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The Structure of Simple Liquids

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Theories of the structure of simple liquids, and the present state of the problem, have been examined. Attention has been paid to the unity of the static and dynamic characteristics of the structure. New results obtained by molecular-dynamic computer modelling, including the use of the ideas of statistical geometry, have been presented. The lack of justification for the quasi-crystalline approach to the structure of short-range order, and the fruitfulness of Bernal's ideas, have been pointed out.

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I. INTRODUCTION

A large amount of information on the properties of different liquids has been obtained in the last ten years. The number of liquids is very large, and is increasing continuously as a result of the synthesis of new compounds. The selection of substances for practical application requires their physico-chemical "classification", and this is becoming more difficult. A reasonable approach involves the use of sufficiently general regular features relating molecular structure to the properties of matter. Considerable progress has been made in reducing the amount of primary information needed by the use of the theory of physical similarity (the generalised law of corresponding states)[1,2].

A liquid, unlike a gas, is a collection of strongly interacting particles. It is distinguished from a crystal by the irregularity of its structure. Since it has not been possible to select a suitable simple model of a liquid, attempts have been made to bring it so "close" to either a gas or a solid crystal that the results based on the corresponding ideal model can be applied to a significant extent.

II. THE SEARCH FOR SIMPLE MODELS

In 1869, the detailed experimental work of Andrews[3] finally established the existence of the critical point (CP) of the liquid–vapour equilibrium as a universal property of matter. Andrews formulated the principal physical consequences of this fact: the possibility of a continuous change from a gas to a liquid in the region of the critical point; the existence of intermediate states above the critical point, which cannot be confidently assigned to any of the states of aggregation, and the unique character of transitions beyond the critical point. Van der Waals' thesis, which appeared four years after the publication of Andrews' work[3], contained

the elementary theory of the gas–liquid state in a very lucid form. Qualitatively, it showed satisfactory consistency with Andrews' discovery.

Boltzmann, in his review "Vorlesungen über Gastheorie"[4], discussed in detail the physical significance of van der Waals' equation and its many consequences. He pointed out the existence of intermediate states of matter in a continuous change from a gas to a liquid. Boltzmann's achievements in the development of the kinetic theory of gases stimulated studies in which the description of liquids was approached "from the direction of the gas".

These achievements provided a basis for bringing a liquid "closer" to the gaseous state (dense fluid states, and not an analogy between a liquid and a rarefied gas, were of course assumed). The range of applicability of the model of a weakly interacting gas was extended to an unjustifiable degree, however, and this led to the concept of the unstructured state of liquid. Experiments on the observation of the scattering of X-rays at small angles[5] (Stuart, Danilov, and their successors) demonstrated convincingly the existence of local ordering of the molecules of a liquid. For an arbitrarily chosen molecule, the neighbours in the first and second layers lie on the average at definite distances; the average number of neighbours in these layers can also serve as a characteristic of the short-range order in a liquid (the coordination number).

The breakdown of the view that liquids are unstructured was used, together with other arguments, to strengthen the position of the "solid" (quasicrystalline) model. This approach was developed most fully by Frenkel in 1945 in a monograph[6] which established an epoch in the physics of liquids. Many experimental facts received a simple explanation. It became possible to carry out elementary estimates of kinetic phenomena in liquids, and this stimulated studies in various branches of physical chemistry. This approach also has significant unsatisfactory features, however, particularly in the study of the structure of liquids, which is often interpreted as quasicrystalline. There is no satisfactory definition of quasi-crystallinity. The term combines a broad spectrum of concepts, from regularity in the arrangement of the atoms, disturbed by thermal motion, to a microcrystalline heterogeneous structure (the microcrystallinity is "softened", and the indefinite concepts of cybotaxes and clusters are introduced).

The adherence of many research workers to quasicrystalline models of liquids is strengthened by the established traditions of the processing and interpretation of the results of diffraction experiments. On the basis of an approximate form of the radial distribution function (RDF), conclusions are reached about the degree of correspondence between the structures of the liquid and the crystal. Although information about the average number of neighbours in the first coordination spheres and about the position of these spheres (layers) is reliably established from the processing of the X-ray diffraction patterns, the investigation of the finer details of the structure comes up against the indeterminate nature of the method. The RDF transforms the three-dimensional distribution of the atoms into a smoothed one-dimensional function. This imposes a fundamental restriction on the possibility of using the method to interpret the structure of the short-range order in a liquid: practically identical RDF can correspond to quite different configurations.

The concept of the quasicrystallinity of liquids does not follow from experimental data, but is rather related to an *a priori* underestimation of the unique character of the dense irregular structure. The existence of long-range order presupposes a quite definite type of short-range order. In the absence of the requirement of regularity (and when there is a certain free volume), the system has access to a new and extensive region of configuration space, and the system spends almost all its time in this region.

Quasicrystallinity is apparently a concept which is just as unacceptable as the unstructured dense liquid picture. Bernal was the first, in the late nineteen-fifties, to begin the battle against these concepts. He concluded that "this short-range order" is "quite different from what might be expected from an analogy with the crystalline state"[7]. Using "natural" (mechanical) models, Bernal demonstrated the existence (and even predominance), in a close-packed random structure, of elements of local ordering which are known to exclude the possibility of the appearance of a regular structure. Bernal's work will be examined in more detail below.

The next major achievement in the study of the structure and properties of simple liquids was associated with the use of the hard sphere model as an object of study by the methods of statistical physics and computer simulation. In this model, the forces of attraction between the particles is neglected, and the repulsion is described by the pair potential of inter-particle interaction $\Phi(r)$, which has the form of a rectangular wall

$$\Phi(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r \geqslant \sigma \end{cases} \qquad (1)$$

Here, σ is the diameter of the sphere, $v_0 = 1/6\pi\sigma^3$ its volume, $\rho/\rho_0 = Nv_0/V$ the proportion of the volume of the system occupied by the spheres (the density of packing), and V the total volume of the system. Allowance for thermal motion in the hard-sphere model leads to a linear temperature dependence; the RDF depends only on the density. The average potential energy of a system of N hard spheres is equal to zero, and the internal energy U is independent of the volume and can be written as for an ideal gas in the form

$$U = 3/2Nk_BT$$

It should not be thought that the theoretical description of the equation of state and the structure of this model is simple. The complexity of the problem is due to the fact that for dense states, the total volume of the spheres makes up a significant proportion of the total volume of the system. The simplicity of the model is sufficient, however, to permit the effective use of the Percus–Yevick approximation and the hyperchain approximation in the theory of correlative functions[8] and to bring the calculations to numerical values. Fig. 1 shows the RDF for "dense" argon, obtained experimentally[9] and calculated by the Monte Carlo method for the hard sphere model[10].

The RDF in the hard sphere model reproduces qualitatively the RDF of a real simple liquid. The dependence of the structural characteristics of the model on the curvature of a Lennard-Jones type potential in the range of small distances has been studied[10]. The splitting of the second peak of the RDF, which is observed for a system of hard spheres (see Fig. 1), takes place at values of the exponent of the repulsive part of the potential $n \geq 75$, whereas the average number of nearest geometric neighbours in the hard sphere model differs by less than 0.1% from the corresponding characteristic of systems with $n \geq 25$. This may indicate that the "geometric" factor has a decisive role in the formation of the irregular compact structure.

Before continuing the examination, it is appropriate to investigate how clearly and completely it is possible to formulate the actual concept of "the structure of liquids". This concept is much broader and deeper than any static

geometric representation. The structure of a molecular system is related to and forms a unity with the thermal motion. An "instantaneous photograph" of a single crystal at a high temperature, fixing the position of its particles, shows little similarity to the structure of the ideal lattice. An approximation to this structure is achieved by increasing the exposure time and averaging the configurational picture. The case of a liquid is even more complicated, because of the constant drift of particles from their immediate environment, and individual motion. Direct photography will give a picture which will become increasingly blurred with increase in the exposure. There arises the question of how to determine the characteristic geometric representation of the liquid in this case. It can be constructed by analysing the dynamic set of configurations formed by the particles of the system in thermal motion. Thus in the examination of the structure of a liquid, the treatment cannot be restricted to the geometric aspect. It is necessary to take into account the dynamic properties of the liquid. Its structure is revealed in different ways in time intervals of different scale.

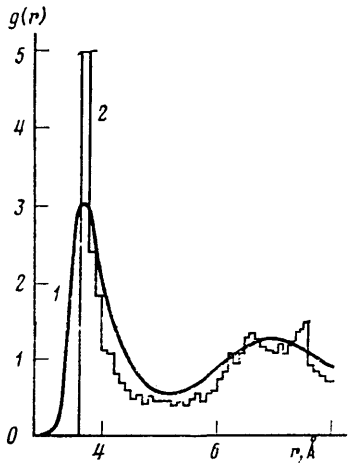


Figure 1. Radial distribution function of liquid argon: *1*) experimental, from elastic neutron scattering at 85 K,[9] *2*) histogram giving the result of a calculation by the Monte Carlo method for the hard sphere model[10].

III. THE STRUCTURE AND DYNAMIC PROPERTIES OF A LIQUID

1. Structure-sensitive Properties

In physicochemical analysis, the concept of "structure-sensitive" properties is often used, but attention is not always paid to which structural aspect is being revealed in the change in the given property. For example, the electrical conductivity of crystalline copper at room temperature is "sensitive" chiefly to constant defects of the structure and the difference between the instantaneous configuration of the ions and their regular average arrangement. With decrease in temperature, the positional "blurring" decreases, and the electrical conductivity σ_e increases. At 5 K it is ~1.5×10^4 times that at 300 K, and ~8.4×10^4 times that close to the melting point (1356 K). Compared with this difference, the change in σ_e on fusion is slight ($\sigma_e^l/\sigma_e^{cr} \cong 2.04$), and indicates a certain similarity between the instantaneous configurations of the liquid and the crystal at a high temperature. The electrical conductivity is a macroscopic characteristic, and represents a certain average value of microscopic variables of the crystal system, but from the structural viewpoint this averaging reflects the degree of irregularity in the "series" of successive configurations. For a macroscopic equilibrium specimen, the averaging of any local characteristic with time is equivalent to averaging with respect to the volume, since in the volume the system contains a vast number of independent sub-systems (microvolumes with linear dimensions greater than the de Broglie wavelength).

An example of a physicochemical property determined by positional and orientational ordering of the particles is the anisotropy. It is characteristic of crystals of low symmetry, and is not shown by ordinary liquids.

The heat capacity is another structure-sensitive property. In compact condensed systems, the heat capacity is determined by the spectrum of the frequencies of the elastic vibrations of the atoms; the main contribution is made by high-frequency modes. The influence of structure on the properties is due to a change in the spectrum of the vibrations in structural rearrangements, and also to a change in the contribution of individual motions to the energy characteristics† of the system. There is no simple relationship between them.

The dynamic structure of a liquid[11] (in momentum space) is related to the configurational structure. Experimental methods exist for the study of the dynamic structure, for example from scattering of neutrons by matter. By determining the elastic (without change in wavelength and energy) and inelastic coherent scattering on the one hand, and the inelastic noncoherent scattering on the other, it is possible to separate the contributions made to the scattering by the collective and individual motions of the particles.

2. The Fluctuational Aspect of Structure

The RDF is the most widely used primary characteristic of the structure of liquids. It is usually found from experiments on the low-angle scattering of X-rays. The scattering power of a liquid as a function of the angle of scattering θ is proportional to the static structure factor ($S(k)$, which carries the necessary information on the averaged configurations of the particles in the volume:

$$I/I_0 N f^2 = S(k)$$

Here, I_0 and I are the intensities of the exciting and scattered radiation respectively; N the number of atoms in the scattering volume V; f the atomic scattering coefficient, which depends on the electron density; $k = (4\pi/\Lambda) \times \sin(\theta/2)$ the modulus of the wave vector of the scattering; and Λ the wavelength of the X-rays.

