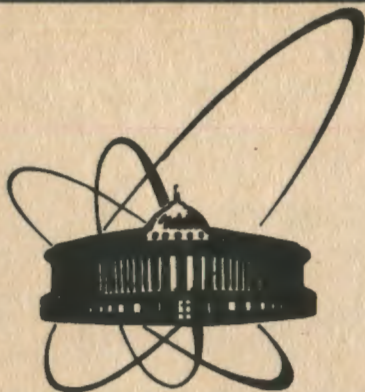


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**ОБЪЕДИНЕННЫЙ  
ИНСТИТУТ  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
ДУБНА**

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**CONSTRUCTION OF THE CONDENSED STATE MODEL.  
CALCULATION OF THERMODYNAMIC PROPERTIES  
OF THE MATTER WITHIN THIS MODEL**

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## 1. INTRODUCTION

Reliable information on thermodynamic properties of various matters used in industry is the basis for developing a more elaborate equipment in chemical and oil industry, mechanical engineering, energetics and others. Moreover, developing and promoting of efficient methods of mathematical simulating and systems of automatic design of different processes increase the necessity of using computer programs for calculations. As a source of information on thermodynamic properties not the tables obtained from experimental and calculational studies are used with increased frequency but the computer programs providing calculations with high accuracy and minimal computer time consuming. The computer program realises an algorithm based on a certain mathematical model describing the laws of behaviour of real matters and their mixtures in a one-phase state and in the region of phase transitions liquid-solid state.

Modern status of the statistical physics opens new possibilities for choosing various approaches in simulating the matter state. However, it is obvious that, for instance, the method based on the solution of an integral equation for the radial distribution function with a subsequent derivation of the state equation is inapplicable due to large computer time consuming. Almost all the available approaches do not admit a consistent description of the liquid-solid state phase transition. To a great extent the problem is complicated in making an attempt to simulate an interaction of nonspherical molecules.

To simulate a condensed state the most universal are thought to be the Monte-Carlo and molecular dynamics methods. They enable one to achieve a qualitative description of all specific features of a phase diagram. Here, one can consistently simulate the interaction of various molecules (of water, polymers, etc.) in various state regions. In particular, the state equation can be calculated in the region of liquid-solid state phase transition in the binary system and is considered in Sec.1.

In simulating mixtures of any molecules the methods of computer simulation have no basic limitations. However, their direct application in practice is hardly possible due to a large computer-time consuming.

At the same time, there are a great many empirical and semiempirical state equations approximating sets of trial data

for various state branches. Equations of the van der Waals-type and the virial equation underlie these approximations. Therefore, they offer certain extrapolation possibilities. However, these models fail to describe the behaviour of the matter in the region of the liquid-solid state phase transition since in the mathematical structure the transition is not taken into account by any means. Introduction of additional terms into the state equation in order to describe one more van der Waals loop for the  $p = p(V, T)$  dependence is not justified. As is shown in ref. <sup>1)</sup>, one can hardly expect any progress in calculating the phase transition parameters in the case when each phase is described by its equation allowing for only one class of configurations: crystalline and liquid. More sensible is a simultaneous inclusion of various states on the basis of a unique equation. However, one cannot advance along this line without a clear differentiation of configurations defining condensed states. Unfortunately, there is no universally accepted criterion to make a constraint. In ref. <sup>1)</sup> a possible separation of the classes of states is demonstrated using the distribution function in the energy space where this distinction amounts to several per cent. Therefore, it becomes clear why this division is impossible on the basis of the radial function in the coordinate space where it is one order of magnitude less (in defining the position of the basic maximum).

In calculating thermodynamic properties the most optimal is thought to be a combination of the methods of computer simulation allowing one to reveal the basic laws of the behaviour of the matter with the methods of constructing the approximating state equations.

## 2. MODEL SYSTEMS IN THE MONTE-CARLO METHOD

The efficiency of the calculational method of thermodynamic properties, determination of the phase transition parameters, manifests itself, as a rule, in studying the behaviour of the many-particle model systems. Most simple but rather essential are the systems of hard particles (spheres, discs, etc.) and of particles interacting by the Lennard-Jones law. For both the systems the whole phase diagram is investigated. Both the systems can be used as the trial ones while passing to real matters through corrections by the methods of perturbation theory or through the introduction of the so-called effective potentials.

The basic result of the computer methods of simulation is the proof of a possible description of the liquid-solid state transition. It is also shown that the difference between the condensed phases is difficult to reveal, especially in the coordinate space. The fact that there is a difference in the values of the energy characteristics (energy attraction and repulsion of the Lennard-Jones particles) cannot unfortunately allow one to formulate a clean-cut criterion of a phase transition. It can be explained by the changes both in the first coordinate sphere and in the subsequent ones<sup>1,2</sup>).

