and finally,

$$m(\tau''-\tau')=\ln v'_c-\ln v''_c$$

$$m=\frac{\ln v'_c-\ln v''_c}{\Delta\tau}, \tag{28}$$

where $\Delta\tau = \tau'' - \tau'$ is the time over which the temperature difference changes in the interval b' − b''. It is convenient to use the galvanometer scale divisions, then

$$m=\frac{\ln N_1-\ln N_2}{\Delta\tau}. \tag{29}$$

Use of Eq. (29) is quite convenient for practical determination of m.

NOTATION

t_a, autoclave temperature; θ, temperature change; V, ρ, c_p, volume, density, and isobaric specific heat of material in ampul; λ, thermal conductivity of heat meter material; F_1, R_1, area and radius of outer ampul surface; c_p', volume isobaric specific heat of material; W', correction required for heat loss along conductive wires and tube; C_b, ballast heat capacity of ampul and other elements; δ, δ', thickness of side and end layers of liquid; a, thermal diffusivity; V_c, core volume.

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THEORY OF BIVACANCY CONTRIBUTION TO THE COEFFICIENT OF SELF-DIFFUSION IN MONATOMIC MOLECULAR CRYSTALS

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On the basis of the statistical theory of a crystal with defects, we calculate the frequency of jumps of an atom for diffusion in the bivacancy mechanism. We obtain an expression for the contributions of different types of bivacancies to the coefficient of self-diffusion. Calculations are carried out for the special case of a Lennard-Jones 6-12 potential.

The vacancy mechanism of diffusion assumes that the coefficient of self-diffusion is determined both by monovacancies as well as complex vacancies. Of the various vacancy clusters, the most important for diffusion are bivacancies, since the concentration of clusters containing a larger number of vacancies rapidly falls off with the number of vacancies.

The known estimates of the contribution of bivacancies to self-diffusion lie in a rather wide range (see for example [1]). The difficulties of such estimates are explained by the fact that they are mostly in the form of independent calculations of two groups of parameters:

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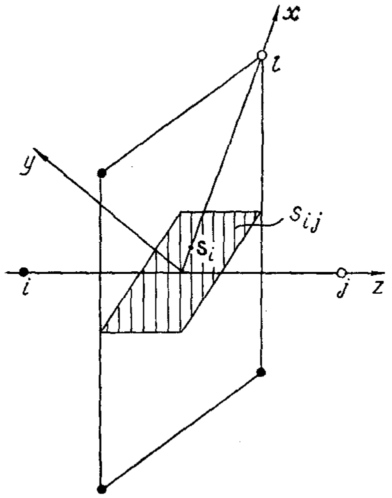

Fig. 1. Schematic diagram of the geometry of a bivacancy-1. The bivacancy is at the lattice points j and ℓ, and an atom, performing the jump, is in cell i.

the formation characteristics of bivacancies and their migration characteristics. In addition, one usually takes into account the contribution of only a single type of bivacancy, composed of vacancies which are nearest neighbors on the lattice and the bivacancy is assumed to migrate without dissociation. In addition such an approach is not consistent from a theoretical point of view. Thus, one can question the reliability of estimates made on the basis of these assumptions.

The purpose of the present paper is to develop a theory to calculate the bivacancy contributions to self-diffusion from "first principles," in the framework of classical statistical mechanics and to analyze the behavior of these contributions as functions of the thermodynamic parameters of a monatomic molecular crystal.

We start from the expression for the coefficient of self-diffusion obtained on the basis of the theory of random walks [2], which for a crystal with a cubic lattice and with the inclusion of bivacancies has the form

$$D = \left(k_1 + \sum_{\alpha} k_2^{(\alpha)}\right) R^2/6, \tag{1}$$

where k_1 is the frequency of monovacancy jumps, and $k_2^{(\alpha)}$ is the frequency of jumps of bivacancies of type α. R is the length of a jump, equal to he distance between the centers of contiguous Wigner–Seitz cells. The frequencies k are calculated using various models (see [1]). The most consistent approach uses statistical mechanics [3]. The frequency k_1 and hence the contribution of monovacancies in the coefficient of self-diffusion has been calculated in [4]. The calculation was based on the statistical theory of a crystal with point defects [5, 6], which generalizes the statistical method of conditional distributions [7] for such systems. In the framework of this theory the dependence of the characteristics of the bivacancies on the thermodynamic parameters of the crystal were considered in [8, 9].

