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MOLECULAR-STATISTICAL DESCRIPTION OF NONUNIFORMLY DEFORMED SPECIMENS. 1. FORMULATION OF THE PROBLEM AND METHOD FOR SOLVING IT

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To describe the structural and mechanical properties of actual deformed crystalline specimens with defects (thermal vacancies), simultaneous use is made of the method of correlative functions of the particle and vacancy distribution over the volume and the method of thermodynamic functionals, which implies solution of the corresponding variational problem in the final stage of statistical investigations. For the first time the tensor of microscopic deformation of the lattice is introduced in governing equations of statistical physics as internal field parameters of the system. As a result, prerequisites for a statistical solution of problems of elasticity theory with simultaneous description of the structure and mechanical characteristics of the elastic properties of the specimens are created.

Introduction. Let us use, as a basis, results obtained in the development of a two-level [1] molecular-statistical description of inhomogeneous media that consists in simultaneous use of the methods of correlative functions of Bogolyubov–Born–Green–Kirkwood–Yvon (BBGKY, see [2]) and L. A. Rott (the method of conditional correlative functions [3]) and the method of thermodynamic functionals [4]. These methods are independent from the point of view of their initial principles and therefore lie at the basis of two quite autonomous statistical directions in contemporary physics. The methods of correlative functions are predominantly used in describing homogeneous systems; in particular, in the theory of the bulk properties of liquids the method of integral equations [5] is widely known, due to which the statistical theory of liquids is just as good as the well-developed theories of gases and perfect crystals. The method of thermodynamic functionals, which implies solution of the corresponding variational problems, is used to study inhomogeneous systems, for example, in the theory of heterogeneous systems with a plane or spherical interface [4, 6].

In both the method of correlative functions and the method of thermodynamic functionals the problem of closing is central. In the first case, it is necessary to close down at some equation an infinite system (chain) of linked integro-differential equations for the correlative distribution functions of the particles of the system in the volume V, while in the second case it is necessary to terminate infinite series that determine the corresponding thermodynamic quantities, for example, the free energy of an inhomogeneous system. It is known that, if one and the same approximation is taken in each of these methods to solve the problem of closing, and the termination of infinite systems or series is always carried out, to a certain extent, rather arbitrarily [1, 5], the results in the indicated methods turn out to be mismatched [1, 7]. In the case of crystals with defects and multicomponent systems, there also occurs the no less important problem of normalization of the correlative functions of mixtures, so that in this direction, too, one has to make use of different approximations, for example, the Bragg–Williams and Kirkwood approximations and the quasichemical approximation [8-10].

In the approach developed, all correlative functions of a condensed medium are represented in the form of a product of two functions. One of them describes the microdistribution of particles within unit cells, into which the entire volume V is mentally subdivided (the method of conditional distributions [2]), and in closing is approximated according to the method of average-force potentials [3]. The other, which describes the distri-

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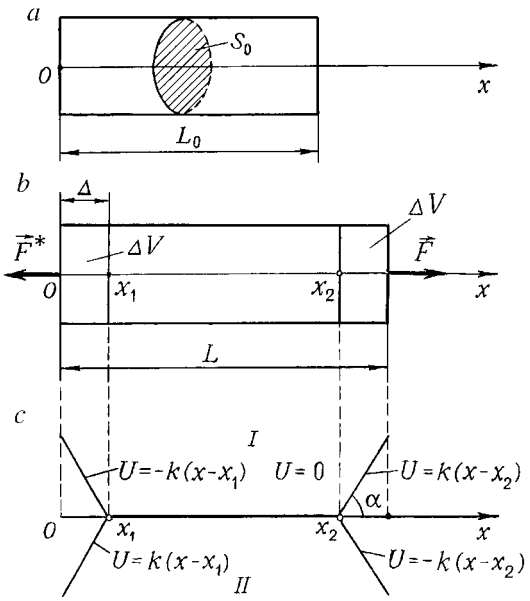

