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Statistical model of the condensed media and it using for a description of phase transitions

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In the frame of the two-level molecular statistical approach a classic statistical model of the condensed system is worked out. A united state equation is obtained on the base of expressions, which are known in the statistical thermodynamics, for a thermodynamic potential, entropy and inner energy of the model. It is allows to build a theoretical phase diagram of the simple molecular medium.

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1. Introduction

On the basis of a two-level molecular-statistical approach which is based on the use of Bogolyubov – Born – Green – Kirkvud – Ivon method of correlative functions, Rott's method of conditional distributions and the method of thermodynamic functionals, a united statistical theory of all phase transitions in molecular systems: crystal – liquid, crystal – gas and liquid – gas is constructed. On the basis of the developed statistical theory of phase transitions [1] we formulate a simple statistical model of a condensed system [2] with the first-order interaction of particles. This interaction is described by Lennard – Johns potential. As a result, an approximate analytical constitutive equation of the system of N particles is obtained. The particles are homogeneously distributed on M microcells in volume ω $(M > N)$ into which the whole volume V of the system is divided. Volume ω should be small enough so that it would be possible to neglect the contribution of states when in cells there are simultaneously two and more molecules in the cells.

The received all-phase state equation contains two parameters of the model: A and ω which are analogous to power parameters and drop-out volume in the known equations of Van-der-Vaals and M. Planck. The constitutive equation is based on approximation which can be neglected, but opportunities of rigorous statistical approaches [3,4], allowing to define parameters A and ω by means of variational methods, can be applied.

2. Construction of the united constitutive equation for molecular systems

At calculating potential energy U of the system of N molecules we shall use an expression which considers correlation in filling pairs of cells with particles. It determines probability n_{ij} of simultaneous filling pairs of cells with two particles in volumes i and j, (two-cell numbers of

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filling) [1]:

$$n_{ij} = n + \frac{1 - \sqrt{1 + 4n(1-n)f_{ij}}}{2f_{ij}} \simeq K_{ij}n^2, \tag{1}$$

where $n = N/M$ – concentration of particles, f_{ij} – average value of function $f(r)$ ($f(r) = exp[-\Phi(r)/(kT)] - 1$). It is received as a result of averaging Mayer function by means of binary distribution function of two particles in two cells.

Correlation factor K_{ij} in formula (1) is expressed by f_{ij}, and so it depends on distance R between the centers of the cells, and consequently on their volume ω ($R = \sqrt[6]{2}\omega^{1/3}$ – for a face-centered cubic lattice) and the coordination sphere number.

The analysis of expression (1) shows, that factors K_{ij} for the first neighbours of the first coordination spheres (K_1) and other spheres ($K_2, K_3, ...$) are not much dependent on concentration n, as volume $x = 4n(1-n)f_{ij}$ in formula (1) is lower than a unit.

In the expression for potential energy U we use average values of potentials of average forces φ_{ij}.They consider effects which are connected with distribution of particles within the cells (localized in a crystal area and delocalized in liquid and gaseous states). So, in approximation of the nearest neighbours for a potential part of the self-energy of the condensed medium (taking into account two-partial correlations) (1) we shall receive the following expression [4,5]:

$$U = \frac{1}{2}\sum_{i=1}^{M}\sum_{j\neq i}^{M}\varphi_{ij}n_{ij} \simeq 6MK_1\varphi_1 n^2 = -M\frac{A^*n^2}{2}, \tag{2}$$

where $A^* = -12K_1\varphi_1(R,T)$. Multiplier 12 defines the number of the nearest neighboring cells which centers belong to the first coordination sphere of a face-centered cubic lattice composed of M microcells.