The expression for the RDF is obtained from $S(k)$ by means of a Fourier transformation:

$$g(r) = 1 + \frac{1}{8\pi^3\rho} \int [S(\mathbf{k}) - 1] \exp(-i\mathbf{kr})\, d\mathbf{k}$$

Here, $\rho = N/V$ is the average numerical density.

†On the fusion of polyatomic (molecular) crystals, the heat capacity may also increase as a result of the removal of the degeneracy from rotational and librational degrees of freedom.

As noted earlier, the RDF gives extremely crude (contracted) information on the structure of a liquid. The important feature for scattering is the non-uniformity of the distribution of the scattering centres (molecules) with respect to the elementary volumes ΔV_i, the linear dimensions of which are of the order of the wavelength of the radiation; N_i is the number of molecules in the volume ΔV. The total effect of scattering with allowance for interference depends on the average value of the non-uniformity $\langle (N_i - \bar{N}_i)^2 \rangle^{1/2}$ in these volumes#. By changing the wavelength of the radiation or the angle of scattering (that is **k**), it is possible to "probe" non-uniformities of different scale. Essentially, the fluctuations in the density and their correlation in the thermal motion are being revealed here. Thus the structure factor, and hence the RDF, carry chiefly the information on the structure of the liquid which is contained in its description in the language of fluctuations. In the long-wave limit, the following relationship exists between the average value of the fluctuations $\langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho}$ and the structure factor of RDF:[12]

$$\lim_{k \to 0} S(k) = 1 + \rho \int [g(r) - 1] \, dV = V \langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho} \qquad (2)$$

On the other hand, statistical thermodynamics makes it possible to express the density fluctuations (naturally, long-wave compared with the internuclear distance) in terms of the isothermal compressibility of the substance $\beta_T = V^{-1} \cdot (\partial V / \partial p)_T$:

$$\langle (\rho - \bar{\rho})^2 \rangle / \bar{\rho}^2 = k_B T \beta_T / V \qquad (3)$$

The quantity β_T can be regarded as a function of the response to a small static perturbation of the system by pressure. It is clear from Eqn.(3) that the response function becomes large where the fluctuations are large, for example close to the critical point of the liquid–vapour equilibrium. Eqns.(2) and (3) can be generalised to the case of short-wave perturbations§ with wavenumber k:[12]

$$S(k) = \rho k_B T \beta_T(k) \qquad (4)$$

Here, $\beta_T(k)$ is the isothermal response function, which depends on k and which characterises the isothermal compressibility for short-wave perturbations.

Liquid argon or sodium are regarded as typical simple liquids. Close to the melting point, the structure factor of liquid argon does not differ greatly from $S(k)$ for liquid sodium (see Fig.2). The structural similarity between the liquid inert gases and the alkali metals was unexpected, since their forces of interaction are quite different. The existence in metals of a sub-system of almost free electrons alters the situation in many respects, for example by leading to the appearance of a long-range oscillating component in the effective potential of the paired interaction $\bar{\phi}(r)$.[12,13] Without going into details, it is found that the structure of the short-range order in a dense liquid is not appreciably sensitive to the form of the function $\phi(r)$. Its similarity to the structure of a system of hard spheres indicates the important role of the "geometric" factor (short-range repulsion forces) in the production of the short-range order of simple liquids. This is also indicated by the one-parameter thermodynamic similarity in the fusion curves of the inert gases and typical metals[14].

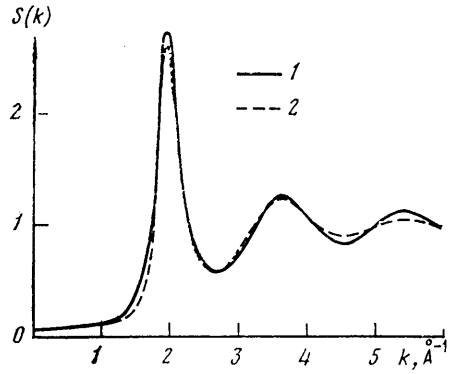


Figure 2. Structure factor for liquid argon at ~85 K [9] (*1*) and for liquid sodium at ~383 K [15] (*2*), close to the melting point.

It is not possible in the present review to carry out a detailed examination of the fluctuations and correlation functions. It is necessary, however, to distinguish the "fluctuational aspect" of the structural description of liquids. It is reflected in condensed form by Eqns.(2)–(4), from which it follows that the spectrum of the density fluctuations contains important information on the supermolecular structure. The dynamics of the fluctuations, the characteristic time of their dissipation, self-diffusion, and collective modes are all related to the structure of the liquid in the broad sense. The positions of two close molecules are statistically correlated not only in space but also in time. The Van't Hoff function $G(\mathbf{r}, t)$ is introduced as the average numerical density of the particles¶; close to the point **r** at moment of time t with the condition that the origin of coordinates coincides with one of the particles at $t = 0$. This function can be used to describe the space–time correlations. To change from $G(\mathbf{r}, t)$ to the RDF, it is necessary to fix the time and put $g(r) = G_d(r, 0)$; $G_d(r, t) = G(r, t) - G_s(r, t)$, where $G_s(r, t)$ is the auto-correlation part of the Van't Hoff function.

Just as the spatial fluctuation of the density represents a superposition of harmonic vibrations of different wavelength, the time "portrait" of the correlation can be expressed by a definite frequency spectrum (ω), using the Fourier transformation of the function $G(r, t)$ relative to the time t. This introduces the dynamic structure factor $S(k, \omega)$:

$$S(k, \omega) = \rho \iint \exp[-i(\mathbf{kr} - \omega t)] G(\mathbf{r}, t) \, d\mathbf{r} dt$$

#The angle brackets or the bar above the letter denote averaging with respect to the ensemble.

§In the present work, the letter k is used to denote both the wave vector of scattering and the Fourier components in the representation of the spatial density distribution by the set of harmonic functions $\rho(\mathbf{k})$ with different wavelength λ, $k = 2\pi/\lambda$. The condition of the first interference maximum when scattering is observed relates the quantities λ and Λ as follows: $\lambda = (\Lambda/2) \sin(\theta/2)$.

¶The terms "molecule" and "particle" are used as synonyms. Simple liquids are primarily monatomic. In this sense it might be possible to give preference to the word "atom", but it is not completely appropriate in the case of metallic liquids.

If the scattering is coherent, then for a given **k**, integration of $S(\mathbf{k}, \omega)$ with respect to all frequencies gives an expression for the static structure factor:

$$S(\mathbf{k}) = \int_{-\infty}^{\infty} S(\mathbf{k}, \omega)\, d\omega$$

The scattering function $S(k, \omega)$ can be calculated using model representations. A particularly important feature, however, is that $S(k, \omega)$ can be found from neutron scattering experiments.

The dynamic structure factors of liquid argon close to the melting point, 83.8 K, and of sodium at 506 K (m.p. = 370.9 K), are given in Fig.3. In spite of the differences in the nature of the interaction between the particles in sodium and argon, the dynamic characteristics of their structures are of the same type. The spectrum of the density fluctuations of sodium has many more high-frequency modes, however, and the spectrum of argon many more low-frequency modes. It may be noted that with decrease in temperature there is a decrease in the width of the range of values of $S(k, \omega)$ with respect to the variable ω. Thus the dynamic structure factors of liquid sodium and argon approach even closer in the region of the melting point.

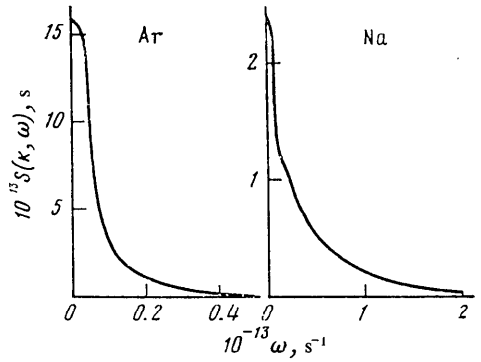


Figure 3. Dynamic structure factor for liquid argon (85.2 K) [16] and for liquid sodium (506 K) [17] with wavenumber $k_1 = 2$ Å^{-1}, corresponding to the position of the first $S(k)$ maximum.

between the particles and which should lead to convolutions in the path of the molecule between two successive hard collisions.

The Frenkel model of a dense liquid[6] assumes another basic mechanism of individual thermal motion: the molecule vibrates about a temporary equilibrium position, and then jumps abruptly to another position, at the foot of the potential well formed by the particles of the new environment. The magnitude of the jumps is close to the average distance between nearest neighbours d. The period of the vibrations τ_0 and the average settled time τ_s are the characteristic time scales in this model of a liquid. Their use together with the parameter d makes it possible to estimate the kinetic coefficients.

The use of molecular-dynamic computer modelling[18-20] has helped to answer questions about the real picture of the thermal motion of the individual particles of a liquid of the argon type close to the triple point, and about the method of study that will make it possible to establish it.

The modelling of simple liquids of the argon type is usually carried out assuming a pairwise central interaction between the particles. The computer is used to calculate numerically the trajectories of the particles with a time step Δt. The results obtained close to the triple point for a model of argon containing in the basic cell 108 interacting (Lennard-Jones potential) particles[21] are given below. The step size in the integration of the equations of motion Δt was 10^{-14} s.

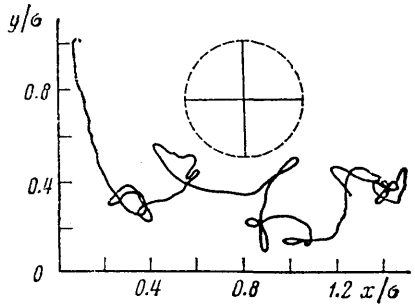


Figure 4. Projection of the trajectory of the motion of a particle on a plane in the molecular-dynamic model of liquid argon[21], 84 K; time interval 10^{-11} s; σ is the effective diameter of the particle (the parameter of the Lennard-Jones potential).

3. The Nature of Thermal Motion in a Liquid

Attention has been drawn to the complexity of the concept of the structure of a simple liquid. To create the correct geometric representation of a structure (this is usually the problem posed), it is necessary to find a method for separating the characteristic indications of the structure from the large number of "transient" configurations arising in the process of thermal motion. This motion has collective and individual components. Ideas about the nature of the thermal motion of individual molecules in a dense liquid have changed with the passage of time. Van der Waals' approach led to the following picture. A particle undergoes hard elastic collisions with the particles of its environment. Between collisions, it moves freely, that is the average field does not change its rate vector significantly; there is no collective component. Some authors also attach importance to "soft" collisions, which are due to the forces of attraction

The motion of each particle resembles the Brownian drift in the field of the changing environment (Fig.4). This motion includes a high-frequency component (Fig.5), but it is difficult to distinguish it in the train of approximately monochromatic vibrations about the temporary equilibrium position and in the jump to a new fixed position. The time interval in Fig.4 contains 10^3 steps in the integration of the equations of motion, so that the picture of the individual motion is obtained with a high resolution. The two sections in the circle, intersecting at right angles (Fig.4) show the magnitude of the displacement of the argon atom in a time of 7×10^{-13} s for motion with an average thermal velocity. For a crystal near the triple point, the motion of the particle is concentrated in the region bounded by the broken circle in Fig.4. The maximum of the spectral density $f(\omega)$ of the

auto-correlation function of the velocity of the particle is observed at $\omega' = 2 \times 10^{12}$ s^{-1}, which corresponds to the most probable frequency of the individual vibrations of the atoms in the liquid. If the gas-dynamic approximation is used, a value close to ω' is obtained for the average number of collisions of the particle. Examination of a selected particle together with its environment, and the dynamic structure factor[20,22], shows, however, that the molecular motion in a dense liquid is essentially collective in character.