Fig. 1. Scheme of the model of the uniaxially deformed state of a specimen: a) undeformed linear specimen; b) nonuniformly deformed linear specimen; c) force field in which the deformed specimen is placed (I, potential well in compression; II, potential well in extension).

bution of the particles of the medium averaged over the unit cells, is a normalization factor for the function of the first type, so that it reflects macroinhomogeneities in the system. These functions in themselves are not subjected to any approximation in solving the problem of closing. Expressions for them are obtained by variation of the free-energy functional by pair, triple, etc. correlations [10]. As a result it has become possible to practically realize the well-known Bogolyubov statement that higher-order correlative distribution functions of particles (and vacancies) are functionals of lower-order ones.

Description of a Statistical Model of a Uniformly Deformed Linear Specimen. Let us investigate the structure and elastic properties of crystalline specimens that have the shape of thin rods of length L_0 and cross-sectional area S_0 in an undeformed state (Fig. 1a).

To produce uniaxial extension or compression, we apply forces $\vec{F}$ and $\vec{F}^*$ that are equal in magnitude and opposite in direction to the ends of the rod (Fig. 1b). We proceed to a description of a statistical model that corresponds to the considered problem of uniaxial extension (compression) in elasticity theory. For this purpose, we place a deformed specimen of length L in a force field that is a potential "well" in the form of a trapezoid (Fig. 1c). The parameters of the latter (Δ, α) that determine the shape of the potential $U(x)$ must be such that the resultant force of the volumetric forces distributed over a thin layer of thickness Δ near the ends is equal to the tensile (or compressive) force F:

$$F = \int_{\Delta V} \left| \frac{dU}{dx} \right| \rho_0 dV = \int_{x_2}^{L} k\rho_0 S_0 dx = k\rho_0 S_0 \Delta . \qquad (1)$$

Here ρ_0 is the average density of the material near the ends of the rod, i.e., at the attaching points in tensile testing machines or presses.

We take into account the fact that, in the method of conditional distributions, the entire volume V of the statistical sum of N particles is mentally subdivided into microcells [5] whose number M is larger than the number of particles N [1]. The centers of these cells for simple molecular systems form a face-centered lattice with a certain concentration of vacant nodes to be determined. Consequently, having performed the procedure of mental subdivision of an undeformed specimen of length L_0 (Fig. 1a) into microcells, we will describe the stressed state of a deformed specimen of length L using the field of the microscopic deformation tensor $\lambda^{\alpha\beta}$

that determines the material gradient [11-13] of the displacement vector $\vec{u}$ of the particles of the medium (in this statistical method, the role of the particles of the medium is played by microcells of volume ω whose size is comparable to the size of the particles (molecules) of the system) [14, 15]:

$$\lambda^{\alpha\beta} = \frac{\partial u_\alpha}{\partial x_\beta}; \quad \alpha, \beta = 1, 2, 3, \tag{2}$$

where x_1, x_2, and x_3 are the coordinates of the centers of the particles in the initial, i.e., undeformed, specimen; u_1, u_2, and u_3 are the projections of the displacement vector $\vec{u}$.

For the one-dimensional model of unixial extension (compression) discussed here, we write a definition of the Poisson coefficient:

$$\mu = -\lambda_\perp / \lambda_\parallel . \tag{3}$$

The character of the distribution of N particles of the molecular system over M cells is described by a set of occupation numbers η_l (l = 1, 2, ..., M) that prescribe the concentration field of cells occupied by one particle and the corresponding field of vacant cells $n_l^b = 1 - n_l$ (the volume ω of the microcells is selected so that statistical states with two-particle and subsequent occupations can be disregarded). In the statistical approach developed, the sought sets of numbers n_l and $\lambda_l^{\alpha\beta}$ are actually internal field variables, and this means that, to determine them, it is necessary to solve a corresponding variational problem that minimizes a certain thermodynamic potential, for example, the functional of the free energy or the functional of the grand thermodynamic potential $\Omega = -pV$.