Statistical Approach. We consider a system of N identical atoms in a volume V in thermodynamic equilibrium with the Hamiltonian function:

$$H_N = \sum_{\mu=1}^{N} \mathbf{p}_\mu^2/(2m) + \left(\frac{1}{2}\right) \sum_{\mu,\nu=1}^{N}{}' \Phi(\mathbf{q}_\mu, \mathbf{q}_\nu). \tag{2}$$

Here $\mathbf{p}_\mu$, $\mathbf{q}_\mu$ are the momentum and coordinate of atom μ; m is the mass of the atom; $\Phi(\mathbf{q}_\mu, \mathbf{q}_\nu)$ is the interatomic interaction potential; the prime on the summation sign means that the summation is carried out subject to the condition $\mu \neq \nu$. The Gibbs distribution function of the system has the form [10]

$$D_N(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N) = Z_N^{-1} \exp\{-\beta H_N\}, \tag{3}$$

where $Z_N = \int d\mathbf{p}_1 \ldots \int d\mathbf{p}_N \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \exp\{-\beta H_N\}$; $\beta^{-1} = (k_B T)$; k_B is the Boltzmann constant; T is the absolute temperature.

We divide the volume V up into $M = N + N_0$ cells of volume $w_i = V/M$ (i = 1, 2, ..., M) and we include only those states of the system in which each of the cells is either empty or contains exactly one particle. Integrating the Gibbs distribution (3), we can introduce a sequence of "partial" distribution functions [11], which determine the probability of different states of groups of cells, subject to the condition that the remaining cells are

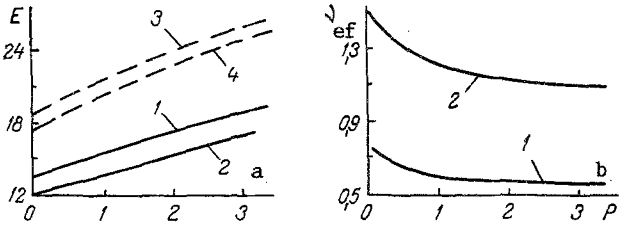

Fig. 2. (a) Activation energy of self-diffusion of monovacancies [curves 1) and 2)] and bivacancies-1 [curves 3) and 4)] for θ = 0.5 [curves 1) and 3)] and θ = 0.7 [curves 2) and 4)]. (b) Effective frequency of monovacancies [curve 1)] and bivacancies-1 [curve 2)] for θ = 0.7 as function of pressure.

either empty or contain one particle. We use the following notation for these functions: each function has indices indicating the numbers of the cells, whose states are described by the function; if the arguments of the function consist of a momentum and a coordinate whose numbers coincide with the number of the cell, then this means that the cell contains an atom; the presence of the index alone indicates that the cell is empty.

In order to illustrate the approach, we consider the set of functions corresponding to the states of a single cell, a pair of cells, and a group of three cells, two of wich are empty: F_i, $F_i(p_i, q_i)$, F_{ij}, $F_{ij}(p_i, q_i)$, $F_{ij}(p_i, q_i, p_j, q_j)$, $F_{ij\ell}(p_i, q_i)$. F_i is the probability that cell i is empty; $F_i(p_i, q_i)$ is the probability density to observe an arbitrary particle in the neighborhood of the point $q_i \in w_i$ with a momentum in the neighborhood of p_i, F_{ij} is the probability that cells i and j are empty; $F_{ij}(p_i, q_i)$ is the probability density of observing an arbitrary particle in the neighborhood of the point $q_i \in w_i$, with momentum p_i; and cell j is empty; $F_{ij}(p_i, q_i, p_j, q_j)$ is the corresponding probability density for two particles in two cells; finally $F_{ij\ell}(p_i, q_i)$ is the probability density that here is an atom in cell i in the neighborhood of the point $q_i \in w_i$ with momentum p_i and cells j and ℓ are empty.