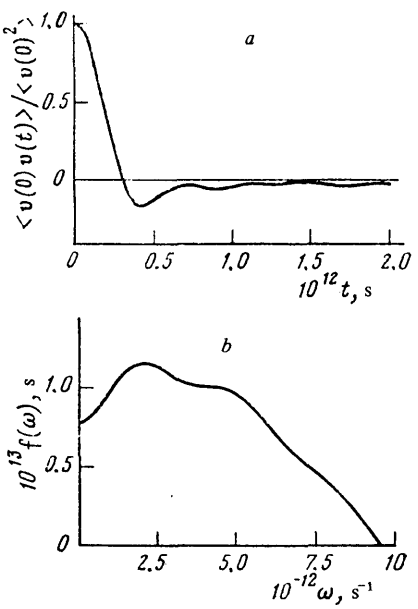


Figure 5. Self-correlation rate function (*a*) and its time Fourier transform (spectral density) (*b*) for the MD model of liquid argon (84 K).[21]

Table 1 gives the characteristic values of quantities related to the static and dynamic structures for two simple liquids, argon and sodium, close to the triple point. Table 1 was compiled using data from Refs.9, 11, 15–17, 21, 22. The average distance between the particles d was obtained as $v^{1/3} = (V/N)^{1/3}$. The positions of the first and second maxima of the RDF give the radii of the first and second coordination spheres r_1 and r_2. The average coordination numbers are determined by the integrals

$$\bar{z}_1 = \int_0^{r_{m1}} d z, \quad \bar{z}_2 = \int_{r_{m1}}^{r_{m2}} d z,$$

where r_{mj} is the position of the jth minimum of the RDF. The local coordination number $\delta z = dz$ is the average number of neighbours in a spherical layer of thickness δr at a distance r from the central particle:

$$\delta z = \frac{4\pi}{v} g(r) r^2 \delta r, \quad \delta r = (r_{i+1} - r_{i-1})/2;$$

the subscript $i = 1, 2, \ldots$ denotes the points of division of the interval in which the RDF was obtained from the experiment. The blurring of the coordination layers is characterised by the second moments of δz_1, δz_2, that is

$$\tilde{\Delta} z = \langle (\delta z - \bar{\delta z})^2 \rangle^{1/2} / \bar{\delta z}$$

The position of the first maximum of $S(k)$ is denoted by k. The average rate of thermal motion $u = (k_B T/m)^{1/2}$, and D is the self-diffusion coefficient. The characteristic frequency of the individual vibrations of the atoms (the position of the principal maximum of the frequency spectrum of the auto-correlation function of the velocity) is denoted ω'. In liquid alkali metals, propagating collective vibrations (modes) with fairly short wavelengths λ are observed (as far as $\lambda \cong 1.5\lambda_1$, where $\lambda_1 = 2\pi/k_1$ is the characteristic wavelength of the order of the interatomic distances). In liquid argon, only modes with $\lambda \geq (5-7)\lambda_1$ can be propagated, but as in liquid sodium, a mode of the relaxation type exists in argon. The characteristic frequency of this excitation ω_C is determined via the half-width of $S(k_1, \omega)$; ω_D is the Debye frequency (it depends on the temperature of the solid for which it is determined), and $\tau_R = \eta/G$ is the Maxwell relaxation time (η is the shear viscosity of the liquid, and the value of the shear modulus G is taken for the solid substance).

Table 1. Space–time characteristics of the structure of liquid argon (m.p. = 83.8 K) and sodium (m.p. = 370.9 K) close to the melting point.

Characteristic	Ar	Na	Characteristic	Ar	Na
T, K	85	373	k_1, Å^{-1}	2.0	2.0
d, Å	4.05	3.76	u, m s^{-1}	133	367
r_1, Å	3.67	3.82	$10^5 D$, cm^2 s^{-1}	1.9	5.8
r_2, Å	6.94	6.9	$10^{-13}\omega'$, s^{-1}	0.2	2.0
$\bar{z}_1$	12.2	13.9	$10^{-13}\omega_C$, s^{-1}	0.06	0.13 (T=506 K)
$\tilde{\Delta} z_1$	0.50	0.54	$10^{-13}\omega_D$, s^{-1}	1.0±0.2	1.5±0.3
$\bar{z}_2$	42.6	45.8	$10^{-13}\tau_R$, s^{-1}	0.3	0.8
$\tilde{\Delta} z_2$	0.40	0.39			

Table 1 shows that the greatest difference is between the principal frequencies of the individual vibrations of the atoms. This is due chiefly to the difference in the strengths of the interactions between the particles in liquid argon and sodium. The Na ions are in a stronger surrounding field than the Ar atoms. Thus the vibrations of the Na ions in this field also take place with a higher frequency than those of the Ar atoms. The characteristics of the static structure of liquid argon and sodium do not differ so markedly.

IV. THE RESULTS OF THE USE OF SIMPLE MODELS

1. Bernal's Model Representations

In the late nineteen-fifties, Bernal[23] stated that the structures of the short-range order in a liquid and in a crystal are essentially different. Bernal pointed out the inadequacy of the quasi-crystalline concept in the theory of simple liquids. He later pointed out[24] the symmetry-related source of this difference: "A necessary geometric property of any lattice or any structure constructed in a lattice, no matter how small its dimensions, is the presence of a definite form of axial symmetry, of second, third, fourth, or sixth order. Symmetry of fifth order is impossible in a crystal lattice, however". In the irregular structure of a liquid, however,

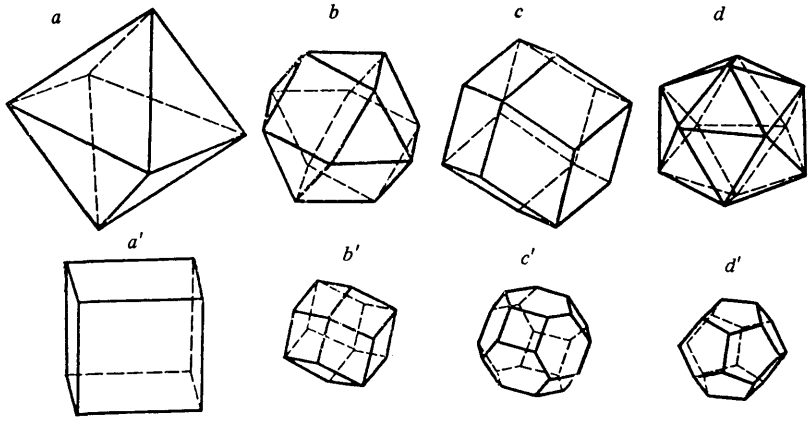


Figure 6. Polyhedra for the nearest neighbours (particles situated at the centre and apices of the polyhedra) in the ideal simple cubic (*a*), face-centred cubic (*b*), and body-centred cubic (*c*) lattices and for icosahedral coordination (*d*). The corresponding Voronoi polyhedra are: cube (*a'*), rhomboidal dodecahedron (*b'*), cubo-octahedron (*c'*), and dodecahedron (*d'*).[21]

other types of symmetry may be found. For example, elements with symmetry of fifth order are characteristic of dense random packing.

Since Bernal was interested in problems of the geometric structure of liquids, he turned to mechanical models, believing that random dense packing is closest to the typical molecular configurations of a simple liquid. Models of different types were used: 1) ball and spoke, 2) wax and plasticine spheres, and 3) steel (non-deformable) spheres. In the first type of model, a random distribution was approached by the successive addition of spokes whose length was selected in accordance with the RDF of argon, or by specifying the coordinates of the centres of the spheres by means of a computer using an established program ensuring a random distribution. The second type of model was subjected to compression, and the spheres were converted into polyhedra (analogues of the Wigner–Seitz cells), whose shape reflected directly the relative arrangement of neighbours. To make the corresponding construction without resorting to deformation of the spheres and replacing them altogether by points, the following procedure was used. Through the centres of the sections connecting the selected point (the centre of the sphere) to the points surrounding it, planes normal to the sections are constructed. The intersection of the planes gives a set of polyhedra round the given point. The convex internal polyhedron, which is not intersected by other planes, is called the Voronoi polyhedron (VP). It reflects the arrangement in space of the points nearest the selected point. The VP is a cube for a simple cubic lattice, a cubo-octahedron for a body-centred cubic lattice, and a rhomboidal dodecahedron for a face-centred cubic lattice. This correspondence between the cell and the VP is shown in Fig.6; to it is added another example—the Voronoi polyhedron for an element of an irregular arrangement of atoms—which can be represented by an icosahedron or by twelve deformed tetrahedra.

Bernal analysed the set of polyhedra obtained in the deformed model. it was found that the average number of faces of the Voronoi polyhedron $\bar{n} = 13.3$ (in the ball and spoke model, $\bar{n} = 13.6$), and of all types of face $3 \leq m \leq 7$ (m is the number of sides of the face), the quadrilateral was encountered most frequently; averaging over all the polyhedra gave $\bar{m} = 4.3$. The existence of five-particle configurations in the model of the liquid (the proportion of pentagonal faces was 27%, whereas the proportion of quadrilateral faces was 48%) is known to exclude the possibility of a regular structure. This characteristic, according to Bernal, reflects a fundamental structural property of a liquid.

The mathematical study of three-dimensional irregular networks[25] gives a higher value $\bar{m} = 5.115$ and a similar value $\bar{n} = 13.56$.

When polyhedra are obtained in close packing by compressing a model, fairly small faces and edges of the polyhedra are revealed ineffectively or not at all. Thus Bernal's analysis does not correspond rigorously to the actual configuration. As shown below, however, the smallest faces apparently should not be taken into account, since they reflect that element of random character which should disappear on appropriate averaging. In the molecular system they arise as the background produced by thermal motion.

Modelling showed that a random close-packed structure is characterised by a certain coordination number distribution function. This was clearly revealed in experiments with steel balls in a balloon[7]. After shaking and compressing the system, paint was poured into the balloon; the paint flowed freely, leaving thicker traces in the form of rings or points at those places on the surface of the spheres where they were in contact or almost in contact with one another. This detected neighbours for which the relative distance between the centres r/σ lay in the range $1 \leq r/\sigma \leq 1.05$.

The next method of studying models of steel balls ($N = 3000$, $\sigma = 6$ mm) was based on the determination of the Cartesian coordinates of each ball using a special measuring device[7]. Similar experiments were carried out by Scott[26] in Toronto. Spheres in a random close-packed structure occupy ~0.64 of the total volume. For a regular close-packed structure, $v_0 N/V = 1/6\pi\sigma^3 N/V = 0.7405$. This corresponds to a ratio of the densities of regular and irregular packing of 1.16. The number obtained is close to the ratio of the densities of crystalline and liquid argon (1.15) close to the triple point. The coordinates of the steel balls measured in

the packing were fed into a computer[27] for the construction and analysis of the Voronoi polyhedra. This gave the values $\bar{n} = 14.28$ and $\bar{m} = 5.16$, which are greater by 5% and 1% respectively than the values of $\bar{n}$ and $\bar{m}$ obtained in Coxeter's theoretical model[25].