Since factor K_1 poorly depends on concentration n, parameter A^* is also little dependent poorly depend on concentration n. Then the approached expression for energy ε^* which defines the change of energy at the fixed values of volume $V = \omega M$ and the number of microcells M ($\omega = V/M = \text{const}$) will become:

$$\varepsilon^* = \frac{\partial U}{\partial N} = \frac{1}{M}\frac{\partial U}{\partial n} \simeq -A^*n. \tag{3}$$

As a result of using potential $\Omega = -pV$ we receive the following constitutive equation of system N of the particles:

$$p = -\frac{\theta}{\omega}\ln\left(1 - \frac{\omega}{\upsilon}\right) - \frac{A^*\omega}{2\upsilon^2} = -\frac{\theta}{\omega}(\ln(\upsilon - \omega) - \ln\upsilon) - \frac{A^*\omega}{2\upsilon^2}, \tag{4}$$

where $\theta = kT$, $\upsilon = V/N$, $\omega = V/M$.

3. Design of an analytical expression for the average value of potentials of average forces

At numerical solution of the integrated equations for potentials of average forces φ_{ij}, with the help of the computer, we mark that in the field of existence of a crystal state of matter the line of pushing away of average forces potential proves to be less "rigid", than that of potential Φ_{ij}.

It arises from averaging potential $\Phi(r)$ on volumes ω_i and ω_j by means of distributional functions of Rott's method of conditional distributions. These functions are strongly localized around the lattice points, i.e. the centers of microcells. The given effect of averaging is considered by means of factors η and λ. These factors are introduced into the expression for Lennard – Johns point intermolecular potential, which is written down in dimensionless variables (distance R in terms of σ , and potential φ_1 in terms of ε ; σ and ε – parameters of Lennard - Johns potential):

$$\varphi(R) = 4\eta\left(\frac{1}{(R\lambda)^{12}} - \frac{1}{(R\lambda)^{6}}\right). \tag{5}$$

In the field of liquid or gaseous conditions distributional functions are delocalized. And so the corresponding potentials of average forces φ of fluid systems should be practically constant within the limits of microcells. So, in the field of phase transition fusion – crystallization potentials of average forces change in steps (sharply) from distance R. We shall write down asymptotes of the average meaning for a potential of average forces at small values R (crystal state) and at big R (gaseous state):

$$\varphi(R) \to \Phi(R) \qquad \text{at} \qquad R \to 0, \qquad \varphi(R) \to \text{const} \qquad \text{at} \qquad R \to R_{\text{kp}} \tag{6}$$

where R_{kp} – distance around the critical point "liquid – gas".

For a sharp change of the form of average forces potential we shall use the following approximations for factors η (power) and λ (linear):

$$\eta = 1 - a(1 - f(\omega)), \tag{7}$$

$$\lambda \simeq 1 + (\omega^{-1/3} - 1)(1 - f(\omega)), \tag{8}$$

$$f(\omega) = \frac{1}{\exp\left[(\omega - \omega_0)/\beta\right] + 1}. \tag{9}$$

Parameters ω_0 and β in formula (9) should be selected so that theoretical thermodynamic parameters of phase transition at a triple point temperature coincide with their experimental values. Parameter a is determined with the use of the expression for critical temperature of the model ($a = 1 - \theta_{\text{kp}}/3$). For defining parameter γ the earlier formulated function [4] is used. Dependence of volume ω on molecular volume by the exhibitor is approximated:

$$\omega = \upsilon \exp\left[-\gamma/\upsilon\right]. \tag{10}$$

For model parameters of the condensed medium ($\omega_0 = 1,2$, $\beta = 0,01$, $\gamma = 6,9$, $a = 0,58$) isotherms of pressure at different temperatures are constructed. In the field of temperatures above the triple point and below the critical point on isotherms of pressure there is a usual Van-der-Vaals loop for transition "liquid – gas". On all isotherms in the field of phase transitions "crystal – liquid" (above the triple point) and "crystal – gas" (below the triple point) the similar loop is found out.

4. Conclusion

The use of phase balance conditions (Maxwell's rule) will allow to construct a theoretical phase diagram in molecular systems.

Thus, for the first time the constitutive equation of the condensed medium, which describes all phase transitions in simple molecular systems is received.

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