STATISTICAL CALCULATION OF THE COEFFICIENT OF
DIFFUSION IN CRYSTALS OF THE NITROGEN TYPE

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On the basis of the statistical theory of a crystal with vacancies we calculate the coefficient of diffusion, the effective frequency, and the activation energy for crystals of the nitrogen type.

We use the statistical method of calculating the coefficient of self-diffusion developed earlier in [1], which is based on the method of conditional distributions [2]. An essential difference from [1] is that in the Hamiltonian of the system we include the dependence of the orientational variables of the molecules and the corresponding contributions to the kinetic energy. In particular, molecular crystals such as nitrogen correspond to Hamiltonians of this type. The theoretical treatment of the problem for crystals of this type is especially important, since, as far as we know, there is no experimental data on the diffusion coefficient for crystals of this type.

Method of Calculation. We consider a system of N identical particles with rotational degrees of freedom in a volume V in thermodynamic equilibrium. The Hamiltonian of the system is written in the form

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

Here I is the moment of inertia of the molecule (modeled as a rigid rotator); $\Phi(x_\mu, x_\nu)$ is the molecular interaction potential, which depends on the five-dimensional vectors $x_\mu = (\mathbf{q}_\mu, \mathbf{e}_\mu)$ where $\mathbf{q}_\mu$ are the coordinates of the center of mass of the molecule and the vector $\mathbf{e}_\mu$ defines its orientation. The prime on the summation sign indicates that the sum is to be evaluated with $\mu \neq \nu$. Following [2], and basing the treatment on the Gibbs distribution function, we describe the statistical method for this system. The total volume V of the crystal is divided up into M equal cells of volume $w = V/M$, where $M = N + N_0$, N_0 is the number of vacancies in the crystal. We only take into account states in which each cell is either empty or contains one molecule. We also assume only pair correlations. Then the system is described by six distribution functions: F_i, $F_i(\mathbf{p}_i, \mathbf{l}_i, x_i)$, F_{ij}, $F_{ij}(\mathbf{p}_i, \mathbf{l}_i, x_i)$, $F_{ij}(\mathbf{p}_j, \mathbf{l}_j, x_j)$, $F_{ij}(\mathbf{p}_i, \mathbf{p}_j, \mathbf{l}_i, \mathbf{l}_j, x_i, x_j)$, where F_i is the probability that the cell is empty; $F_i(\mathbf{p}_i, \mathbf{l}_i, x_i)$ is the probability density that in cell i there is a molecule near the point l_i with orientation q_i, momentum e_i and angular momentum p_i. The pair functions (the last four functions of the above set) determine the corresponding probabilities for pairs of cells. If the function has an index with no corresponding arguments, this means that the cell with this number is empty, i.e. it contains a vacancy.

In equilibrium statistical mechanics, the momenta, angular momenta, and coordinates are distributed independently:

$$F_i(\mathbf{p}_i, \mathbf{l}_i, x_i) = F(\mathbf{p}_i) F(\mathbf{l}_i) F_i(x_i), \tag{2}$$

$$F_{ij}(\mathbf{p}_i, \mathbf{p}_j, \mathbf{l}_i, \mathbf{l}_j, x_i, x_j) = F(\mathbf{p}_i) F(\mathbf{p}_j) F(\mathbf{l}_i) F(\mathbf{l}_j) F_{ij}(x_i, x_j).$$

The following exact probability relations can be written for the configurational parts of the distribution functions:

$$F_i = F_{ij} + \int_j dx_j F_{ij}(x_j), \quad F_i(x_i) = F_{ij}(x_i) + \int_j dx_j F_{ij}(x_i, x_j) \tag{3}$$
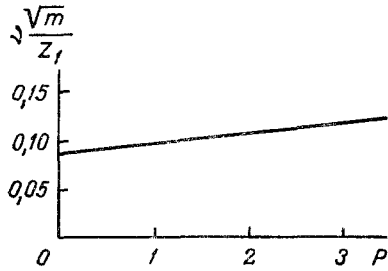
Fig. 1. Effective frequency as a function of pressure.

where these relations follow from the definitions of the distribution functions. Here and below all integrals are evaluated over the five-dimensional space representing the union of the center-of-mass position variables and the orientational variables.