As for practical applications, one of the basic problems is the absence of recommendations on propagating the methods for describing mixtures. There are no papers on a direct calculation of the state equation for mixture in the region of phase transitions. As a rule, the calculations are made of the excess thermodynamic functions in the one-phase state. The comparison

with experimental data for matters close to the properties of the Lennard-Jones fluid is satisfactory. Similar results have been obtained within the theories where the mixture is simulated by an individual matter with average characteristic parameters<sup>3)</sup>. However, it is obvious that in the cases when molecules of the matter in the mixture differ essentially its description on the basis of averaging of this type leads to unsatisfactory results, which is especially obvious in determining the phase transition coordinates.

Now we consider how the results<sup>4)</sup> change for the model of the argon+krypton mixture of different compositions. The model is a mixture of particles interacting through the Lennard-Johns potential. The ratio of the energy parameters  $\epsilon_{Kz} / \epsilon_{Az} = 1,335$  and of the scale parameters  $\sigma / \sigma_{Az} = 1.075$ . The interaction of molecules of different types was determined by the parameters of the same potential,  $\sigma_{Az-Kz} = \frac{\sigma_{Az} + \sigma_{Kz}}{2}$  and  $\epsilon_{Az-Kz} = (\epsilon_{Az} \cdot \epsilon_{Kz})^{\frac{1}{2}}$ . The basic cell was chosen as a face-centered cubic lattice; the particles of both the types were not mixed in this case. The computer experiments were performed for three compositions (25%, 50% and 75% component). An additional difficulty in comparison with the simulation of a pure matter<sup>4)</sup> was the determination of the initial values of the attraction (A) and repulsion (R) energies. The table gives their values for the radius of the potential cut-off  $R_c = \frac{L}{2}$ , where  $L$  is the edge of the basic cell.

T a b l e

Initial values of the attraction and repulsion energies and the number of generated chains for various compositions of the LD mixture simulating the argon-krypton mixture

Mole fraction of argon	$A_0$	$B_0$	$N$
1.00	6.046875	12.7500	16
0.75	7.448742	14.25957	19
0.5	9.044937	16.29419	27
0.25	10.64158	18.33363	21

The change of the  $A$  and  $B$  parameters was investigated in the limits  $A_m \leq A \leq A_m + \Delta A$ ,  $B_n \leq B \leq B_n + \Delta B$  where  $\Delta A = 0.04$ ,  $1 \leq m \leq 12$  and  $\Delta B = 0.14$ ,  $1 \leq n \leq 32$ . The optimal values of  $m$ ,  $n$ ,  $\Delta A$  and  $\Delta B$  were chosen empirically. The choice criterion was the completeness of the cell filling ( $A_m$  and  $B_n$ ) reliable from the statistical viewpoint and sufficient for further calculations. Each generated chain contained 128000 configurations.

The MC calculations provided the histograms determining the number of states with different values of  $A$  and  $B$ . According to them, simple calculations gave the dependences  $\rho = \rho(V, T)$  and the distribution functions of the most probable values of  $A$  and  $B$  that can serve as an analog of the radial distribution function in the energy space. The isotherms calculated for the pure matter and mixtures are represented in Fig. 1 in the given coordinates:  $\theta = k_B T / \epsilon A \epsilon$ ,  $\tau = V / \sigma A \epsilon^3$  and  $\mathcal{T} = \frac{\rho \sigma A \epsilon^3}{\epsilon A \epsilon}$ . Fig. 2 shows the cross section of the surface  $Q(A, B_{max})$  versus  $A$  while the reduced density changes from  $\tau = 1.25$  (liquid state) to  $\tau = 1.12$  (solid state).

Separation of the liquidus and solidus lines by integrating over energies turned out to be a more difficult task for the mixtures than for the pure matter. Therefore, the temperature-composition diagram for the fixed pressure  $\mathcal{P} = 11.08$  should be considered approximate (Fig. 3). At the same time, the specific volume of the mixture up to the line of hardening is very close to the value defined as

$$V_m = X_{Ar} \cdot V_{Ar} + X_{Kr} \cdot V_{Kr}$$

which is in agreement with experimental data:  $\Delta V_{ex} \rightarrow 0$  with increasing pressure<sup>5)</sup>.

However, these results do not allow one to make any assumptions as to the transition mechanism, to determine rather precisely the limit of existence of a homogeneous phase. This phenomenon can be explained by the "softness" of the Lennard-Johns potential.