In equilibrium statistical mechanics the momentum and coordinate distributions are independent [10]:

$$\begin{gathered} F_i(\mathbf{p}_i,\ \mathbf{q}_i) = F(\mathbf{p}_i) F_i(\mathbf{q}_i),\ \ F_{ij}(\mathbf{p}_i,\ \mathbf{q}_i) = F(\mathbf{p}_i) F_{ij}(\mathbf{q}_i), \\ F_{ij}(\mathbf{p}_i,\ \mathbf{q}_i,\ \mathbf{p}_j,\ \mathbf{q}_j) = F(\mathbf{p}_i) F(\mathbf{p}_j) F_{ij}(\mathbf{q}_i,\ \mathbf{q}_j), \\ F_{ijl}(\mathbf{p}_i,\ \mathbf{q}_i) = F(p_i) F_{ijl}(\mathbf{q}_i), \end{gathered} \tag{4}$$

and

$$F(\mathbf{p}_i) = [\beta/(2\pi m)]^{3/2} \exp\{-\beta \mathbf{p}_i^2/(2m)\},\ \ \int d\mathbf{p}_i F(\mathbf{p}_i) = 1. \tag{5}$$

The functions $F_i(q_i)$, $F_{ij}(q_i)$, $F_{ij}(q_i, q_j)$ describing the distribution of particles in configuration space, together with the functions F_i and F_{ij}, satisfy the following rigorous equations, which follow from their definitions:

$$\begin{gathered} F_i + \int_i d\mathbf{q}_i F_i(\mathbf{q}_i) = 1,\ \ F_i = F_{ij} + \int_j d\mathbf{q}_j F_{ij}(\mathbf{q}_j), \\ F_i(\mathbf{q}_i) = F_{ij}(\mathbf{q}_i) + \int_j d\mathbf{q}_j F_{ij}(\mathbf{q}_i,\ \mathbf{q}_j), \end{gathered} \tag{6}$$

where the integration is carried out over the volume of the cell.

Using the concept of mean field potentials and quasipotentials [7, 12, 13] and also the procedure of closure, the functions can be represented in the form

$$\begin{gathered} F_i = (n_0/Q_0) \exp\{-\beta\varphi_i\},\ \ F_i(\mathbf{q}_i) = (n/Q) \exp\{-\beta\varphi_i(\mathbf{q}_i)\}, \\ F_{ij} = \exp\{\beta[\varphi_{i,j} + \varphi_{j,i}] F_i F_j, \end{gathered} \tag{7}$$

$$F_{ij}(\mathbf{q}_i) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{j,i}]\} F_i(\mathbf{q}_i) F_j,$$

$$F_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{j,i}(\mathbf{q}_j) - \Phi(\mathbf{q}_i, \mathbf{q}_j)]\} F_i(\mathbf{q}_i) F_j(\mathbf{q}_j),$$

$$F_{ijl}(\mathbf{q}_i) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{j,i} + \varphi_{i,l}(\mathbf{q}_i) + \varphi_{l,i} + \varphi_{j,l} + \varphi_{l,j}]\} F_i(\mathbf{q}_i) F_j F_l,$$

$$Q_0 = \exp\{-\beta\varphi_i\}, \quad Q = \int_i d\mathbf{q}_i \exp\{-\beta\varphi_i(\mathbf{q}_i)\}. \tag{8}$$

Here $n_0 = N_0/M$ is the concentration of empty cells, and $n = 1 - n_0$. The mean field potentials $\varphi_i(q_i)$ and the quasipotentials φ_i are sums of the form

$$\varphi_i(\mathbf{q}_i) = \sum_{m \neq i}^{M} \varphi_{i,m}(\mathbf{q}_i), \quad \varphi_i = \sum_{m \neq i}^{M} \varphi_{i,m}. \tag{9}$$

In order to obtain a closed system of equations for the potentials $\varphi_{i,m}(q_i)$ and the quasipotentials $\varphi_{i,m}$ it is sufficient to substitute the expressions for the functions (7) into the last two equations of (6) and we thus obtain

$$\exp\{-\beta\varphi_{i,j}\} = \exp\{\beta\varphi_{j,i}\} F_j + \int_j dq_j \exp\{\beta\varphi_{j,i}(\mathbf{q}_j)\} F_j(\mathbf{q}_j), \tag{10}$$

$$\exp\{-\beta\varphi_{i,j}(\mathbf{q}_i)\} = \exp\{\beta\varphi_{j,i}\} F_j + \int_j dq_j \exp\{\beta[\varphi_{j,i}(\mathbf{q}_j) - \Phi(\mathbf{q}_i, \mathbf{q}_j)]\} F_j(\mathbf{q}_j). \tag{11}$$

The solution of this system of nonlinear integral equations determines all of the functions (7), and through the free energy

$$F = -(M/\beta)[n_0 \ln(Q_0/n_0) + n \ln(Q/n)] \tag{12}$$

also all of the thermodynamics of the system.