Closed System of Integral Equations for Correlative Distribution Functions of Particles and Point Defects in a Deformed Crystal. We write equations that relate the distribution functions of the BBGKY method (the functions F_1, F_2, etc. are defined throughout the volume of the system studied – the deformed specimen) to the functions F_{11} of the method of conditional distributions (the F_{11}-approximation). The domain of the latter is microcells of volume ω for an undeformed specimen in which the centers of the cells form a regular lattice with occupied and unoccupied (vacant) cells (a modified F_{11}-approximation [1, 3]).

For this purpose, we use corresponding general expressions that are also true for a nonuniformly deformed specimen (see formulas (10) and (11) from [10]) and apply a scaling transformation to the space variables [14, 15] for the points of the medium in the deformed and undeformed specimens:

$$\vec{\tilde{r}} = \vec{f}(\vec{r}) . \tag{4}$$

This transformation of the variables is a generalization of the Bogolyubov λ-transform that is well known in statistical physics and characterizes uniform deformation of the system (see, for example, [3]). As a result of transformation (4) the distribution functions F_{11} of the method of conditional distributions [3] for an inhomogeneous deformed system with vacant and occupied cells [14, 15] will functionally depend not only on the field of the occupation numbers n_l but also on the field of the components of the deformation tensor $\lambda_l^{\alpha\beta}$(α, β = 1, 2, 3; l = 1, 2, ..., M).

The indicated equation of relation for the unary (single-particle) distribution functions $F_1(\vec{r})$ and $\hat{F}_{11}$ has the following form [10] (here and subsequently we will omit the vector sign, i.e., the arrow above the corresponding symbols, in cases where this involves no misunderstanding in representations):

$$F_1(\tilde{r}_l) = n_l \hat{F}_{11}\left(r_l, \{n_k\}, \{\lambda_k^{\alpha\beta}\}\right), \quad l, k = 1, 2, ..., M . \tag{5}$$

Here $\tilde{r}_l$ is the radius vector of a certain point A of the medium (Fig. 2) in the deformed specimen ($\tilde{r}_l \subset \tilde{\omega}_l$) while r_l is the radius vector in the undeformed specimen ($r_l \subset \omega_l$) that corresponds to it, so that the vector of the displacement field is $u = \tilde{r}_l - r_l$.

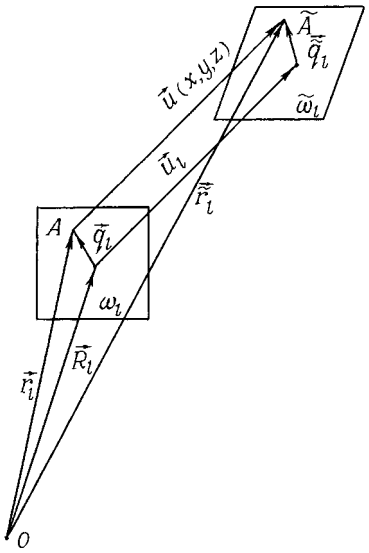

Fig. 2. Scheme of the relative position of a microcell with the number l in deformed ($\tilde{\omega}_l$) and undeformed (ω_l) states.

The point A of the medium has the coordinates x, y, z in the undeformed specimen; therefore the vector u of displacements of the points of the medium depends on these coordinates and describes the deformation field $u = u(x, y, z)$. Transformation (4) with allowance for the definition of the displacement field u can be written as

$$\tilde{r}_l = r_l(x, y, z) + u_l(x, y, z), \quad l = 1, 2, ..., M. \tag{6}$$

In formula (5), the braces in the arguments of the correlative function $\hat{F}_{11}$ indicate its functional dependence on the field of the occupation numbers of the cells ω_k (a discrete set of numbers $\{n_k\}$) and the field of the deformation tensor of the crystalline specimen (a discrete set of components $\{\lambda_k^{\alpha\beta}\}$). To shorten the representation of the subsequent equations, we will omit, in isolated cases, the braces with the corresponding set of the numbers n_k and $\lambda_k^{\alpha\beta}$.