Following the procedure described in detail in [1], we obtain a closed system of non-linear integral equations:

$$\exp\left(-\beta\varphi_{i,j}\right) = \exp\left(\beta\varphi_{j,i}\right)F_j + \int_j dx_j \exp\left[\beta\varphi_{j,i}(x_j)\right]F_j(x_j),$$

(4)

$$\exp\left[-\beta\varphi_{ij}(x_i)\right] = \exp\left(\beta\varphi_{j,i}\right)F_j + \int_j dx_j \exp\left\{\beta\left[\varphi_{j,i}(x_j) - \Phi(x_i,\ x_j)\right]\right\}F_j(x_j).$$

Here $\varphi_{i,j}$ and $\varphi_{i,j}(x_i)$ are the quasipotential and potential of the mean force due to cell j on empty cell i and on the particle in cell i, respectively. All cells are equivalent in an infinite system, and hence $\varphi_i \equiv \varphi$, $F_j \equiv n_0$ (j = 1, 2, ..., M), where $n_0 = N_0/M$ is the concentration of vacancies, and

$$\varphi_j = \sum_{m \neq j}^{M} \varphi_{j,m},\quad n_0 = \exp\left[-\beta\left(\varphi + Pw\right)\right],\quad \varphi_j(x_j) = \sum_{m \neq j}^{M} \varphi_{j,m}(x_j),$$

(5)

$$F_j(x_j) = (1 - n_0)\exp\left[-\beta\varphi_j(x_j)\right]/\int_j dx_j \exp\left[-\beta\varphi_j(x_j)\right],$$

which, together with (4), forms a closed, self-consistent system of equations. The Helmholtz free energy per cell and the pressure can be expressed in terms of the solution to this system of equations:

$$f = -\beta^{-1}\ln\left\{(Q_0/n_0)^{n_0}\left[Q/(1 - n_0)\right]^{1-n_0}\right\},\quad Q_0 = \exp\left(-\beta\varphi\right),$$

(6)

$$Q = \int_j dx_j \exp\left[-\beta\varphi_j(x_j)\right],\quad P = -(\partial f/\partial w)_{\beta, n_0}.$$

As a first step in obtaining an approximate solution of the system (4) we use the fact that $n_0 \ll 1$; therefore the solution can be written as a power series in n_0. In the zeroth approximation in n_0, (4) takes the form

$$\exp\left(-\beta\varphi_{i,j}\right) = \int_j dx_j \exp\left[\beta\varphi_{j,i}(x_j)\right]F_j(x_j),$$

(7)

$$\exp\left[-\beta\varphi_{i,j}(x_i)\right] = \int_j dx_j \exp\left\{\beta\left[\varphi_{j,i}(x_j) - \Phi(x_i,\ x_j)\right]\right\}F_j(x_j),$$

(8)

and

$$F_j(x_j) = Q^{-1}\exp\left[-\beta\varphi_j(x_j)\right].$$

(9)

The solution of (7) and (8) can be obtained by the method of steepest descent [3], using the fact that the function $F_j(x_j)$ has a sharp maximum at the lattice point for the equilibrium orientation δ_i . The equilibrium position of the molecule at lattice point i is written as the five-dimensional vector $a_j = (n_i, \delta_i)$, where n_j is the coordinate vector of the lattice point and δ_i is the equilibrium orientation. Then application of the method of steepest descent with the leading asymptotic term taken into account gives

$$\varphi_{i,j}(x_i) = \Phi(x_i, a_j) - \varphi_{j,i}(a_j), \qquad (10)$$

$$\varphi_{i,j} = -\varphi_{j,i}(a_j) = -\Phi(a_i, a_j)/2, \qquad (11)$$

and

$$\varphi_{i,j}(a_i) = \varphi_{j,i}(a_j). \qquad (12)$$

Hence the mean potentials are expressed in terms of the pair interaction potentials. Therefore the distribution functions can be found, from which it is possible to compute the diffusion coefficient for a nitrogen crystal.

We have for the momentum and angular momentum distribution functions

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

$$\iint d\mathbf{p}_i dl_i F_i(\mathbf{p}_i, 1_i, x_i) = F_i(x_i), \quad \iint d\mathbf{p}_i dl_i F_{ij}(\mathbf{p}_i, 1_i, x_i) = F_{ij}(x_i), \qquad (13)$$

$$\iiiint d\mathbf{p}_i d\mathbf{p}_j dl_i dl_j F_{ij}(\mathbf{p}_i, 1_i, \mathbf{p}_j, 1_j, x_i, x_j) = F_{ij}(x_i, x_j).$$

Diffusion processes in solids are usually described as a random walk with the use of various assumptions. For cubic crystals the coefficient of self-diffusion has the form [4]

$$D = kR^2/6, \qquad (14)$$

where R is the length of the molecular jumps and is equal to the distance between nearest neighbors on the cubic lattice.