It is most probable that the transition from the liquid state into the crystalline one is mostly due to the interaction of the hard cores of molecules - their repulsion. The repulsion slightly manifesting itself in the condensation at the critical point plays a crucial role in the structure formation in the many-particle system. Probably, the formation of a hard phase at sufficiently low temperatures is smoothed out by the effect of a still strong attraction of particles. Therefore, the pattern of the liquid-crystal transition in the Lennard-Johns model is smoothed out.

In the light of the afore-said the study of crystallisation in the hard particle system is of particular interest.



Investigations of certain models for these systems<sup>6-9</sup>) demonstrated their principal importance for the development of the statistical physics. The hard particle model admitting an exact solution in the one-dimensional case was known to be used for verifying various theories. In particular, because of the simplicity of the potential interaction function for solving integral equations for the radial distribution function. However, since various approaches of the statistical physics are based on the assumptions of the interaction smallness, a possibility of expanding the functions over the interaction energy parameter in a power series and the decisive contribution of binary interactions are a priori inapplicable to the hard particle model. On the contrary, in this case an infinitely strong interaction takes place at a certain distance. At the same time, under a strong compression this system of particles behaves as cluster in which a multiparticle interaction cannot be neglected. Undoubtedly, the theory aspiring to success in describing "solid" liquid, the process of hardening, should have a possibility of describing the behaviour of the hard particle system as a starting point of investigation. Here, the problems of space geometry, the package and arrangement of particles, are brought to the fore, i.e., the mathematical basis in this case in the theory of geometric probabilities. This fact has first been pointed out by Bernal<sup>6</sup>). The random dense package introduced by Bernal is treated as a model for liquid. The difference between the density of a package of this type found by Bernal and the density of the ordered package corresponds approximately to the difference of the densities of liquid and hard phases

of noble gases. The properties of the random dense package and its structure were studied in detail in many papers in order to reveal differences from the regular structure. However, practical results were not obtained. At the same time, investigations in the framework of the Monte-Carlo method have shown that the density of the Bernal model does not determine the density of liquid in the process of hardening<sup>7)</sup>. Obviously here the situation described above takes place as well: a small resolving power of the method based on the study of the particle distribution in the coordinate space around a randomly chosen particle. It is to be mentioned that the basic results in the Bernal model were obtained by an experimental realisation of random densely packed structures.

The most dense random package is not yet strictly defined; therefore, theoretical investigations by the computer simulation provide ambiguous results. It is clear that in a dense package particles touch each other. At the same time one did not succeed in introducing geometrical probabilities as yet. As regards the theory of geometrical probabilities in the considered case the distances between the points, angular distribution of the nearest neighbours around the central particle, are thought to be random elements. However, it is difficult to choose unambiguously the probability measure of these elements in the two- and three-dimensional space<sup>10,11)</sup>. If the whole variety of configurations is made discrete with the basic properties of the model preserved, one can obtain rigorous estimates.

In refs. 8,9) the models have been considered in which the use was made of an exact solution for the one-dimensional system of hard particles and in the second degree of freedom a discrete distribution is introduced instead of the continuous one. This provides a possibility of using combinatorial methods, which simplifies the problem considerably. At the same time, the model preserves the basic property of the system of hard discs (or spheres). The degree of a maximally possible compression of the model is determined by a mutual arrangement of particles.

The basic results of the investigation of the state equation of the models<sup>8,9)</sup> are the following. The density of the random densely packed structure is a random quantity but not a fixed one as in ref. 6). It is distributed by the Gauss law around the mean value of  $V_2$ . If the value of the system density equals this mean value, then one can observe a sharp turn on the isotherm. It can naturally be identified with the liquid-solid state transition. By analogy with the Bernal model the value of the density of the random dense package should correspond to the bending point on the isotherm (Fig. 4).

As will be seen further, a large role in constructing the state equation is played not only by the value of this critical density but also by the index  $\alpha$  in the Gauss function  $\exp[-\alpha(V_k - V_2)^2]$  which defines the distribution.

It has been attempted in ref. 12) to calculate these quantities for the system of hard discs and to obtain for it the state equation. The main purpose in this case is the calculation of the distribution function of random densely packed configurations. With this one can unambiguously obtain the statistical sum,

and consequently, the state equation. The scheme of reasoning underlying the approach developed in refs. 8,9,12) is the following.