The exact construction of the Voronoi polyhedra (with allowance for the small faces and edges) for the model of a simple liquid showed that pentagonal configurations predominate over other arrangements of the spheres. For the steel-ball models, the RDF was constructed and found to show satisfactory agreement with the RDF for liquefied inert gases and alkali metals. The independent determination of the RDF by Bernal and by Scott gave identical results. Thus the model of irregular close packing reflects essential features of the geometric structure of simple liquids. The theoretical study of the hard sphere model (the calculation of the RDF, mentioned above), and also computer modelling[28], lead to the same conclusion. Another conclusion is as follows. The form of the RDF of liquid argon or sodium close to the triple point is not determined by the need for a quasi-crystalline structure of the short-range order. Models show that the RDF arises from a large number of configurations, where there is a predominance of elements of short-range order excluded from the small set of coordinations allowed by the construction of a regular close packed structure.

Bernal also used other geometric methods of studying models. For example, he examined the shapes of the cavities between the spheres, which are clearly revealed in a system constructed from balls and spokes. The cavities (holes), bounded by planes passing (in contrast to the Voronoi polyhedra) through sections connecting nearest neighbours, form a certain set of polyhedra. Their variety is not particularly large, if the examination is restricted to the case where cavities into which a sphere can enter freely are not formed. The random close-packed model is characterised by a much larger number of types of polyhedra than the regular structure, however. In both cases, the predominant form of cavity is the tetrahedron. This reflects a high density of packing, since the tetrahedral coordination of four atoms corresponds to the highest local density (0.7795). A very compact formation is obtained by the connection of several tetrahedra. Bernal called these formations pseudo-nuclei. The prefix "pseudo" is related to the fact that a regular structure cannot be constructed from tetrahedra, but slightly curved chain formations of tetrahedra are possible.

The study of the angular distribution of neighbours in the models revealed the existence of groups of 4–6 atoms arranged almost in straight lines. These randomly oriented "collinear formations", according to Bernal, are a characteristic sign of irregular close packing.

Thus the use of mechanical models has proved extremely valuable in the investigation of a dense irregular structure. The absence of restrictions associated with regularity permits a large number of additional coordinations not characteristic of the crystal, and these configurations predominate. In this approach (for which there is justification) the structure of the short-range order of simple liquids is contrasted with the crystal structure.

2. Clusters with Minimum Energy

In the purely geometric approach to the determination of the structure of liquids, the role of inter-particle interaction and thermal motion is underestimated. In hard sphere models, the impenetrability of the spheres is equivalent to the introduction of repulsive forces (1), but forces of attraction are ignored. The more realistic Lennard-Jones and Morse potentials have been used to determine the optimum structure of clusters from a small number of interacting atoms. The configuration with the minimum potential energy U_{min} was found. For $N = 2$ there is one configuration. With increase in N there is an increase in not only the total number of configurations but also the number of relatively stable forms. Even for $N > 4$, the search for the spatial arrangement of the particles corresponding to the absolute minimum energy becomes difficult. Fig.7 shows the sequence of optimum figures for clusters containing up to 13 atoms[29].

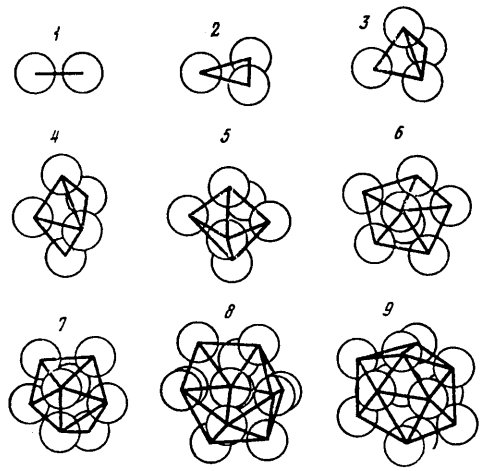


Figure 7. Sequence of small clusters with optimum shape: *1*) dimer (*2*), *2*) equilateral triangle (*3*), *3*) tetrahedron (*4*), *4*) twinned tetrahedra (*5*), *5*) octahedron (*6*), *6*) pentagonal bipyramid (*7*), *7*) bipyramid *6* brought up to eight atoms (*8*), *8*) bipyramid *6* brought up to 12 atoms (*12*), *9*) icosahedron (*13*); the number of atoms in the sequence is given in parentheses.

Most stable configurations are of the non-crystalline type, that is they cannot be elements of a regular lattice; they may, however, be present in an irregular structure of the liquid type. In this sense, the study of clusters with a free surface is also of interest for the investigation of the structure of liquids.

The use of modern fast computers makes it possible to increase the number of optimum figures to values $N > 13$. The examination of a given sequence of configurations is partly replaced by restricted or even free relaxation of the system. For example, a published algorithm[30] provides for the motion of each atom in the direction of the acting force in steps whose length is proportional to the magnitude of the force.

The initial configuration of the model of a cluster containing several tens of particles can be selected in accordance with the packing of tetrahedra[31], which determines the variety of forms of a cluster and its symmetry. In spite of the fact that the tetrahedron is an element of a regular (face-centred cubic) structure (together with the octahedron), it is impossible to fill an appreciable proportion of space by tetrahedra alone in compact form (without cavities). Twenty tetrahedra, combined in a convex compact figure (the centre of the figure is a common apex of the tetrahedra) form a

minimum of eleven pairs of non-contacting planes, giving gaps of different volume. If these gaps did not exist, that is if all the faces of the tetrahedra touched, an icosahedron would be obtained. For this to happen, however, it is necessary to deform the tetrahedra by reducing all the distances from the centre of the figure to its apices by a factor of ~1.048, leaving the distances between adjacent external angles unchanged.

It is assumed that atoms are situated at the centre of the figure and the apices (existing and assumed) through which a five-fold axis of symmetry passes. If this 13-atom cluster is allowed to change its configuration ($U \to U_{min}$), the result of relaxation will be an arrangement of atoms corresponding to an icosahedron. Seventeen tetrahedra, combined in definite fashion[31], after structural relaxation form a cluster of fourteen atoms with the symmetry of the tetrahedron (four three-fold axes of rotation). The same symmetry is shown by 26- and 38-atom clusters. A cluster formed by the packing of tetrahedra can also have the complete (33 atoms) and partial (45 atoms) symmetry of the dodecahedron, that is twelve five-fold axes of symmetry. High symmetry, however, does not guarantee an increased stability of the cluster. In a cluster containing $N < 50$ atoms, an arrangement of particles obtained from the packing of tetrahedra is more favourable than face-centred cubic or hexagonal close packing. The stability of clusters of large dimensions depends markedly on the form of the interaction potential responsible for the structural relaxation. The estimation of the equilibrium form of the cluster is made difficult by the fact that for short-range potentials (of the Lennard-Jones type), the main contribution to the energy is made by the first two layers of neighbours, and the difference in the contributions between the third and higher-lying layers is small.

The icosahedron is a structural formation with minimum energy among clusters of the same size (N). A cluster with icosahedral packing may have not only 13 atoms but also 55, 147, 309, 561, ... particles.. When the struture is optimised using a computer, icosahedral symmetry is apparently preserved in subsequent ($N > 561$) clusters for a long-range potential (of the Morse type). In the case of the Lennard-Jones potential, this symmetry may disappear. The symmetry of the icosahedron does not allow it to be the unit cell in a periodic lattice. The icosahedron is used as the basic structural unit in models of dense irregular extended phases such as amorphous metals[32].

In the construction of large clusters, the method of combination is sometimes used[33]. An example of a cluster constructed in this way is the 485-atom dodecahedron obtained by the structural relaxation of a 55-atom icosahedron surrounded by twenty 26-atom clusters with tetrahedral packing. Subsequent "additions" to the cluster brings its "size" up to 4000 atoms.

Increase in the size of the cluster is accompanied by a definite structural rearrangement, which wipes out the differences between its physical properties and those of an extended phase, determined by the high value of the ratio of the surface energies for the cluster and the volume. These differences concern chiefly the nature of the close packing of small groups (clusters) and the changes in their thermophysical properties. The particles of noble metals (dimensions 30–150 Å, that is $N \sim 10^4$–10^6) have been studied by electron microscopy and electron diffraction[34]. The clusters on nucleation had icosahedral packing, but subsequently their structure changed so that the electron diffraction pattern showed a similarity to the face-centred cubic structure. Metallic particles with shapes close to both icosahedral and dodecahedral were observed, possibly due to repeated twinning. The melting point and the Debye temperature for the small particles were lower than for the massive material[35]. The vibrations of the surface atoms in the cluster take place with a larger amplitude and a lower frequency than the vibrations of the atoms in the bulk. This is responsible for the change in the vibrational spectrum and the increase (relative to the massive specimen) in the heat capacity of the cluster.

Molecular-dynamic modelling of the structure of clusters of Ar, Kr, and Xe,[36] formed by 4, 7, and 16 layers of neighbours round a central atom (face-centred cubic lattice) established that in the smallest of these clusters (55 atoms), even at $T \cong 0.16$ m.p.* (m.p.* is the melting point of the cluster), a structural phase transformation takes place, leading to the structure of an icosahedron. Larger clusters (135 and 429 atoms), however, retained the face-centred structure as far as the melting point. The limiting size of a cluster with a structure having stable pentagonal symmetry is not yet known even for the simplest potentials, since this requires the determination of the free energy of a very large number of isomers.

3. Phase Transformations of the Fusion Type in the Hard Sphere Model

In the theory of the liquid state, the view has developed that the hard sphere model reflects the most important features of a dense irregular structure[37]. The chief advantage of the model is its simplicity: the spherical symmetry of the molecules, hard collisions, and free motion between collisions. In a system of hard spheres, the pressure p and the temperature T are proportional to the sum of the squares of the velocities of the spheres, averaged with respect to time or with respect to the ensemble, that is for a given density of packing, the ratio p/T remains constant for any finite values of the velocities. In other words, for the hard sphere model, all the isotherms on coordinates $p/T-V$ are equivalent.

The hard sphere model is widely used in the solution of the integral equations of statistical theory. Here, however, it either does not describe the phase transformation or predicts a disordering transition at densities not corresponding to the real densities. A phase transformation of the fusion type for the hard sphere model was detected in a computer experiment[38]. Computer calculations[39,40] showed that this transformation also exists for a two-dimensional model, that is for a hard disc model. Calculations for a cellular model of the crystal were carried out by the Monte Carlo method[41]. Identical cells filled compactly the space occupied by the particles. The centres of the cells coincided with the sites of the ideal crystal lattice. The cell represented a rhomboidal dodecahedron in the three-dimensional model, and an equilateral hexagon in the planar case. The condition of constant occupancy of the cells was used, that is it was assumed that in the motion of each particle, its centre did not go beyond the limit of the cell assigned to it. A break on the isotherm, indicating a phase transformation, is observed only when the region of the transformation is approached from the direction of the solid (see Fig.8). In the compression of a liquid consisting of hard spheres, a phase transformation was not observed either in computer calculations or when Pade's approximation[41] or Woodcock's equation[42] were used.

In a Monte Carlo experiment, Hoover and Ree[43] located a transition, which they interpreted as fusion, in a system of hard spheres by equating the chemical potentials of the liquid and crystalline phases (the line ab in Fig.8). The

sections of the isotherm *af* and *bc* correspond to metastable states: the supercompressed liquid and the stretched crystal. Table 2 gives the densities found in this way for the liquid and crystalline phases (their ratios to the density of close packing), the values of the pressure and the entropy changes on fusion, and also the corresponding values obtained in the self-consistent cellular model using a cluster expansion[44], and the experimental parameters of the fusion of argon[45] at $p = 1324$ MPa and $T = 295.7$ K. It is assumed that for these values of p and T, the Ar atoms can be described by hard spheres with diameter $\sigma = 3.405$ Å, that is compression leads to changes only in the distances between the atoms, and the size of the atoms themselves remains constant. Soft interaction between the atoms is replaced by hard interaction, and forces of attraction are neglected. It can be seen that the experimental values of $\Delta\rho$ and ΔS for Ar show much better agreement with those calculated by the Monte Carlo method than with those calculated using the self-consistent cellular model. The exponent of the repulsive potential[46] has a strong influence on the change in entropy, free energy (ΔF), and internal energy (ΔU) on fusion, but has little influence on the Lindemann fusion parameter. Thus with change in the exponent of the potential from 4 to ∞ (hard spheres), the values of ΔF increased by a factor of 2.5, whereas the value of $\langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle^{1/2}$ decreased by not more than 20%.

