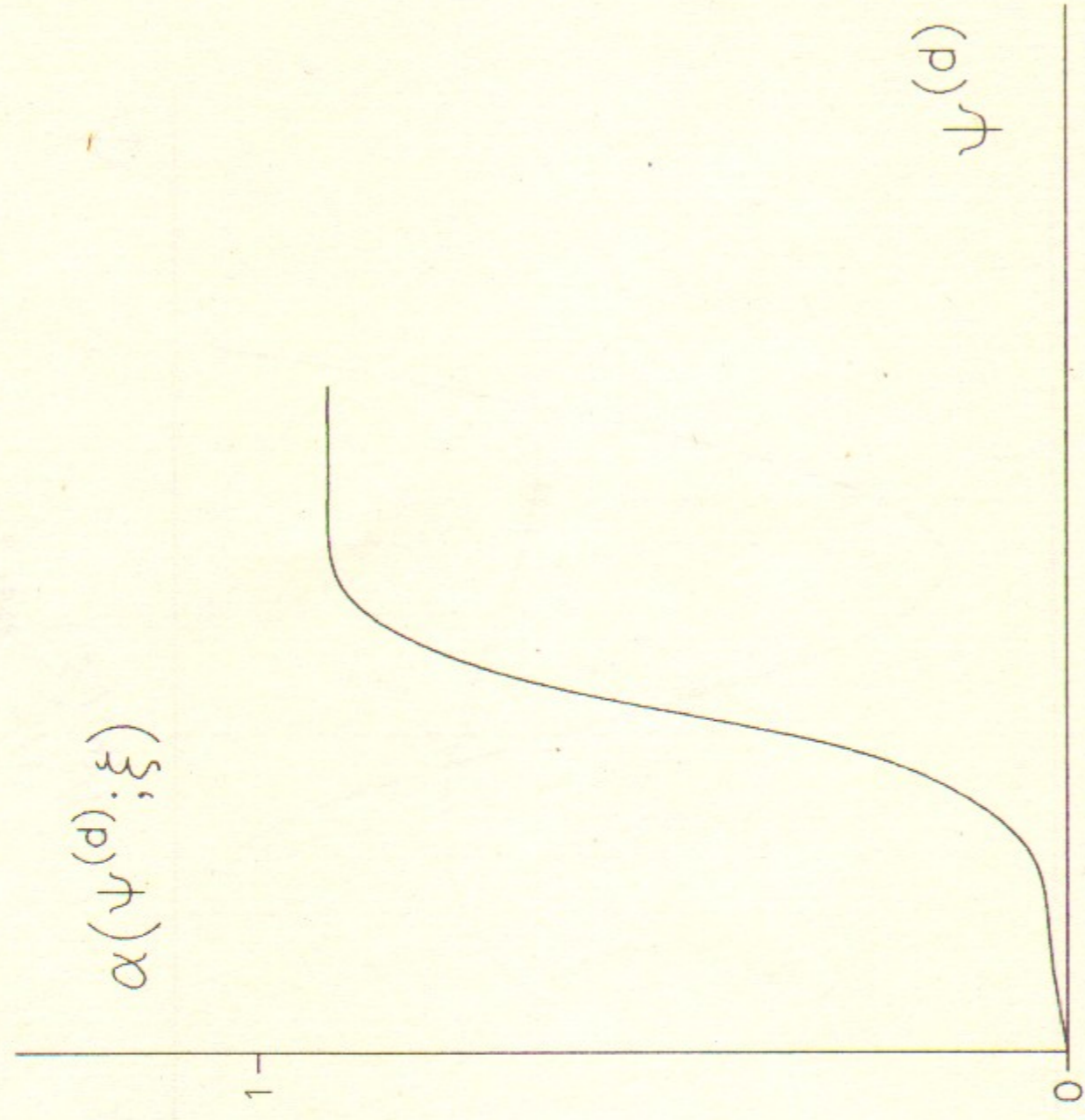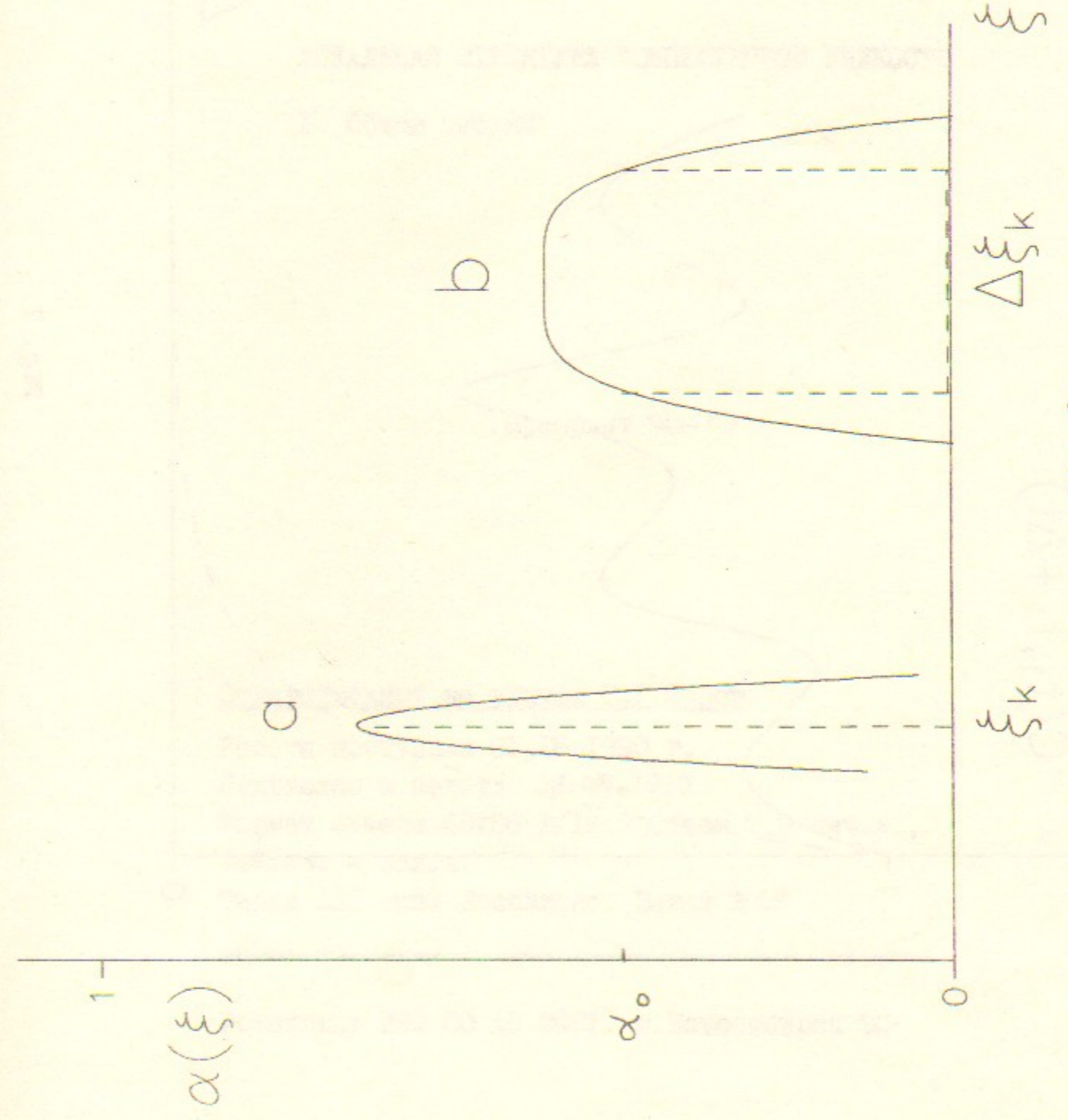
Fig. 6

Fig. 7

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ЛОКАЛЬНАЯ СТРУКТУРА КОМПЬЮТЕРНОЙ ЖИДКОСТИ

I. Общая теория.