The ensemble of states of the many-particle system which will be used for calculating macroquantities can be represented as a set of topologically ordered systems, i.e., the systems in which a sequence of particle coordinates does not change under compression or expansion of the system volume  $V$ . In the topologically ordered system the number of accessible states is proportional to  $(V - V_c)^N$  where  $V_c$  is the condensate volume, i.e. of such a state of the system of  $N$  particles when none of the particles can be shifted without changing the position of its nearest neighbours. The condensate is an analog of the random densely packed structure. Of the largest density is the condensate that is a hexagonal regular package (on the surface) or a face-centered one (in the three-dimensional space). The configuration in the volume  $V$  can be formed by successive transpositions of particles without violating their topological order from the condensate of the volume  $V_c < V$ . Consequently, the formation probability of a configuration is proportional to  $\Omega(V, V_c) (V - V_c)^N$ , where  $\Omega(V, V_c)$  is the formation probability of a condensate of the volume  $V_c$ .  $\Omega(V, V_c) = P(V_c) / \int_{V_c}^V P(V_c') dV_c'$ , where  $P(V_c)$  is the distribution function of the condensate density, and  $V_c$  is the volume of a crystalline condensate. The function  $\Omega(V, V_c)$  is the Gauss function with the centre  $V_c = V/2$ ; therefore, it is obvious that  $\Omega(V, V_c)$  at  $V_c > V/2$  and  $\Omega(V, V_c)$  increases sharply at  $V_c \leq V/2$  (the contribution of the configurations close to a regular package increases). This specific feature of the function  $P(V_c)$  manifests itself in calculating the state equation (Fig. 4).

The criterion of a phase transition under such a consideration is formulated as follows. Under the compression of the system a liquid state exists as long as the volume of the system is larger than the volume of the most probable random dense package. This can be realised only in the metastable region. Further compression leads to the rearrangement of a condensate with increasing role of the states close to a regular lattice.

In the usual case the transition parameters are determined on the basis of the Maxwell rule. It is seen that the density of the Bernal package is larger than the liquid density and less than the solid state density in the phase transition. It has been shown in ref.<sup>12)</sup> that the curve of the state equation is symmetric at the points  $p = p_2$ ,  $V = V_2$  with respect to the vertical passing through the point  $V_2$ .

Now let us consider one of the most widely spread state equations - the van der Waals equation

$$p = \frac{RT}{(V-b)} - \frac{a}{V^2}. \quad (1)$$

It is known that the first term of the equation allows for the repulsion while the second term for the attraction between the molecules. The first term is specific of more complex and exact equations obtained in<sup>13)</sup>. By the equality,  $b''$  we mean a minimally possible volume of the system of hard spheres<sup>14)</sup>. However, it is obvious that for the liquid this role should be played by the volume of the most probable condensate and  $b'$ . The pressure should tend to infinity in the solid phase not specific of the liquid state. In ref.<sup>12)</sup> the condensate volume is determined from the condition of maximum production  $\Omega(N, V_c)$ .

$\cdot \exp[-\alpha (V_c - V_L)^2]$  Then, for the liquid state region

$$p = \frac{RT}{\frac{V - V_L}{2} + \left( \left( \frac{V - V_L}{2} \right)^2 + \frac{1}{\alpha^2} \right)^{1/2}} + \frac{a}{V^2}; \quad V \geq V_L. \quad (2)$$

The state equation obtained (2) can immediately include the hardening line, where  $V_L \sim V_L(T)$  and  $\alpha \sim P_S(T)/T$ , where  $P_S$  and  $V_S$  are the coordinates of the phase transition points.

To use (2) for practical calculations one should determine  $V_L$  and  $\alpha$ . For pure matters one can use the procedure described in refs.<sup>15,16)</sup> where the parameters of the state equation are calculated in the process of optimization. The best agreement of calculations with experimental data on thermodynamic properties of pure matters is the best criterion of optimisation. However, this possibility does not eliminate the problems one encounters in extending eq.(2) to mixtures.

It would be most consistent to determine the density of the Bernal package for each given mixture. However, taking account of both the principal difficulties of the method, mentioned above, and purely technical ones, arising due to the inclusion of a small number of particles<sup>12)</sup>, one cannot admit this way to be optimal. At the same time, the results<sup>6,12)</sup> indicate that the volume of one particle obeys the Gauss-type distribution. The particle volume in this case is the volume of a polygon (or polyhedron) of Voronoj, which is formed by perpendiculars erected from the midpoint of intercepts connecting the central and neighbouring particles. The volume of such a polygon is just the effective particle volume. To the point, each of the topologically ordered system can be represented as a system of the

Voronoi polygons (mosaic) shifting under the volume expansion without rotations and change of relative arrangement in the space. The particles always touch by the same edges. It is natural to assume that in realising a random process with a correctly given probability measure the effective particle volume in a random package can be determined by simulating only its nearest neighbourhood. In particular, in the two-dimensional space a particle may interact with 4-6 particles. The interaction in this case is assumed as the influence on the form of the Voronoi polygon (number of edges). Consequently, a large number of experiments requiring a small time consuming could rather accurately estimate one of the most important parameters of the state equation. This concerns both the pure matter and mixtures with any composition.