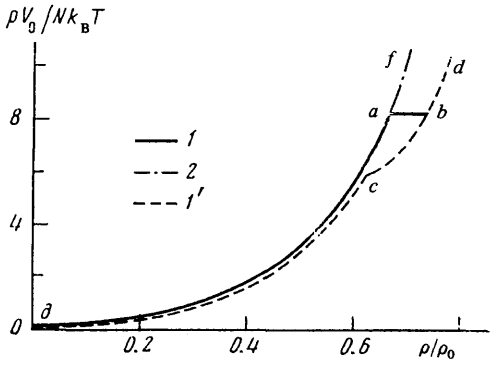


Figure 8. Isotherms for the liquid *ef* (*ec*) and the crystal *cd* in the hard sphere model: *1*) calculation by the Monte Carlo method[41] and using the Pade approximation[41]; *2'*) calculation using the equation of Ref. 42; *1'*) MC calculation in the cellular model[41], the line *ab* corresponds to equality of the chemical potentials of the liquid and solid phases; $V_0 = N\sigma^3\sqrt{2}/2$ is the volume of the close packing.

Table 2. Fusion parameters of hard sphere models and experimental fusion data for crystalline argon at a pressure of 1324 MPa.

Parameter	Monte Carlo method (Refs. 43, 46)	Self-consistent cellular model (Ref. 44)	Experiment (Ref. 45)
ρ_{cr}/ρ_0	0.736±0.003	0.747	0.851
ρ_l/ρ_0	0.667±0.003	0.650	0.805
$\Delta\rho/\rho_0$	0.069	0.097	0.046
pV_0/Nk_BT	8.27±0.13	8.84	9.05
$\Delta S/Nk_B$	1.16	1.77	1.05

The absence of attractive forces and soft interaction makes it possible to regard the disordering transformation in a system of hard spheres (or discs) from purely geometric viewpoints. This can be done most simply for the planar model (in the one-dimensional case, a transition of type I is not observed). In the computer modelling of a system of hard discs, a transformation of the fusion type takes place at the same density of packing as in the static model, when fusion is related[47] to the slipping of a number of discs relative to one another. The same mechanism of fusion is proposed for the three-dimensional model.

V. THE STUDY OF THE STRUCTURE OF A LIQUID BY MOLECULAR-DYNAMIC MODELLING

1. Molecular-Dynamic Modelling Using the Computer

Computer experiments by Monte Carlo (MC) and molecular dynamics (MD) methods have an important place in the study of condensed states of matter. The MC method is generally used to calculate the equilibrium (with averaging with respect to the assembly) properties of a substance, whereas the MD method (averaging carried out with respect to time) can also be used to determine kinetic characteristics (coefficient of self-diffusion, viscosity, thermal conductivity, etc.). Moreover, in the detailed study of the structure of a substance, the MD method has an undoubted advantage over the MC method, in that the configurations of the particles obtained with time are closer to the real values than those obtained by random rearranging of the particles. In this section, particular attention will be paid to the problem of a dense liquid and the crystal⇌liquid phase transformation, that is the range of states for which a theoretical description is difficult.

The MD method is based on the determination of the trajectories of the motion of the particles in the model by numerical integration of the equations of motion. The most widely encountered numerical methods for solving the equations of motion using a computer is the method of prediction and correction[18]. To obtain sufficient accuracy and a satisfactory speed of calculation, two iterations are usually carried out for the accelerations, momenta, and coordinates of the particles. The reliability of the results obtained is controlled from the value of the internal energy U, which should remain constant (in practice, a change in U by ~1% after 10000 time steps is permissible). The principal cell of the three-dimensional model is generally cubic, and contains from several tens to several hundreds (sometimes thousands) of particles. In the study of the properties of a liquid close to the crystallisation range, the number of particles N in the basic cell is selected in accordance with the number of sites of the lattice included in it, which reflects the average positions of the particles in the crystal. For the face-centred cubic lattice, it is assumed that $N = 4n^3$, where $n = 2, 3, 4, 5, 6, \ldots$, that is $N = 32, 108, 256, 500, 864$, etc. In the case of the body-centred cubic lattice, $N = 2n^3$. For the initial arrangement of the particles in the cell when modelling a liquid, either their random distribution or their arrangement at the sites of a given lattice is selected. The direction and magnitude of the initial velocity of the particles is given by a set of random numbers. The absolute values of the velocities for all the particles are corrected in accordance with the selected temperature.

The properties of the macroscopic phase are calculated by applying to the cell periodic boundary conditions to decrease the surface effects due to the small size of the system. By means of the periodic boundary conditions, the main cell is

surrounded by translationally symmetric images (at least 26 of the same cells). The constancy of the particles in the cell is preserved by the periodic boundary conditions; when a particle goes beyond the limits of the cell through one face, an anlogous particle appears in the cell through the opposite face. The interaction of the particles in the model of liquefied inert gases is more frequently described by an effective paired potential $\Phi(r)$ of the Lennard-Jones type. To keep the energy constant, the mutual penetration of the particles is restricted. Usually, the shortest distance r_{min} to which the particles can approach is selected from the condition: $\Phi(r_{min}) \cong 40k_B T_T$, where T_T is the temperature of the triple point. This gave the value $r_{min} \cong 0.822\sigma$ for argon[18].

At distances greater than ~2.5σ, the interaction between the particles becomes very weak, $\Phi(r)$ amounts to less than 2% of the depth of the potential well, and the direct calculation of the interaction energy is replaced by the introduction of a constant correction determined by the static environment. The correction for a liquid is calculated in the approximation of a uniform distribution of the particles of the periphery, and for a crystal the arrangement of the particles at the sites of an ideal lattice is adopted. The main inaccuracy in the modelling is due[18] to the lack of correspondence between the potential of the interaction between the particles, used in the calculations, and the potential describing the interaction in a real substance. For the Lennard-Jones potential, a time step $\Delta t = 10^{-14}$ s ensures the required accuracy of the calculation of the trajectories for the motion of the particles. For high values of Δt, strong overlap of the volumes of the particles is possible, leading to a change in energy in the system.

The evolution of a system takes place according to the laws of motion of classical mechanics. Usually, in a time interval corresponding to several hundred time steps, a distribution of the particle velocities close to the Maxwellian is established, and the internal energy of the system remains constant with time, that is, the system reaches internal equilibrium. From this moment it is possible to proceed to the calculation of the thermodynamic, structural, and also kinetic properties of the substance being modelled.

Fusion in the three-dimensional model of Lennard-Jones particles has been studied in considerable detail by many authors (see, for example, Refs.20, 48, 49). Similar melting points were established[20] for the MD model and in actual crystalline argon (m.p. $\cong$ 84 K, $p \cong 0.1$ MPa). The complex mechanism of fusion is still not fully understood, however. Analysis of the results of MD calculations from any single viewpoint not only does not clarify but sometimes on the contrary confuses the picture of the real phenomenon.

Cotterill and co-workers[48] studied the mechanism of disordering on the basis of the assumption that spontaneous formation of extended defect-dislocations takes place in the crystal. Although considerable progress has been made in this field (for example, the change in volume on fusion for Ar and Kr crystals was ~15%, in good agreement with the experimental data), nevertheless the dislocation interpretation of fusion must be approached with some care. The description of fusion in this approach is based exclusively on the properties of the ordered phase; the unique nature of the structure of the liquid is ignored. Melikhov and co-workers[49] studied the breakdown of a crystal† within the framework of the cluster model of a liquid. The clusters in the MD model were determined via a correlation function of the distances, which can be calculated in the approximation of the Frenkel mechanism of the motion of the atoms[6] in the solid and liquid phases. The mechanism, convenient for theoretical models, of the motion of the atoms in a liquid as vibrations about equilibrium positions and jumps into new equilibrium positions was not confirmed by MD modelling[20]. The conclusions reached[49] appear doubtful, however. Thus it is assumed[49] that fusion is due to the production of the nuclei of an irregular structure, and that the critical nucleus should contain one or two particles. The concept of "structure" (in its geometric sense) clearly has no meaning for such small "formations".

It has been shown[50,51] that the breakdown of the lattice of a face-centred cubic crystal is due primarily to displacements of the particles in a close-packed plane; a body-centred cubic crystal with a Lennard-Jones interaction of the particles is also unstable with respect to displacements in the most highly pupulated plane, which is the (110) plane (in contrast to the (111) plane for the face-centred cubic crystal).

2. The Crystallisation and Stability of a Supercooled Liquid

In recent years, considerable effort has been directed to the study of the crystallisation of a supercooled liquid by MD modelling. Rahman and co-workers[52-55] studied processes of vitrification and crystallisation in Lennard-Jones systems. The vitreous state of argon was obtained[52] in a system of 500 particles, and the transition to the glass was studied in more detail for a system of 108 particles. The radial distribution function $g(r)$ of vitreous argon (see Fig.9) has a clearly defined double peak with maxima at $r/\sigma \cong \sqrt{3}$ and 2, indicating random close packing of the particles in the system. A simple explanation has been proposed[56] for the production of these peaks, using the concepts of contacts between hard spheres. Thus the peak at $r/\sigma \cong 2$ is due to contacts between spheres with a gap which does not allow them to approach more closely. The peak at $r/\sigma \cong \sqrt{3}$ is observed for the contacts of four hard spheres when the two equilateral triangles which they form have a common edge, around which they are able to rotate through an angle which defines the blurring of the peak. Close to the triple point for a face-centred cubic crystal or argon, the maxima of the second and third peaks of $g(r)$ correspond to values $r/\sigma \cong 1.6$ and 2, and for the liquid, $g(r)$ has a second peak which is not split, with a maximum at $r/\sigma \cong 2$. The splitting of the second peak of $g(r)$ on the vitrification of argon (broken line in Fig.9) begins at $T \cong 50$ K ($p = 8.6$ MPa).

In spite of the satisfactory approximation of the RDF of vitreous argon within two coordination spheres by the function $g(r)$ for a body-centred cubic crystal with Lennard-Jones interaction of the particles, the microstructures of these states are different[57]. The shear viscosity of vitreous argon[52], determined from the Einstein–Stokes relationship (via the calculated coefficient of self-diffusion $D = 10^{-9}$ cm^2 s^{-1}) is ~100 Pa.s. This value is ~37 times the viscosity of liquid argon close to the triple point.

The crystallisation process has been studied[53-55] for systems of 108, 256, and 500 Lennard-Jones particles. From the value of $S(k)$ at different points in the space occupied by the particles, it was found that the critical nucleus should contain ~40–70 particles. The type of nucleating strongly-defect crystal structure depends on the nature of the interaction between the particles. In a model of 500 particles of supercooled rubidium (shielding by electrons was taken into account in the potential), the transition to a body-centred cubic crystal was detected[55]. After crystallisation, the

†In fact, Melikhov and co-workers[49] studied not the fusion but the spinodal breakdown of an argon crystal superheated by a factor of 2.86 relative to the melting point ($p \cong 105$ MPa).

potential for rubidium was replaced by a short-range potential (only the repulsive branch of the potential for rubidium, the Lennard-Jones potential, and its repulsive part were used), as a result of which the structure relaxed into the face-centred cubic lattice.