Taking into account definition (2) for the deformation tensor and the notation in Fig. 2, we represent expression (6) in a form that introduces an explicit functional dependence on the deformation tensor $\hat{\Lambda}_k = \{\lambda_k^{\alpha\beta}\}$ in all statistical equations that describe the structure and thermodynamic properties of a deformed medium [16] (the components $\lambda_k^{\alpha\beta}$ characterize local deformation of the medium in the vicinity of the center of the cell ω_k):

$$\vec{\tilde{r}}_l = \vec{R}_l + \vec{u}_l + \vec{\tilde{q}}_l = \vec{R}_l + \vec{u}_l + (1 + \hat{\Lambda}_l) \cdot \vec{q}_l, \tag{7}$$

where $\vec{R}_l$ is the radius vector of the center of the cell ω_l, i.e., the node of the lattice in the undeformed specimen; $\vec{u}_l$ is the displacement vector of this node in the deformed specimen; $\Delta\vec{u} = \hat{\Lambda}_l\vec{q}_l$ is the displacement of the point A with the coordinates x, y, z relative to the new position of the node.

Using (7), we express the radius vector of the relative position of the two points of the deformed crystal $\tilde{r}_{lm}$ in terms of the components of the deformation tensor $\hat{\Lambda}$ for the cells ω_l and ω_m; we take into account that the vector of relative displacement of the centers of these cells is $\vec{u}_{lm} = \vec{u}_m - \vec{u}_l$, while the radius vector of their relative position in the basis (undeformed) lattice is $\vec{R}_{lm} = \vec{R}_m - \vec{R}_l$:

$$\vec{\tilde{r}}_{lm} = \vec{r}_m - \vec{r}_l = \vec{R}_{lm} + \vec{u}_{lm} + (1 + \hat{\Lambda}_m) \cdot \vec{q}_m - (1 + \hat{\Lambda}_l) \cdot \vec{q}_l. \tag{8}$$

Considering the problem of statistical description of the deformation of a crystalline specimen, we use a closed integral equation for the potentials φ of the average forces of an inhomogeneous deformed medium [1] that is obtained as a result of termination of an infinite chain of integro-differential equations for the cor-

relative functions F_{11} with single-particle occupation of the cells ω by molecules (with allowance for the presence of vacant nodes in a deformed crystal lattice [10, 14-16]):

$$n_l \exp\left\{-\frac{1}{\theta}\varphi_{lm}(q_l)\right\} = n_{lm}^{aa}\int\limits_{\omega_m}\exp\left\{-\frac{1}{\theta}\Phi(\tilde{r}_{lm})\right\}\hat{F}_{11}^{*}(q_m)\,dq_m +$$

$$+ n_{lm}^{ab}\int\limits_{\omega_l}\exp\left\{-\frac{1}{\theta}\varphi_{lm}(q_l)\right\}\hat{F}_{11}^{*}(q_l)\,dq_l\,. \qquad (9)$$

Here $\hat{F}_{11}^{*}$ is an auxiliary function normalized to unity, using which the averaging over the molecular positions in the cells ω_l and ω_m is performed ($q_l \subset \omega_l$ and $q_m \subset \omega_m$). This function is expressed in terms of the sought average-force potentials, for example,

$$\hat{F}_{11}^{*}(q_m) = \frac{\exp\left\{-\frac{1}{\theta}\sum\limits_{k\neq l,m}^{M}\varphi_{mk}(q_m)\right\}}{\int\limits_{\omega_m}\exp\left\{-\frac{1}{\theta}\sum\limits_{k\neq l,m}^{M}\varphi_{mk}(q_m)\right\}dq_m}\,. \qquad (10)$$