To fulfill the basic property of a dense package (condensate), each particle should touch directly at least four neighbours. Four-five particles of the first coordination sphere can have coordinates (angles given as random numbers) uniformly distributed in the interval  $(0, 2\sqrt{r})$ . The main problem is to occupy the second coordination sphere. Here, the following variants are possible: the first when the particles are arranged maximally close to a chosen centre touching simultaneously two particles of the first sphere (Fig. 5a), and the second when the second sphere is occupied by random pairs (Fig. 5b).

It turned out that in the first case the mean volume of the principal cell (the Voronoi polygon) is several per cent larger than in an absolutely correct lattice. In the second case, we have obtained for this volume a value approximately equal to the

mean one (2% less) obtained in ref.<sup>12)</sup> for a system of  $\sim 100$  particles. Taking into account that in ref.<sup>12)</sup> the particles of the first sphere had, due to the imposed "crystallinity", an effective volume somewhat less than the mean one, then this coincidence indicates that configurations of the type shown in Fig. 5b are typical of the most probable random condensate. Though particles in ref.<sup>12)</sup> were added so that each particle touched simultaneously the two other particles, a stochastic nature of the process manifested itself in choosing one continuation out of several possible ones.

For the mixture one can calculate the effective volume of a particle of any kind. The environment of the particle is of the "i"th kind and turns out to be proportional to the mole portion  $X_i$  of particles of the given kind in the mixture. Assuming the uniformity of filling, for the effective  $V_i$  volume we get the estimate

$$V_i = \left[ \sum_j \frac{\sigma_i + \sigma_j}{2} X_j A_{ij} \right]^2,$$

where  $\sigma_i$  and  $\sigma_j$  are the diameters of the "i"th and "j"th particles and  $A_{ij}$  is the maximal number of particles of the "j"th kind around the "i"th particle. For  $A_{ij}$  in ref.<sup>17)</sup> for hard spheres the following estimate has been obtained;

$$A_{ij} = 12 \left( \frac{\sigma_i}{\sigma_j} \right)^{1.2}. \quad (3)$$

Then, for the averaged effective volume of a molecule in the mixture we have

$$\langle V \rangle_{mix.} = \sum_i X_i \left[ \sum_j \left( \frac{\sigma_i}{\sigma_j} \right)^{1.2} \frac{\sigma_i + \sigma_j}{2} X_j \right]^3. \quad (4)$$



The relation (4) gives for  $\langle V \rangle_{mix}$  values more close to the volume typical of the largest particles than the mean ones over

$$\langle V \rangle_{mix} = \left[ \sum_{ij} \frac{\sigma_i + \sigma_j}{2} \right]^3 \quad (5)$$

The difference is more essential the larger is the difference between the diameters of molecules of the components. This is in agreement with the fact that in the mixture of effective spheres the effective size of particles of a smaller size is always larger than the proper size. For the most-used relations  $\sigma_i/\sigma_j < 1.1$  the calculations showed that the specific volume of a condensate can be calculated by the linear relation  $\langle V \rangle_{mix} = \sum_i x_i V_i$ , which coincides with the results obtained within the Monte - Carlo method. For the mixture of hard particles with similar dimensions relations (4) and (5) give equivalent results. At  $\sigma_i/\sigma_j > 1$  the distribution function  $\langle V \rangle$  has not one sharp but several smeared extrema, which does not allow one to estimate  $\langle V \rangle_{mix}$  unambiguously.

### 3. CALCULATION OF THERMODYNAMICAL PROPERTIES

As has already been mentioned above, one of the most universal methods used for calculating thermodynamical properties and the parameters of phase equilibriums is the method of the state equation. As a rule, the mathematical structures are obtained empirically by analysing the available experimental data on the pressure of saturated vapor, density in the liquid and vapor phase, etc. Especially, this concerns the dependence of