Of particular interest is the function $F_{ij\ell}(p_i, q_i)$, which has the form

$$F_{ijl}(\mathbf{p}_i, \mathbf{q}_i) = [\beta/(2\pi m)]^{3/2} \exp\{\beta[-p_i^2/(2m) + \varphi_{i,j}(\mathbf{q}_i) + \varphi_{j,i} + \varphi_{i,l}(\mathbf{q}_i) + \varphi_{l,j} + \varphi_{l,i} + \varphi_{j,l}]\} F_i(\mathbf{q}_i) F_j F_l. \tag{13}$$

Jump Frequency of Bivacancies. We consider now an elementary act of diffusion of a bivacancy. For definiteness we first consider diffusion without dissociation, where the bivacancy maintains its structure. A bivacancy composed of two vacancies which are α-th neighbors on the lattice will be called a bivacancy-α. We first consider the self-diffusion of a bivacancy-1 (nearest neighbors on the lattice) for which the elementary act of diffusion reduces to a rotation of its axis by 60°; one of the vacancies remains fixed (in cell ℓ) and the second goes from cell j into the neighboring cell i, where there was an atom (actually, of course, the atom goes from cell i into cell j). The coordinate system is shown in Fig. 1. The self-diffusion of other types of bivacancies, both with dissociation and without it, can be considered in a similar way.

We will assume that an elementary act of diffusion of a bivacancy is completed if the atom in cell i reaches its boundary S_{ij} with cell j and has a positive component of momentum along the z axis. Correspondingly, the vacancy jumps from cell j into cell i. Hence the jump frequency of bivacancies-1 is given by the expression

$$k_2^{(1)} = 4 \sum_{j=1}^{z_1} \int_{-\infty}^{\infty} d(p_i^x/m) \int_{-\infty}^{\infty} d(p_i^y/m) \int_0^{\infty} d(p_i^z/m) \int_{S_{ij}} dq_i F_{ijl}(\mathbf{p}_i, \mathbf{q}_i)(p_i^z/m). \tag{14}$$

In a similar way we can determine the jump frequency for other types of bivacancies. There will be differences in the number z_α (the number of atoms on the α-th coordinate sphere) and in the numerical coefficient in front of the summation sign; this factor is related to the symmetry of the transition.

Using the explicit form of the function $F_{ij\ell}(p_i, q_i)$, the integration over momentum can be done directly. Also in an infinite crystal the probability that a given cell is empty does not depend on the number of the cell and hence $F_i = F_j = n_0$. Then (14) can be written in the form

$$k_2^{(1)} = 4z_1(2\pi m\beta)^{-1/2}(1 - n_0) n_0^2 \exp\{\beta[\varphi_{j,i} + \varphi_{j,l} + \varphi_{l,j} + \varphi_{l,i}]\} \times$$
$$\times \int_{S_{ij}} d\mathbf{q}_i \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{i,l}(\mathbf{q}_i) - \varphi_i(\mathbf{q}_i)]\} / \int_{\omega_i} d\mathbf{q}_i \exp\{-\beta\varphi_i(\mathbf{q}_i)\}. \tag{15}$$

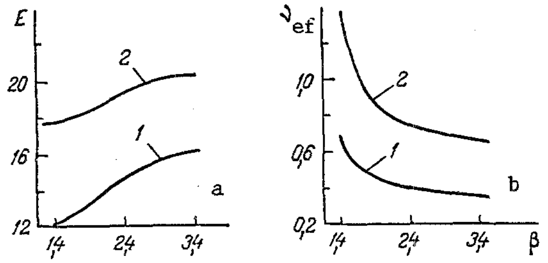

Fig. 3

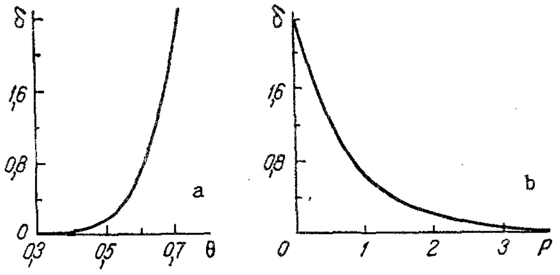

Fig. 4

Fig. 3. (a) Energy of activation of the self-diffusion of monovacancies [curve 1)] and bivacancies-1 [curve 2)]; (b) effective frequency of monovacancies [curve 1)] and bivacancies-1 [curve 2)] as functions of the inverse temperature for $p = 0$.