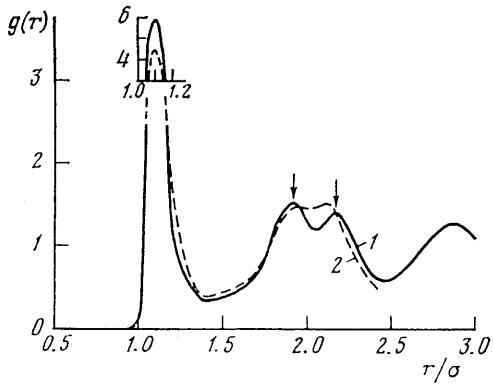


Figure 9. Radial distribution function of vitreous argon, obtained in the MD model: *1)* $T = 12.9$ K, $\rho = 1.596$ g cm^{-3},[52] the arrows indicate the positions of the two maxima of the split peak at $r/\sigma = 1.93$ and 2.16; *2)* $T = 48.8$ K, $\rho = 1.667$ g cm^{-3}.[57]

The actual identification of the crystalline nucleus presents considerable difficulty in the MD experiment. It has been suggested[58] that in MD modelling, the following factors have a decisive influence on the production of a regular structure: 1) the error of the method of integrating the equations of motion; 2) the rounding-off error of the computer calculation; and 3) the periodic boundary conditions. In the MD models, however, crystallisation was observed for different (including short-range) potentials of intermolecular interaction, so that the errors in the integration and the application of the periodic boundary conditions can hardly play a decisive role, since these errors have a smaller order of smallness than the perturbations associated with a change in the potential.

The computer experiments[53–55] may have detected not genuine crystallisation but a preceding stage of heterogeneous fluctuations in the supercooled system in which an ensemble of prenucleation formations is produced and relaxes to the stationary state.

Schneider and co-workers[59] proposed to study the possibility of another mechanism of crystallisation. It is assumed that a supercooled liquid may be unstable with respect to perturbations of the density, taking place throughout the volume of the liquid and having a wavelength of the order of the interatomic distances. Schneider's hypothesis was verified[60,61] in a study of a Lennard-Jones liquid with respect to external time-independent perturbations. In both the planar[60] and the three-dimensional[61] cases, when a periodic perturbing potential was applied, ordering of the particles in the model was obtained. As soon as the potential was removed, however, the system returned to the internal-equilibrium liquid state.

The response of a system to an external perturbation is closely related to the fluctuations in the density, taking place in the system itself (fluctuation–dissociation theorem). Thus the reaction of a system to external perturbations can be found via the calculated spectrum of the density fluctuations. A criterion of the thermodynamic stability of the isotropic phase (in the long-wave limit) is the fulfilment of the inequality[62,63]:

$$T/C_p > 0, \quad -(\partial p/\partial V)_T = (V\beta_T)^{-1} > 0$$

According to Schneider[59], in the static case the system will be stable with respect to perturbations of arbitrary wavelength with the condition

$$\beta_T^{-1}(\mathbf{k}) = \rho k_B T/S(\mathbf{k}) > 0 \qquad (5)$$

Here, $\beta_T(\mathbf{k})$ is the isothermal response function for a time-independent perturbation.

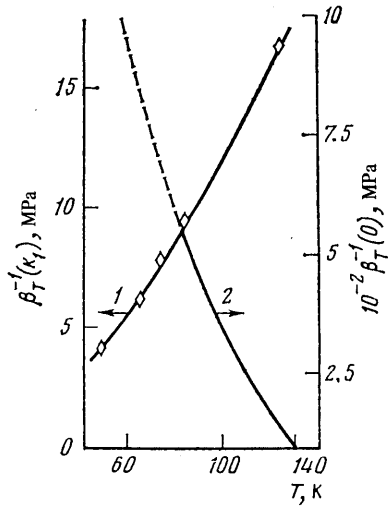


Figure 10. Elasticity of the liquid with respect to long-wave ($\beta_T^{-1}(0) \equiv \beta_T^{-1}$) and short-wave [$\beta_T^{-1}(k_1)$] perturbations: *1)* result of molecular-dynamic calculation[22], *2)* experiment[64]; the broken line corresponds to the extrapolation of the experimental data.

The elasticity of a simple liquid towards short-wave perturbations decreases with decrease in temperature, whereas the thermodynamic (long-wave) elasticity increases (see Fig. 10).[22] In the temperature range studied (with a deep descent into the metastable range), condition (5) is fulfilled both for $k = 0$ and for $k = k_1$. The increase in the mechanical stability to long-wave perturbations ($\beta_T^{-1}(0)$ increases), together with the fulfilment of the thermal stability condition $T/C_p > 0$,[21] indicates the absence of a boundary of appreciable instability (spinodal for the supercooled liquid). Attention was first drawn to this fact by Skripov and Baidakov[65]. The essential feature of this statement is that if the treatment is restricted to an examination of small (continuous) perturbations of the type of fluctuations in the density and energy, the liquid retains its internal stability to as low a temperature as desired. In a real experiment, breakdown of stability may take place as a result of the spontaneous production of a crystalline nucleus (a perturbation of special form) or as a consequence of dynamic instability.

To detect the dynamic (phonon) instability of a liquid, it is necessary to determine the temperature dependence of the dynamic structure factor $S(k, \omega)$ in the deep descent to the range of metastable states. If with change in the thermodynamic state of a system the complex frequency of any collective vibration decreases to zero (soft mode), the system approaches the limit of stability[66]. The frequency of the collective mode Γ_c [half-width $S(k, \omega)$], determined in the MD model of argon[22], decreases more rapidly with temperature than Γ_c calculated in the central field approximation[67] or the generalised Pathak–Singwi approximation[68] (Fig.11). The explicit form of the $\Gamma_c(T)$ relationship was obtained in the form of a polynomial of second degree on treatment of the results of the MD calculation by the least-squares method

$$\Gamma_c(T) = -2.36 + 0.045T - 0.00012T^2 \qquad (6)$$

(in units of 10^{12} s^{-1}). The $\Gamma_c(T)$ relationship in the form of Eqn.(6) is given by the broken line in Fig.11. At $T \cong 64$ K, the polynomial in Eqn.(6) becomes zero. This result, however, apparently cannot be interpreted as the attainment of the limit of dynamic stability of the simple liquid ($k \cong k_1$). At low temperatures ($T < 65$ K for Ar), vitrification of the supercooled liquid takes place, accompanied by a marked increase in the relaxation time. This leads to a no less marked decrease in the half-width of the first (quasi-elastic) peak for $S(k, \omega)$, compared with that for the change to crystalline order. The instability of the liquid can be judged from the decrease in Γ_c when it is certain that the decrease in Γ_c is not due to some other factor.

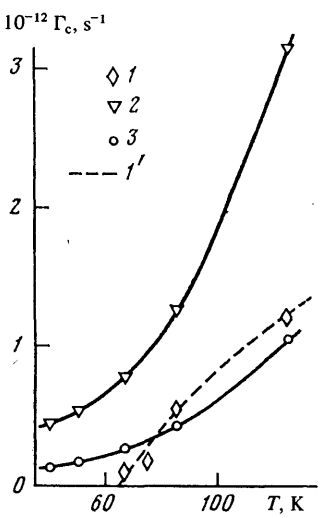


Figure 11. Temperature dependence of the frequency of the collective mode Γ_c: *1*) data from a computer experiment[22], *1'*) result of the approximation of $\Gamma_c(T)$ by the polynomial *6*; *2*) central field approximation[67]; *3*) Pathak–Singwi approximation[68].

The above examination was restricted to simple liquids. For substances with complex molecules, in the description of the structure of the condensed phases, it is necessary to take into account the orientational effects and internal degrees of freedom. The latter influence the "external" dynamics of the system as a consequence of the exchange of energy between different degrees of freedom[69].

3. The Method of Statistical Geometry (Developed for the Computer)

Statistical geometry involves the analysis of the geometric elements characterising the packing of the atoms, based on the construction of Voronoi polyhedra (the Dirichlet region) or Delaunay tetrahedra. The definition and method of construction of the Voronoi polyhedra (VP) were given above in the description of Bernal's mechanical models. Another method of breaking down the space occupied by the particles is associated with the name of Delaunay and is based on the construction of irregular tetrahedra (IT) or, more accurately, triangular pyramids. The method used by Bernal to study the structure of simple liquids by examining the shapes of the cavities formed by the particles reduces to the Delaunay-tetrahedra method. The apices of the IT coincide with the centres of four closely situated particles. For the case of the packing of hard spheres, the IT combines both spheres in direct contact with one another and spheres separated by a small gap (see Fig.12). The section connecting the centres of two spheres in contact is called an edge of the IT,[70] and the section connecting spheres not in contact is called a diagonal of the IT. Each additional particle placed inside the IT leads to the appearance of four smaller IT. For an ensemble of randomly close-packed hard spheres of equal size, the probability of the appearance of a new edge of the IT is 3/4, and that for a diagonal is 1/4. Any IT can be represented by a Delaunay diagram, which describes the nature of the contact between the particles forming it. For a random arrangement of the particles, it is possible to calculate the frequency of the appearance of a given type of IT.

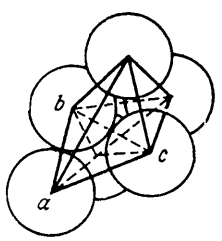


Figure 12. Delaunay tetrahedra for the packing of hard spheres: *ab*—edge of the IT, *ac*—diagonal of the IT.

This method of examination is convenient for the description of the packing of particles of different size, since the distance between the particles is itself an object of statistical analysis. For the study of the regular features of the packing of particles of equal size, however, the method based on the construction of the VP has been more widely used. The methods of describing the structure of the packing of particles on the basis of the VP and the IT are closely related. Thus the number of faces of the VP is determined by the sum of all edges and diagonals passing through an apex "common" to a group of IT (with allowance for all

acceptable versions of the breakdown of space into IT). In a structural analysis using the computer, the VP method is more convenient than the IT method, in that it relates to one definite particle and characterises its environment; the VP carries information on the number and relative arrangement of the nearest geometric neighbours.

Various exact and approximate methods for the computer construction of the VP exist[71-75]. The method proposed by Galashev[75] can be described as follows. The configuration of the system of particles, obtained in the MD experiment for a given step, was known; VP were constructed around the centres of individual particles in the model. Intersecting planes were constructed for the particle environment selected round the centre being considered. From the centre O, a sphere of radius OM was drawn at half the distance to the nearest neighbour; ~200 points were arranged uniformly over the sphere. The points M_c at which the rays, starting at the centre, which had passed through the points arranged on the sphere, meet the set of intersecting planes were then found (see Fig.13). The planes nearest the centre formed the VP. The number of points used ensured that account was taken of all the faces and edges of the VP with area $s > 0.01\bar{s}$ and length $l > 0.1\bar{l}$ respectively, where $\bar{s}$ is the average area of a face, and $\bar{l}$ the average length of an edge of the VP. The accuracy of the construction of the VP can be made as high as desired, by increasing the number of reference points (nodes of the net).

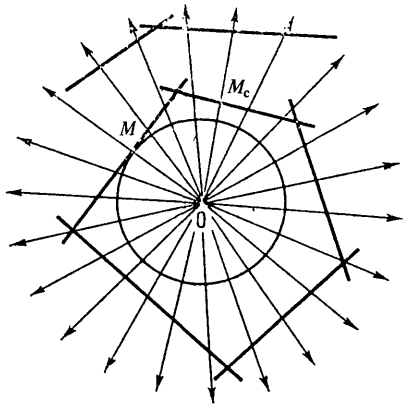


Figure 13. Construction of the VP and its faces by an approximate method[75] (projection of three-dimensional specimens on a plane): *OM* is the radius of a sphere equal to half the distance to the nearest neighbour; the straight lines represent planes passing at right angles through the centres of sections joining the central particle *O* to its neighbours; the arrows leaving the point *O* are the rays; M_c represents the points where the rays meet the planes. The construction used to determine the faces of the VP has a similar form.