the state equation coefficients on temperature. The dependence on the density is chosen either in the form of the van der Waals structure or the equation (BVR)<sup>18)</sup>. The first is based on the particle impenetrability model; and the second, on the expansion of the statistical sum over the density powers. At present, these approaches are being developed by determining the dependence of the state equation coefficients on temperature. It is to be emphasized that in the elaboration of the so-called few-constant equations (of the van der Waals equation) the main problem is a more accurate description of the experimental data on phase equilibriums in the mixture, whereas in the construction of many-constant equations (of the BVR-type) the problem of exact calculation of the thermodynamical properties of mixtures is solved by adding new terms. It is obvious that in the first case the purpose is justified since in the technological programs a rapid and exact calculation of the phase equilibrium parameters is very important for calculating the equipment. Since in determining these parameters the chemical potentials of components (the volatility coefficients) are calculated, i.e., the integral quantities, inaccuracies in the state equation are not so strongly reflected. However, the gain in time and simplicity of programming computer operations is essential. Investigations devoted to the modification of many constant state equations are based on a natural assumption that with increasing accuracy of the calculation of equilibrium properties in a wide range of the phase diagram one can achieve a high accuracy of the calculation of phase equilibriums as well<sup>19)</sup>.

Realization of this idea in practical problems encounters

numerous technical difficulties. First, this is the problem of selecting experimental data, attributing statistical weights to these data which define the degree of their importance, the choice of the region of defining data, etc.

Obviously, the chosen mathematical problem should provide an adequate description of the P-V-T data in a wide range of temperatures  $\theta = T/T_c$  at  $\theta \gg 1$  and  $\theta \leq 1$ .

In refs. 15, 16) the algorithm has been suggested which allows adaptation of the chosen state equation to the conditions of a concrete problem. It was used as a basis for elaborating a computer code package actively used for providing matter mixtures with the technological data on the thermodynamical properties. However, this adaptation does not always solve the problem as well. Therefore, the search for new analytical dependences is still urgent.

Following the modification of the BVR equation

$$\pi = \tau \cdot \theta + (B_0 \theta - A_0 - C_0 \theta^{-3}) \tau^2 + (b \theta - a) \tau^3 + \alpha \tau^6 + c \tau^3 \theta^{-2} [1 + \gamma \tau^2] \exp(-\gamma \tau^2),$$

in the Starling version<sup>20)</sup>

$$\pi = \tau \cdot \theta + (B_0 \theta - A_0 - C_0 \theta^{-2} + D_0 \theta^{-3} - E_0 \theta^{-4}) \tau^2 + (b \theta - a - d \theta^{-1}) \tau^3 + \alpha (a + d \theta^{-1}) \tau^6 + c \tau^3 \theta^{-2} (1 + \gamma \tau^2) \exp(-\gamma \tau^2)$$

and then in a more complex one<sup>19)</sup>

$$\pi = \tau \theta + (B_0 \theta - A_0 - C_0 \theta^{-2} + D_0 \theta^{-3} - E_0 \theta^{-4}) \tau^2 + (b \theta - a \theta^{-1} - e \theta^{-4} - f \theta^{-23}) \tau^3 +$$

$$+d(a+d\theta^{-1}+e\theta^{-4}+f\theta^{-23})\tau^6 + (c\theta^{-1} + \\ +g\theta^{-8} + h\theta^{-17})\tau^3(1+\gamma\tau^2)\exp(-\gamma\tau^2)$$

we can note that the basic problem is to guarantee a satisfactory description of the dependence  $p(\rho, \tau)$  for the temperatures  $\theta$  at  $\theta \gg 1$  and  $\theta < 1$ . Since the matter behaves differently in these regions, the equation is also added by functions of the type  $\theta^{-n}$  ( $n > 1$ ) in which the point  $\theta = 1$  separates the branches of different slope. The exponents are chosen empirically and the coefficients are determined from the regression analysis.

In approximating trial data the methods of nonlinear programming<sup>15)</sup> allow variation of a set of functions.

In particular, for the state equation<sup>20)</sup> a considerable decrease in errors of description is achieved by the following modification ( $t \approx 2$ ,  $x \approx 8$ ):

$$\pi = \tau \cdot \theta + [B_0 \theta + (B_1 + B_2 \sqrt{\theta}) \exp(-\frac{t}{\theta^2}) - \\ - A_0 - C_0 \theta^{-2} + D_0 \theta^{-3} - E_0 \theta^{-4}] \tau^2 + (b \theta - a - \\ - d \theta^{-1}) \tau^3 + \alpha (a + d \theta^{-1}) \tau^6 + c \tau^3 \theta^{-3} (1 + \gamma \tau^2) \exp(-\gamma \tau^2).$$

The efficiency of modification can be judged from a joint approximation of the data on the density and heat capacity, density and pressure of saturated vapors of nitrogen, argon and methane in the range of temperatures 80-150 K<sup>0</sup> and pressures up to 100 bar. An average error in describing these properties is two-three times less than the state equation<sup>20)</sup>.