Fig. 4. Relative contribution to the coefficient of self-diffusion of bivacancies-1 as a function of temperature for $p = 0$ (a) and pressure for $\theta = 0.7$ (b); δ, %.

Therefore, the determination of the coefficient of self-diffusion for bivacancies reduces to two problems. The first is to determine the mean field potentials and the quasipotentials; the second is to calculate the integrals in (15) over the surface S_{ij} and over the volume w_i.

In order to determine the potentials and quasipotentials we must solve the system of nonlinear integral equations (10) and (11). We can obtain an approximate solution of this system by using the fact that $n_0 \ll 1$ ($n_0 = 10^{-3}$-10^{-4} near the triple point). Thus, we seek a solution in the form of a series in n_0 [14]. Limiting ourselves to the zeroth approximation and calculating the integrals by the method of Laplace [15] (the function $F_i\,(q_i)$ has sharp maxima at the lattice points) we obtain an expression for the mean field potentials

$$\varphi_{i,j}(\mathbf{q}_i)=\Phi(\mathbf{q}_i,\ \mathbf{n}_j)-\varphi_{j,i}(\mathbf{n}_j)-\beta^{-1}\ln\{1+\sigma^{-1}\{\Delta\varphi_{j,i}(\mathbf{n}_j)-\Phi''(\mathbf{q}_i,\ \mathbf{n}_j)-$$
$$-2\Phi'(\mathbf{q}_i,\ \mathbf{n}_j)/|\mathbf{q}_i-\mathbf{n}_j|+\beta[\nabla\varphi_{j,i}(\mathbf{n}_j)+\Phi'(\mathbf{q}_i,\ \mathbf{n}_j)(\mathbf{q}_i-\mathbf{n}_j)/|\mathbf{q}_i-\mathbf{n}_j|]^2\}\} \tag{16}$$

and the quasipotentials

$$\varphi_{i,j}=-\Phi(n_{ij})/2+\beta^{-1}\ln\{(1-\Gamma_{ij})^{1/2}/[1+(\Delta\varphi_{i,j}(\mathbf{n}_i)+\beta k_{i,j}^2)/(2\sigma)]\}. \tag{17}$$

Here $\mathbf{q}_j = \mathbf{n}_j + \mathbf{u}_j$, where $\mathbf{n}_j$ is the coordinate of a lattice point, $\mathbf{u}_j$ is the displacement of the atom from the lattice point, and $\mathbf{u}_j \in w_j$; $n_{ij} = |\mathbf{n}_j - \mathbf{n}_i|$; Δ is the Laplacian operator; $\Gamma_{ij} = [\Delta\Phi(\mathbf{n}_{ij}) - \Delta\varphi_{i,j}(\mathbf{n}_i) - \beta g^2{}_{ij}]/(2\sigma)$; $g_{i,j} = k_{i,j} + \Phi'(n_{ij})$; $k_{i,j} = |\nabla\varphi_{i,j}(\mathbf{n}_i)|$; $\sigma = \sum\limits_{j\neq i}^{M} \Delta\varphi_{i,j}(\mathbf{n}_i)$.