We find the frequency of jumps using the distribution function $F_{ij}(\mathbf{p}_i, 1_i, x_i)$, which is the probability density of observing a molecule at the point $x_i(\mathbf{q}_i \in w_i; \mathbf{e}_i)$ with momentum $\mathbf{p}_i$ and angular momentum 1_i when cell j is empty (i.e. contains a vacancy), subject to the condition that all states of the remaining M-2 cells are taken into account.

Let cell i contain a molecule and cell j be empty and let these cells be nearest neighbors on an fcc lattice. We choose the coordinate system such that the origin is at the center of cell i, the z axis is directed along the line joining the centers of cells i and j, and the x and y axes are perpendicular to the z axis.

We will assume that the atom in cell i makes a transition to the empty cell j if it reaches the boundary S_{ij} between the cells and if the component of its momentum along the z axis is positive for arbitrary angular momentum. Then the frequency of jumps is given by the expression [5, 1]

$$k = \sum_{j=1}^{Z_1} \frac{1}{m} \int_0^\infty dp_i^z \int_{-\infty}^\infty dp_i^y \int_{-\infty}^\infty dp_i^x \, p_i^z \int dl_i \int_{S_{ij} \oplus A} dx_i F_{ij}(\mathbf{p}_i, 1_i, x_i), \qquad (15)$$

where A is the two-dimensional subspace of orientations $\mathbf{e}_i$. This expression is different from the analogous result in [5]. First, here we have considered molecules with rotational degrees of freedom; second, in [5] essentially isolated vacancies were considered, i.e. it was assumed that all of the surrounding cells contain particles, whereas here, according to (15), each of the M-2 cells can either be empty or contain one molecule.

The integration with respect to momentum and angular momentum in (15) can be carried out directly, taking into account the explicit form of the function $F_{ij}(\mathbf{p}_i, 1_i, x_i)$

$$F_{ij}(\mathbf{p}_i, 1_i, x_i) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp[-\beta \mathbf{p}_i^2/(2m)] \times$$

$$\times \exp\{\beta[\varphi_{i,j}(x_i) + \varphi_{j,i}]\} F_i(x_i) F(1_i) F_j. \qquad (16)$$

Hence

$$k = Z_1 (2\pi\beta m)^{-1/2} \exp(\beta\varphi_{j,i}) F_J \int_{(S_{ij} \oplus A)} dx_i \exp[\beta\varphi_{i,j}(x_i)] F_i(x_i). \qquad (17)$$

This last expression can be rewritten in the form

$$k = Z_1 (2\pi\beta m)^{-1/2} n_0 (1 - n_0) \exp(\beta\varphi_{j,i}) \int_{(S_{ij} \oplus A)} dx_i \exp\{\beta[\varphi_{i,j}(x_i) - \varphi_i(x_i)]\} Q^{-1}. \qquad (18)$$
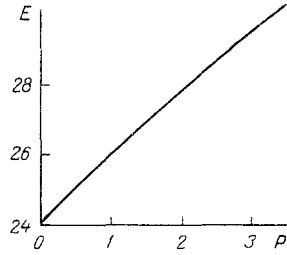
Fig. 2   Fig. 3

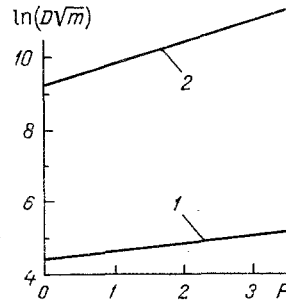Fig. 2. Activation energy of self-diffusion of a monovacancy in an N_2 crystal as a function of pressure.

Fig. 3. Logarithm of the coefficient of self-diffusion of monovacancies in an N_2 crystal as a function of pressure for the temperatures $\theta = 0.1$ (1) and 0.3 (2).