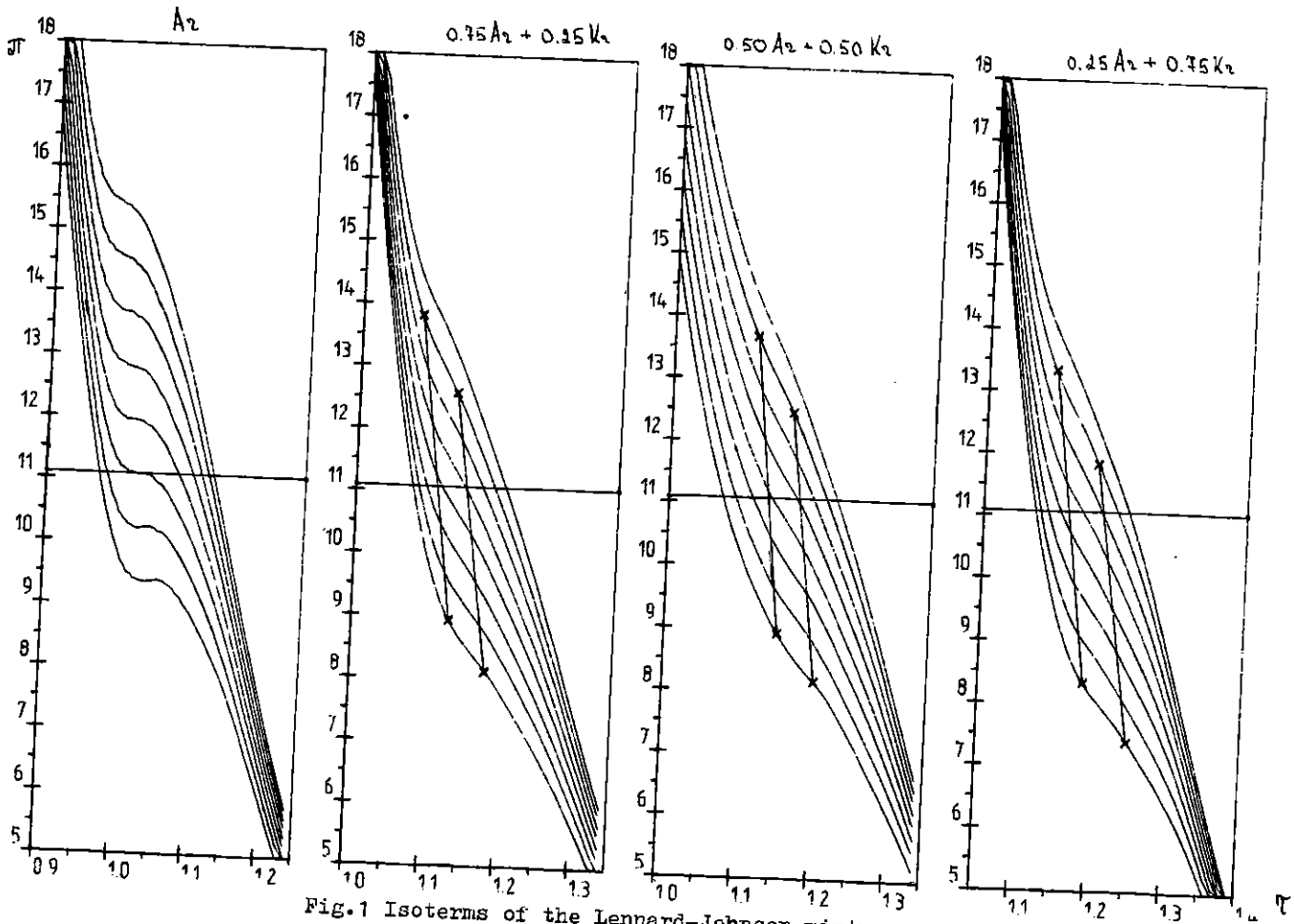


Fig.1 Isotherms of the Lennard-Johnson mixture.

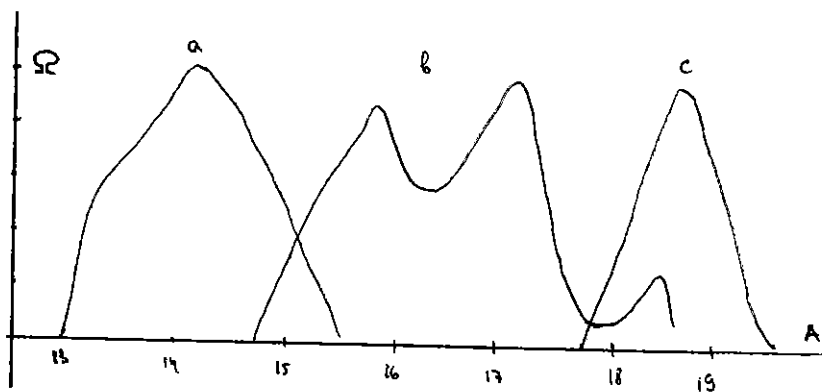


Fig.2. The function  $\Omega(A, B_{\max})$ ; a) is a crystal, b) is the two-phase region and c) is liquid.