The derivatives $\varphi_{j,i}(\mathbf{n}_j)$ entering the right hand side of (16) can be calculated by differentiating the potential $\varphi_{j,i}(\mathbf{q}_j)$ the necessary number of times and then putting $\mathbf{q}_j = \mathbf{n}_j$. We then obtain a system of transcendental equations which can be solved numerically for a given iteratomic potential. The second problem is to calculate the integrals in (15). This problem is also solved by the method of Laplace. The volume integral in the denominator of (15) is

$$\int\limits_{w_i} d\mathbf{q}_i \exp\{-\beta\varphi_i(\mathbf{q}_i)\} = [2\pi/(\beta\sigma)]^{3/2}\exp\{-\beta\varphi_i(\mathbf{n}_i)\}. \tag{18}$$

It is somewhat more difficult to evaluate the surface integral in the numerator of (15). The problem, however, is facilitated by the knowledge of the explicit form of the integrand. We analyze the behavior of the function in the exponent of the integral over S_{ij}:

$$\psi(\mathbf{q}_i) = \varphi_i(\mathbf{q}_i) - \varphi_{i,j}(\mathbf{q}_i) - \varphi_{i,l}(\mathbf{q}_i). \tag{19}$$

Symmetry considerations and the explicit form of this function show that it has a minimum in the plane S_{ij} forming the boundary of the cells i and j. Let the point at which the minimum of the function $\psi(q_i)$ occurs be s_i. By symmetry this point must lie on the x axis. We expand the function ψ in a series in x, keeping the quadratic terms:

$$\psi(x) = \psi(0) + [\partial\psi(0)/\partial x]\,x + (1/2)\,[\partial^2\psi(0)/\partial x^2]\,x^2 + \cdots \tag{20}$$

Differentiating this expression with respect to x and equating the result to zero, we find

$$|\mathbf{s}_i| = -[\partial\psi(0)/\partial x]/[\partial^2\psi(0)/\partial x^2]. \tag{21}$$

The minimum of $\psi(x)$ corresponds to the maximum of the integrand, and we can again apply the method of Laplace. We then obtain

$$\int_{S_{ij}} dq_i \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{i,l}(\mathbf{q}_i) - \varphi_i(\mathbf{q}_i)]\} = [2\pi/(\beta\sigma_s)] \exp\{\beta[\varphi_{i,j}(\mathbf{s}_i) + \varphi_{i,l}(\mathbf{s}_i) - \varphi_i(\mathbf{s}_i)]\}, \tag{22}$$

where $\sigma_s = [(\partial^2\psi(s_i)/\partial x^2)(\partial^2\psi(s_i)/\partial y^2)]^{1/2}$. And so we obtain the following expression for the frequency of bivacancy jumps

$$k_2^{(1)} = \nu_2 \exp\{-\beta E_2\}, \tag{23}$$

where

$$\nu_2 = 4z_1(1-n_0)(\sigma/m)^{1/2}[\sigma/(2\pi\sigma_s)], \tag{24}$$

$$E_2 = g_2^{(1)} + \{[\varphi_i(\mathbf{s}_i) - \varphi_{i,j}(\mathbf{s}_i) - \varphi_{i,l}(\mathbf{s}_i)] - [\varphi_i(\mathbf{n}_i) - \varphi_{i,j}(\mathbf{n}_i) - \varphi_{i,l}(\mathbf{n}_i)] - \{[\varphi_{i,l}(\mathbf{n}_i) + \varphi_{l,i}] + [\varphi_{i,j}(\mathbf{n}_i) + \varphi_{j,i}]\}. \tag{25}$$

Here $g_2^{(1)}$ is the Gibbs potential of the formation of a bivacancy, and is given by

$$g_2^{(1)} = \varphi_j + \varphi_l - \varphi_{j,l} - \varphi_{l,j} + 2Pw, \tag{26}$$

where P is the pressure. The concentration of bivacancies $c_2^{(\alpha)}$ is

$$c_2^{(\alpha)} = (z_\alpha/2)\exp\{-\beta g_2^{(\alpha)}\}. \tag{27}$$

We analyze (25) for the activation energy of self-diffusion. The contribution of the energy of formation of a bivacancy is given by (26). The rest of the expression can be interpreted as the migration activation energy of bivacancies:

$$E_2^{(m)} = \{[\varphi_i(\mathbf{s}_i) - \varphi_{i,j}(\mathbf{s}_i) - \varphi_{i,l}(\mathbf{s}_i)] - [\varphi_i(\mathbf{n}_i) - \varphi_{i,j}(\mathbf{n}_i) - \varphi_{i,l}(\mathbf{n}_i)]\} - \{[\varphi_{i,l}(\mathbf{n}_i) + \varphi_{l,i}] + [\varphi_{i,j}(\mathbf{n}_i) + \varphi_{j,i}]\}. \tag{28}$$