The study of the structure of a simple liquid by the method of statistical geometry using a computer led to the discovery of a number of interesting regular features. Thus Rahman[19] established that the average number of geometric neighbours (or the number of faces in the polyhedra) in a simple liquid increases according to a linear law with change in the order of the layer of neighbours from one to five. The magnitude of the calculated average displacement vector, determined as the sum of the vectors drawn from the centre to the apices of the VP, coincides with that of the displacement of the central particle in a time of $\sim 5 \times 10^{-13}$ s. Finney[76] studied the types of VP encountered for a simple liquid in the mechanical hard sphere model and for modelling by the MC method[10]. The predominant VP in the liquid had a relatively simple form, containing, for example, only four-, five-, and six-sided faces.

Statistical geometry was recently used to study the nucleation of a crystalline phase. The states were identified beforehand from the topological characteristics of the VP. The configurations of 108 and 500 particles, averaged over a time interval of 5×10^{-13} s, were analysed[77]. For the model of a liquid with only repulsive interaction (exponent 12), the number of VP having a set of four-, five-, and six-sided faces for a total number of faces of 13 or 14 reached ~5% of the total number of VP (see Fig.14). Fig.14 also shows that for a supercooled liquid the picture is almost identical, although the number of definite groups of 13- or 14-faced VP having only four-, five-, and six-sided faces is close to 10%. In a face-centred cubic crystal, the fraction of characteristic types of VP amounted to up to 20%. For the body-centred cubic crystal, more than 90% of all the VP belong to the class of the cubo-octahedron. The difference in the number of VP of characteristic type for regular packing is due to the fact that the cubo-octahedron (see Fig.6*c'*) is stable with respect to thermal vibrations of the particles, whereas the rhomboidal dodecahedron (Fig.6*b'*) is completely unstable to these displacements[55].

The initial stage of crystallisation has been studied. In a supercooled liquid, discrete "nuclei" combining several particles were detected; the VP of these groups belonged to the class of the cubo-octahedron. With the passage of time, the nuclei grew to form a large particle of irregular shape, containing several tens of atoms with a distorted body-centred cubic structure. When uniform compression of the system was applied along a definite axis[78] (the degree of compression was varied from 0.90 to 0.71), structural relaxation to the face-centred cubic structure took place in it after ~2000 time steps. Hsu and Rahman[55,79] consider, on the basis of the MD experiment carried out, that the crystallisation of liquid argon begins with the simultaneous formation of face-centred cubic and hexagonal close-packed structures, whereas for rubidium the body-centred cubic lattice is formed.

Up to the present, only the positive features of the method of structural analysis based on the VP have been noted. This method, however, has a serious disadvantage. The statistics (frequencies of appearance) of the faces and edges of the VP are essentially topological, and not metric characteristics. It is therefore sometimes difficult to interpret the results of the analysis of the VP. Thus the distortions of the VP brought about by the thermal vibrations of the particles do not make it possible to identify the face-centred cubic structure reliably. Finney and Wallace[80] studied the structure of non-crystalline close packing using a characteristic which is very sensitive to both topological and metric changes—the correlation function for the cavities formed by the particles. They examined two types of cavity[80], a distorted tetrahedron and a distorted octahedron, and concluded that other types of Bernal cavity are rarely encountered in systems with soft interaction, because of the existence of a relatively large (compared with the packing of hard spheres) free volume corresponding to one particle.

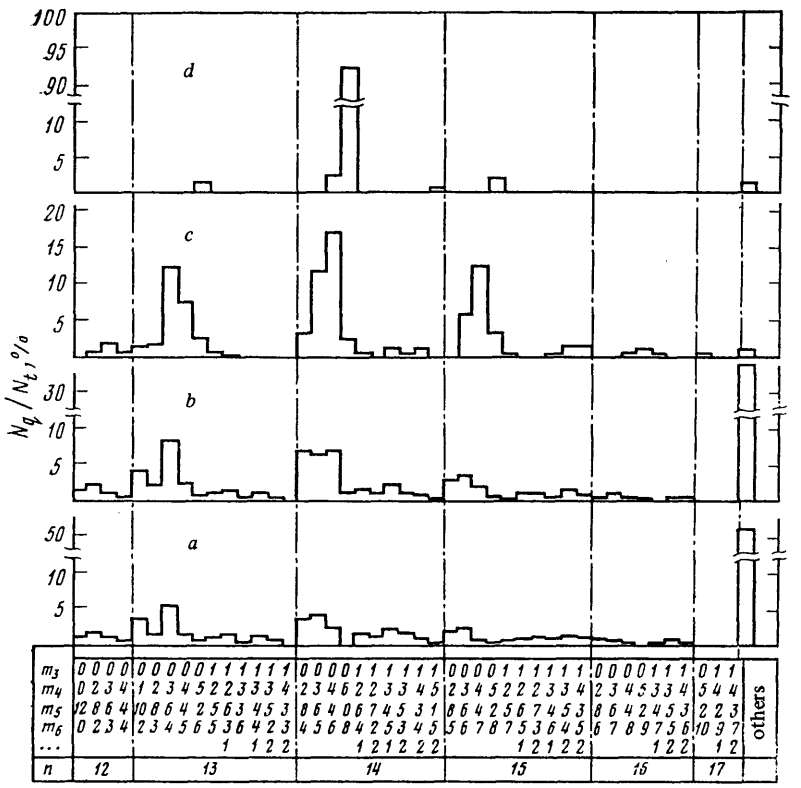


Figure 14. Distribution of the types of VP encountered in the MD models of systems with purely repulsion interaction of the particles[77]; $\Sigma m_i = n$, m_i is the number of i-sided faces in the VP with n faces; N_q/N_t is the relative number of VP containing n faces with i sides; *a*) equilibrium liquid (T = 96.2 K, ρ = 1.511 g cm^{-3}); *b*) supercooled liquid (T = 52.9 K, ρ = 1.847 g cm^{-3}); *c*) face-centred cubic crystal (T = 57.7 K, ρ = 2.099 g cm^{-3}); *d*) body-centred cubic crystal (T = 56.2 K, ρ = 2.099 g cm^{-3}); the values of T and ρ, given in brackets, were calculated for the parameters of the interaction potential σ and ε corresponding to argon.

4. The Structures of the Short-Range Order of the Crystal and the Liquid (the Argon Model)

The short-range coordination of atoms in a liquid has been established from experiments on the diffraction of electrons, neutrons, and X-rays. This coordination does not reduce to crystalline coordination, and is produced by a much larger set of configurations of neighbours. The studies of Bernal, devoted to the investigation of the variety of structures in simple liquids, were discussed above. At the present time, in addition to the alternative approach[7,24], ordering in a liquid is still being interpreted as quasi-crystalline. Use is made, for example, of the models of blurred lattices[81] and floating microcrystallites[82], cluster models in the form of sets of body-centred cubic and face-centred cubic structures[83], etc. The view[84], based on the concept of the quasi-crystallinity of a liquid, that polymorphism exists in liquid metals, is widely encountered. These views are based on an *a priori* under-estimation of the difference between the liquid and the crystal.

From a geometric analysis of mechanical models of irregular packing, Bernal concluded that the most important characteristic of the structure of a simple liquid, distinguishing it from a crystal, is related to the existence of a five-fold rotational axis of symmetry. In fact, pentagonal faces are frequently encountered in the VP of irregular random packing. To confirm this important characteristic of the structure for more reliable models, it is necessary to find for them the distribution of the faces of the VP with respect to the number of sides. Calculations carried out by the MC [10] and MD [19] methods in fact detected a predominance of pentagonal faces in the Voronoi polyhedra for a liquid. It would appear that an essential feature of the structure of a liquid had been reliably determined, but computer calculations[10] raised some doubt about this. The fact is that pentagonal faces are most frequently encountered in the VP not only for instantaneous configurations of the liquid, but also for the crystal. The factor leading to the predominance of five-fold symmetry in both disordered and regular structures has still to be determined. It is natural to relate it to the thermal motion of the atoms. Five-fold symmetry, inadequate for the crystal, can be avoided by changing from an analysis of instantaneous configurations of the particles to an examination of configurations averaged with respect to time.

This method of averaging for a crystal with a large atom settling time is quite acceptable, and gives a positive result. The elements of five-fold symmetry disappear for an averaging time $\tau \gg \tau_0$, where τ_0 is the period of the vibrational motion of the atoms. In a liquid, however, in contrast to a crystal, there are no equilibrium positions of vibrational

motion of the atoms. With developed translational motion of the atoms, averaging over a large time interval may lead to an unnatural configuration with marked overlap of the particles#. This can be avoided by decreasing the averaging time interval, but there is no guarantee that this procedure corresponds to the desired goal.

Averaging with respect to a short time interval was also carried out for the configurations of particles obtained in the MD model of a liquid[77]. The averaging time[77] was 5×10^{-13} s for a time step $\Delta t = 10^{-14}$ s. Displacement of the particles of the immediate environment in a liquid cannot take place in this short time interval. The particles are displaced on the average a distance $r \leqslant 0.1\sigma$. The time of 5×10^{-13} s is close to the average period of the vibrational motion of the atom in a liquid, so that the configurations of the particles, averaged over this time interval, should not differ greatly from the instantaneous configuration§.

Thus in the study of the structure of an equilibrium liquid, direct averaging with respect to time is not effective. To obtain structural characteristics which show little sensitivity to thermal fluctuations, another method of analysis using VP was proposed independently[55,96]. In a study of the crystallisation of supercooled argon, to record the face-centred cubic structure more accurately, small edges ($l \leqslant 0.3\sigma$) in the VP were excluded[55].

To establish the differences in the arrangement of the nearest neighbours in a simple liquid and a crystal, the small faces and edges in the VP were excluded[86]. The application of this procedure to the VP for crystalline argon brings the n- and m-distributions closer to the results obtained by averaging with respect to time. This indicates the physical justification (acceptability) of the procedure involving the rejection of the small edges and faces. The n- and m-spectra of liquid and crystalline argon, constructed after excluding the small geometric elements (see Figs.15 and 16), differ considerably. Thus the difference between the dispersions of the n- and m-distributions of the liquid and the crystal increased by average factors of 2.5 and 3.5 respectively. The proportion of pentagonal faces in the VP for the liquid remained high, whereas for the crystal it decreased considerably. After excluding the faces with $s \leq 0.2\bar{s}$ and the edges with $l \leq 0.4\bar{l}$, four-sided faces predominate in both the crystal and the liquid. The ratio of the numbers of five- and four-sided faces was 0.81 in the liquid, however, whereas for the crystal it was 0.14.