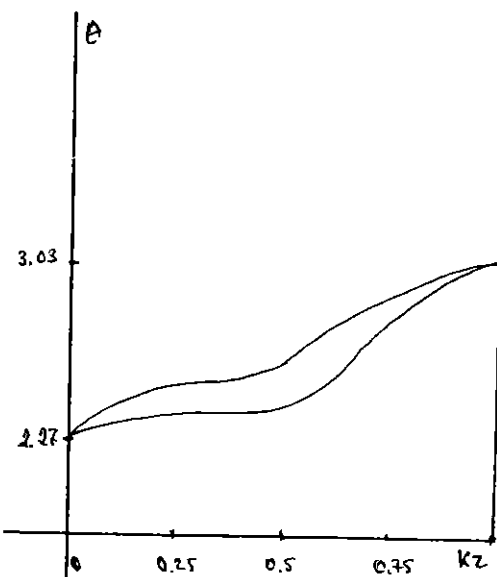


Fig.3. The  $(\Theta - x)$  diagram of the mixture Ar-Kr, ( $\mathcal{N} = 11.08$ ).

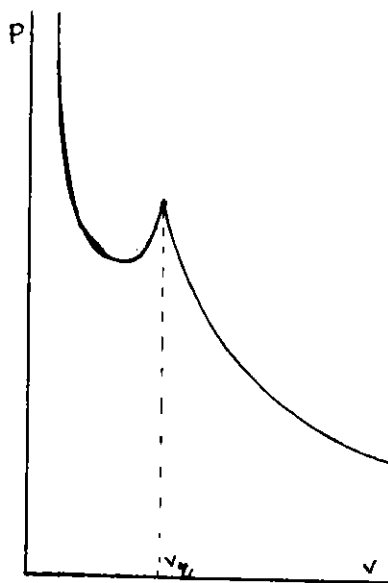
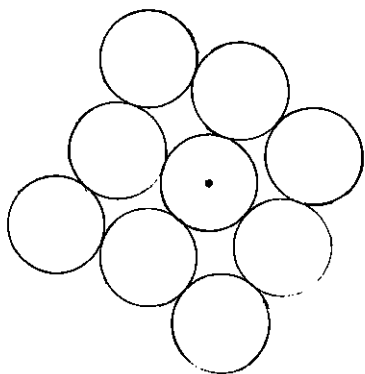
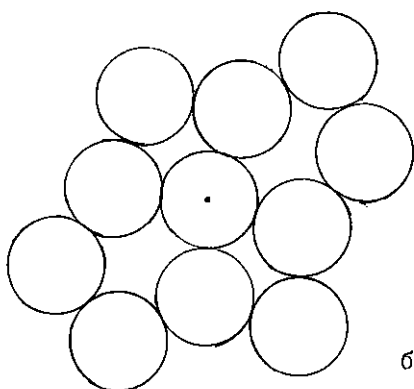


Fig.4. The state equation of the system of impenetrable particles.

Fig.5. Variant of the closest packing.



a



b

Thus, based on the results of investigations of the model systems in the Monte - Carlo methods aimed at defining the contribution of the interaction of hard particle nuclei in the state equation and on the approximation of the contributions determining the attraction between molecules, we can propose the following new form of the state equation:

$$P = \frac{\theta}{(\tau - \tau_0)^{1/2} + \left( \left[ \frac{\tau - \tau_0}{2} \right]^2 + \frac{1}{4} \right)^{1/2}} + \frac{a \exp\left(-\frac{b}{\theta^n}\right)}{\tau^m}$$

The equation parameters  $a$ ,  $\tau_2$  and  $\alpha$  can be defined as the temperature functions. The model can be used for calculating thermodynamical properties and parameters of phase equilibriums, limits of existence of liquid and gaseous mixtures.

In conclusion, we should like to note that approach to the construction of the state equation for pure matters and mixtures, which are based on the lattice models, did not exhaust themselves<sup>21)</sup>. They have recently been generalised to the mixture of molecules of  $\zeta$  - mer. ( $\zeta$  - is the number of cells of the lattice occupied by the molecule with contact parts of different types)<sup>22)</sup>. This allowed a satisfactory description of the thermodynamical properties of hydrocarbon mixtures of alkanes.

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