The function $\hat{F}_{11}^{*}(q_l)$ is similarly defined, while the quantities n_{lm}^{aa} and n_{lm}^{ab} characterize the distribution of N molecules over all possible pairs of cells ω_l and ω_m from all M cells of the lattice; $N_b = M - N$ is the number of vacant cells. The numerical value of n_{lm}^{aa} assigns, in its physical meaning, the probability that there is one molecule each in the cells ω_l and ω_m, while the numerical value of n_{lm}^{ab} assigns the probability of the cell ω_l being occupied by a molecule on condition that the cell ω_m is unoccupied (vacant). Consequently, the quantities n_{lm}^{aa} and n_{lm}^{ab} are two-cell analogs of ordinary occupation numbers. They can be interpreted as probability functions of the integral arguments l and m subject to determination that satisfy a normalization condition of the form

$$n_{lm}^{aa} + n_{lm}^{ab} = n_l\,, \quad l, m = 1, 2, ..., M\,. \qquad (11)$$

CONCLUSIONS

1. We obtained a closed system of integral equations for the potentials φ of the average forces that describe the interaction of the particles of the medium in a deformed specimen and determine the particle-distribution functions in a deformed crystal with vacancies.

2. For the first time we were able, within the framework of a developed two-level molecular-statistical description of the properties of inhomogeneous systems, to proceed to consideration of a typical problem of elasticity theory by the methods of statistical physics. Since the basis is provided by an integral equation [9] that contains functionals of the concentration field of the particles and vacancies and the field of the components of the deformation tensor, the statistical elasticity theory developed is nonlocal and takes simultaneous account of competing entropy and force factors.

NOTATION

L_0 and L, length of the undeformed and deformed specimens, respectively; S_0, cross-sectional area of the specimen in the undeformed state; $\vec{F}$ and $\vec{F}^{*}$, vectors of the forces that extend or compress the specimen; Δ, linear dimension of the parts of the specimen near its ends that are acted upon by the external-force field; α,

slope of the straight line that governs the form of the potential of the external force field to the axis along which the extension or compression of the linear specimen occurs; U, potential of the external force field that provides the deformation of the specimen in extension or compression; V, volume of the statistical system; N, number of particles of the given system; M, number of microcells into which the entire volume of the system is mentally subdivided; $\hat{\Lambda}_k$, microscopic deformation tensor; $\lambda_k^{\alpha\beta}$, components of this tensor; $\vec{u}$, displacement vector of the particles of the medium in the microcells; μ, Poisson coefficient; $\lambda_{||}$ and $\lambda_{\perp}$, relative deformations in the longitudinal and transverse directions of the specimen; n, concentration of the number of particles in the vicinity of the lattice node; p, pressure; F_1, F_2, etc., chain of correlative distribution functions in the BBGKY method; F_{11}, conditional correlative distribution functions of particles near nodes of the lattice with vacancies (the first F_{11}-approximation); $\vec{\tilde{r}}$ and $\vec{r}$, radius vectors of the point of the medium in the deformed and undeformed specimens; $\vec{R}$, radius vector of the center of the microcell in the undeformed specimen; $\vec{\tilde{q}}$ and $\vec{q}$, radius vectors of the point of the medium relative to the centers of the cells in the deformed and undeformed specimens; $\Delta\vec{u}$, displacement of the particle of the medium; φ, potential of the average forces of interaction of the particles (molecules or atoms) of an inhomogeneous deformed medium; Φ, paired intermolecular Lennard-Jones potential; $\theta = kT/\varepsilon$, dimensionless temperature (k, Boltzmann constant, T, absolute temperature, and ε, depth of the potential well that describes the interaction of two particles (molecules) of the medium). Subscripts and superscripts: 0, initial (undeformed) state; α and β, components of tensors of the first and second ranks; 1, 2, and 3, numbers of the components of the corresponding tensors; $||$ and $\perp$, longitudinal and transverse direction, respectively; a, microcell occupied by a molecule; b, unoccupied (vacant) cell; l, k, and m, numbers of the microcells; 11, first statistical approximation, in which all microcells are occupied by no more than one particle (molecule); ~ , membership of the corresponding quantities in the deformed specimen; $\hat{}$, normalization to unity; *, auxiliary nature; lm, pairs of cells; aa, two microcells with the numbers l and m (or k) are occupied by one particle (molecule) each; ab, the microcell with the number l is occupied by one particle, while the microcell with the number m or k is unoccupied (vacant).

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