If the system is compressed and cooled rapidly, the vitreous state of the element is produced in the MD model[52,57]. In this case the particles undergo only vibrational motion about the irregular equilibrium positions, and in the structural analysis it is possible to study the configurations of the particles averaged with respect to time. A comparison of the configurations, averaged with respect to time, of regular and irregular face-centred cubic and body-centred cubic structures has been carried out[57]. The n- and m-distributions for these configurations, shown in Fig.17, were obtained with an averaging time $\tau \cong 8 \times 10^{-11}$ s and 3×10^{-11} s for vitreous argon and the ordered structures respectively. The differences in the spectra are obvious. The dispersion of the n-distribution for the irregular structure is 6.5 times that for the face-centred cubic structure. Pentagonal faces predominate in the m-distribution of vitreous argon. Four-sided faces predominate in the face-centred cubic crystal, and hexagonal faces in the body-centred cubic crystal. The structure of vitreous argon was found to be non-uniform. Its spatial non-uniformity is reflected by the VP, shown in Fig.18. The shape and size of the Voronoi polyhedron characterising the intermediate "structural granule" (Fig.18*b*) are close to those of the most probable VP for an equilibrium liquid at the melting point; the differences between their volumes and surface areas are very small (~0.7% and 2.2% respectively). The intermediate configuration has a distorted structure, and its dimensions are smaller than those of the critical crystalline nucleus, which contains ~50 particles[53].

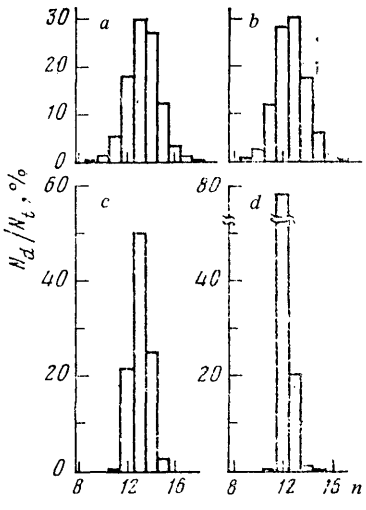


Figure 15. Distribution of VP with respect to the number of faces before (left) and after exclusion of the faces with area $s \leqslant 0.2\bar{s}$ [86] (*a*, *b*—spectra of liquid argon at 83.7 K; *c*, *d*—crystalline argon at 81.1 K); N_d/N_t is the relative number of VP with a definite number of faces.

Yet another method for determining the structural differences in the short-range order of a liquid and a crystal has been proposed[87]. This version of the structural analysis involves not the direct comparison of the packing

#In the case of liquid argon, the averaging time should be shorter than the time $\tau_\sigma = 1 \times 10^{-11}$ s, after which the particle is displaced on the average through a distance σ.

§The results of an analysis of VP constructed for the instantaneous configurations of the particles of the MD model of liquid Al at the melting point and with superheating by ~200 K have been interpreted[85] as confirming the possibility of structural transformations in the melt, analogous to the transformations in the solid phase. The face-centred cubic and body-centred cubic phases were detected in the melt[85] only from the topological characteristics of the VP, but the dimensional (metric) characteristics of the VP were not examined. This method of identifying the structure is not unambiguous[55]. Even if it is assumed that the proportions of VP of the face-centred cubic and body-centred cubic types have been determined correctly, it can still hardly be concluded that a structural transformation takes place in the melt, since the number of VP of these types is small (reaching ~5%).

of particles in a liquid and a crystal, but an intermediary—an ideal crystal lattice corresponding to an average density $\rho = N/V$. The essential feature of the method is the mapping of the particles in the model on to the sites of this lattice. The number of sites is greater than the number of particles mapped on to them. The lattice penetrates the sphere distinguished in the basic MD cell. The sphere is drawn around one of the particles selected randomly in the calculation. For the liquid, this procedure is repeated after every 50 time steps ($\Delta t = 10^{-14}$ s); the total calculation time is 5×10^{-12} s. In the case of the crystal, one configuration of the particles was analysed. The volume of the sphere contained the particles of the first two coordination spheres in the liquid (an average of 57 particles), and three in the crystal (43 particles). The central particle was superimposed on a site of the lattice; for the other particles present in the sphere, the distances to the nearest sites of the lattice were determined. With this correspondence between the particles and the lattice sites, two or even three particles of the liquid were assigned to some of the sites.

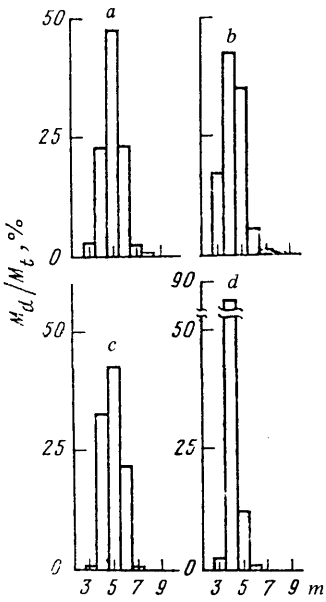


Figure 16. Distribution of the faces of the VP with respect to the number of faces without restriction on l and s (left) and with the exclusion of edges with $l \leq 0.4\bar{l}$ and rejection of faces with $s \leq 0.2\bar{s}$;[86] *a–d*) see Fig. 15; M_d/M_t is the relative number of faces with a definite number of sides.

Another method of mapping involves searching for the nearest unoccupied site for each particle. In this case a one-to-one correspondence was achieved between the particles and the lattice sites. The configurations of the particles averaged over time intervals of 5×10^{-13} s for the liquid and 10^{-11} s for the crystal were analysed. The results of the mapping of the particles on to the sites of a face-centred cubic lattice are shown in Fig. 19 (N_r/N_t denotes the relative number of particles situated at a distance Δr from the lattice sites, and d the distance between nearest neighbours in the ideal face-centred cubic lattice). For a liquid, two distributions with respect to the distances from the lattice sites are obtained, depending on the method of mapping. For a crystal there is only one distribution, independent of the method of mapping. The distribution for the liquid, corresponding to one-to-one mapping, extends as far as distances greater than d. The proportion of particles which for the transformation to a regular structure must be moved through distances greater than d is ~0.7%. This means that it is impossible to obtain the crystal from the liquid only by local displacements of the atoms. In exactly the same way it is impossible to obtain the liquid from the crystal by random small displacements of the particles from the lattice sites (blurred lattices). An appreciable proportion of the atoms in these transitions are displaced through a distance of the order of the interatomic distance.

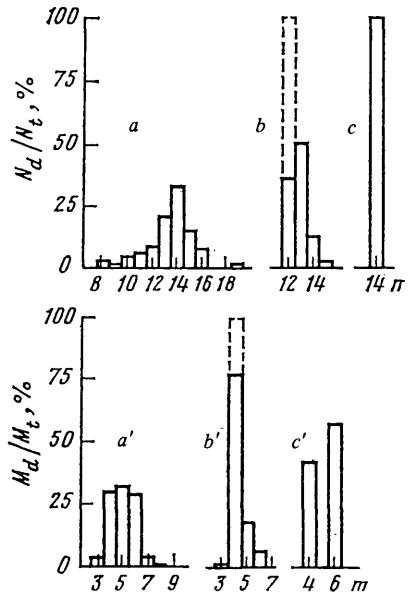


Figure 17. Distribution with respect to the number of faces of the VP and of faces with respect to the number of edges[57]: *a,a'*) vitreous argon at 48.8 K; *b,b'*) face-centred cubic crystal at 41.4 K; *c,c'*) body-centred cubic crystal at 48.4 K; Broken line—ideal face-centred cubic lattice.

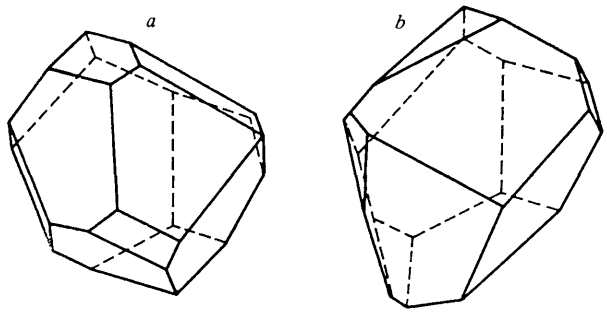


Figure 18. Voronoi polyhedra for the averaged configuration of vitreous argon[57]: *a*) for one of the particles of the uniform part of the volume; *b*) for a particle in the region of the "structural granule".

The results[57,86,87] obtained by the MD method do not confirm the quasi-crystallinity concept in the theory of the liquid state. This is also indicated by the experimentally observed avalanche-like character of the phenomenon of crystallisation and the extensive supercooling of liquids. The structure of the short-range order is different for a liquid and for a crystal. For the production of a crystal-like nucleus in a liquid, "continuous" local rearrangement of the atoms of the immediate environment of the uniform deformation type is insufficient. The conclusion from the study of random packing that five-fold symmetry plays a significant role is confirmed. When this symmetry is present, a regular crystal cannot be constructed.

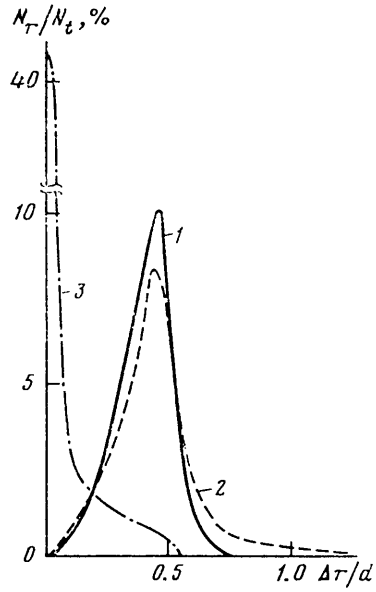


Figure 19. Radial distributions of the particles of a liquid (*1*, *2*) and a crystal (*3*) relative to the ideal face-centred cubic lattice[87]: *1*) with the possibility of repeated action of the lattice sites; *2*) for one-to-one correspondence between the particles and the lattice sites.

VI. SUMMARY

There is as yet no exhaustive answer to the question of how a liquid is constructed. The efforts of research workers are revealing new knowledge, refining old ideas, and developing an overall picture.

A liquid, as a dense irregular structure, is more unique than assumed by quasi-crystalline representations. It is characterised by more numerous and "free" local configurations than an ordered regular structure. The high mobility of the particles and the presence of small groups of particles (with a local density exceeding the crystalline density) create favourable conditions for the exchange of energy and molecular rearrangements.

Attention has been drawn[88] to the structural aspect of chemical transformations in a condensed phase. The principal restriction on the reaction rate is seen in the deficit of free volume for the reacting atoms, and their low mobility. The value of the activation energy in this sense can be regarded as "generalised" and it is not always an exact indicator of the structural-dynamic restrictions in chemical kinetics. The variety of packings of the particles in a liquid is revealed in the excess entropy of the state compared with the crystal. An adequate theory of the elementary chemical act must be constructed with allowance for the local structural-dynamic characteristics of the liquid.

New and interesting facts have been observed in the study of the kinetics of chemical transformations at low temperatures[89]. The reaction rate in the liquid phase decreases with decrease in temperature. When the solution is frozen, however, in some cases it begins to increase very strongly, reaches a maximum, and decreases again on further cooling of the system. This behaviour is not exceptional; it is observed for many reactions involving substitution, decomposition, oxidation, and polymerisation[89]. A significant role in the kinetics of a transformation is apparently played by the phase non-uniformity of multi-component systems. Because of this, conditions are created for the high mobility of groups of particles. The high mobility has been related[89] to the existence of local liquid-like regions ("liquid microphase") in the heterogeneous frozen system. The new facts necessitate a detailed analysis of the structural-dynamic causes of the "anomalous" chemical behaviour of solutions in the region of the heterogeneity and the phase transformation. The state of the supercooled liquid permits a large number of local rearrangements of the particles in a large number of configurations of the non-crystalline type. Decrease in temperature most frequently leads of the production of very compact formations of several molecules, facilitating chemical reaction.

The structure of simple liquids exhibits a certain universality. This is reflected in the existence of thermodynamic similarity in the properties of substances in the liquid state. The marked difference in various properties of metallic and non-metallic liquids is due chiefly to the influence of the electronic sub-system.

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