The migration activation energy is composed of two parts. The expression in the first set of curly brackets represents the difference between the energies of an atom on the cell boundary (at the saddle point s_i) and an atom in the center of the cell (lattice point) where the fact that cells j and ℓ are occupied by the bivacancy is taken into account. In essence this is a barrier height which must be overcome by the atom in order to go into one of the cells occupied by the bivacancy. In the second set of curly brackets there are two terms, corresponding to correlations between an atom at the lattice point and each of the vacancies making up the bivacancy. By definition these terms are related to the correlation functions [8]:

$$\begin{aligned} g_{ij}(\mathbf{n}_i) &= \exp\{\beta[\varphi_{i,j}(\mathbf{n}_i) + \varphi_{j,i}]\} - 1, \\ g_{il}(\mathbf{n}_i) &= \exp\{\beta[\varphi_{i,l}(\mathbf{n}_i) + \varphi_{l,i}]\} - 1. \end{aligned} \tag{29}$$

To illustrate the approach in a specific case, we calculated the coefficient of self-diffusion of bivacancies-1 in a crystal whose atoms interact according to a Lennard-Jones 6-12 potential:

$$\Phi(r) = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6]. \tag{30}$$

All calculated quantities are represented in dimensionless form: the energy characteristics are expressed in units of ε, the dimensionless temperature is $\theta = k_B T/\varepsilon$; the inverse temperature is $\beta = \theta^{-1}$ (for this quantity we use the same notation as for the corresponding dimensionless quantity); the linear characteristics are expressed in units of r_0, the volume characteristics are in units of r_0^3, and the pressure characteristics are in units of ε/r_0^3. For an fcc lattice, into which the inert gases crystallize (we do not consider helium here), we calculated the quantities $\nu_2[\sqrt{m}/(4z_1)]$, E_2, and $\delta = D_2^{(1)}/D$, where $D_2^{(1)}$ is the contribution of bivacancies-1 to the coefficient of self-diffusion. All of the characteristics of bivacancy self-diffusion are compared with the corresponding characteristics for the self-diffusion of monovacancies. In the form given here, all results are correct for arbitrary ε, r_0, m.

Computational Results. As evident from Fig. 2, the activation energy and the effective frequency for bivacancies are higher than the corresponding quantities for monovacancies, although the dependence is practically identical.

In Fig. 3 we show the same quantities as functions of the inverse temperature for P = 0. We note that although ν_2 and E_2 are normally taken as constants in the analysis of experimental data, both of these quantities depend on β, and this dependence is significantly nonlinear. In Fig. 4 we show the relative contribution of bivacancies-1 (completing jumps without dissociation) to the coefficient of self-diffusion, as a function of the pressure and temperature. The assumption of no dissociation means that after a jump the bivacancy-1 maintains its structure. From these figures it is evident that at the triple point this contribution is about 2.4%.

In view of the geometry of the lattice, bivacancies-3 and bivacancies-5 can also diffuse without dissociation (in the approximation used here bivacancies-6 and higher order bivacancies were not taken into account and it was assumed that their binding energies were equal to zero). In these cases the pairs of cells (i, ℓ) and (j, ℓ) are separated by third and fifth neighbor distances, respectively, and cells i and j are nearest neighbors. An elementary act of self-diffusion occurs as in the case of bivacancies-1, however, the angle of rotation of bivacancy is less than 60°. In addition, there are 16 types of transitions for self-diffusion of bivacancies with dissociation. Bivacancies-1, after completing an elementary act of self-diffusion, become bivacancies-α (α = 2, 3, 4). Bivacancies-2 can become bivacancies-α (α = 3, 5) after an elementary jump, bivacancies-3 can become bivacancies-α (α = 4, 5) and bivacancies-4 can become bivacancies-5. Naturally the inverse processes are also possible. The structure of the transitions is determined by the geometry of the lattice, the range of the correlations between vacancies and by the fact that an elementary act of self-diffusion as considered here, is limited to transitions of the atom to one of the nearest lattice points. For all the transitions listed above, numerical calculations were done for the triple point of argon. The calculations showed that the total contribution of bivacancy self-diffusion can reach 9% at the triple point. Using the data in Fig. 4, one can see that the bivacancy contribution to the coefficient of self-diffusion begins to become important only when we approach the melting line.

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