Evaluating the integral in (18) approximately, using the method of steepest descent, we obtain the following formula for the frequency of jumps:

$$k = \nu \exp\left(-\beta E\right), \tag{19}$$

where the so-called effective frequency is

$$\nu = Z_1 (\sigma/m)^{1/2} [\sigma^2/(2\pi\sigma_s^2)], \tag{20}$$

$$E = \varphi + P\varpi + \{[\varphi_i(s_i) - \varphi_{i,j}(s_i)] - [\varphi_i(a_i) - \varphi_{i,j}(a_i)] - [\varphi_{i,j}(a_i) + \varphi_{j,i}]\} \tag{21}$$

and where E is a quantity having the dimensions of energy; s_i is a five-dimensional vector defined such that the function $\varphi_i(x_i) - \varphi_{i,j}(x_i)$ has a minimum at the boundary between cells i and j when $x_i = s_i$; the quantities σ and σ_s are defined by the relations

$$\sigma = \left\{\det\left[\frac{1}{2}\sum_j \partial^2\Phi(x_i,\ a_j)/\partial x_i\partial x_i\right]_{x_i=a_i}\right\}^{1/5}, \tag{22}$$

$$\sigma_s = \left\{\det\left[\frac{1}{2}\sum_j \partial^2\Phi(x_i,\ a_j)/\partial x_i\partial x_i\right]_{x_i=s_i}\right\}^{1/4}. \tag{23}$$

Numerical Calculation of the Coefficient of Self-Diffusion. Calculations were carried out for a crystal consisting of particles interacting according to the potential [6]:

$$\Phi(x_i,\ x_j) = V_1\left[(e_i n_{ij})^2(e_j n_{ij})^2 - \frac{1}{3}(e_i n_{ij})^2 - \frac{1}{3}(e_j n_{ij})^2 + \frac{1}{9}\right] +$$

$$+ V_2\left[(e_i n_{ij})(e_j n_{ij})(e_i e_j) - \frac{1}{3}(e_i n_{ij})^2 - \frac{1}{3}(e_j n_{ij})^2 + \frac{1}{9}\right] +$$

$$+ V_3\left[(e_i e_j)^2 - \frac{1}{3}\right] + V_4\left[(e_i n_{ij})^4 + (e_j n_{ij})^4 - \frac{2}{5}\right] + \Phi_{LJ}. \tag{24}$$

Here e_i is the orientation of molecule i; n_{ij} is a unit vector directed from lattice point i to lattice point j; Φ_{LJ} is the Lennard—Jones potential. Energies are expressed in units of the Lennard—Jones potential well depth ε, volumes are in units of the cube of the linear potential parameter r_0, and pressures are in units of ε/r_0^3.

It was assumed in the calculations that the function $\varphi_i(x_i) - \varphi_{i,j}(x_i)$ has a minimum near the midpoint of the line joining the centers of cells i and j; the orientation of the molecule corresponding to the extremum was selected numerically.

The effective frequency and activation energy are shown in Figs. 1 and 2 as functions of pressure P. These dependences are seen to be practically linear.

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In the approximations adopted here both the effective energy and the frequency are independent of temperature. This means that the Arrhenius expression for the coefficient of self-diffusion is valid:

$$D = D_i \exp(-\beta H). \qquad (25)$$

Figure 3 shows the dependence of the logarithm of the coefficient of self-diffusion on pressure; note the monotonic increase of the diffusion coefficient with increasing pressure.

NOTATION

N, number of particles; V, volume of the system; $\mathbf{P}_\mu$, momentum; $\mathbf{l}_\mu$, angular momentum; m, mass of a molecule; x_μ, five-dimensional vector; $\Phi(x_\mu, x_\nu)$, molecular interaction potential; w, cell volume; β, reciprocal of the temperature; φ_i, pseudopotential; $\varphi_i(x_i)$, potential of the mean force; P, pressure; n_0, concentration of vacancies; D, coefficient of self-diffusion; k, frequency of jumps; R, length of a molecular jump; A, two-dimensional space; s_{ij}, boundary between two cells; ν, effective frequency; E, activation energy of self-diffusion; n_{ij}, unit vector; e_i, unit orientation vector of a molecule; ε, Lennard-Jones potential well depth; r_0, linear parameter in the Lennard-Jones potential; Z_1, number of nearest neighbors.

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OPTIMIZING HOT PRESSING FOR

COLD-PRESSED POROUS BLANKS

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A model is used for three-stage hot pressing, which is based on the effective characteristics for the porous cold-pressed blanks and is used to optimize the process as a whole.

1. Powder metallurgy is important because it not only economizes in metal and reduces costs but also provides composites with unique properties. Sometimes, one component here is hot pressing for cold-pressed porous blanks, in which the powder sinters.

Long sintering at high temperatures can cause selective recrystallization, or recrystallization embrittlement in the more typical refractory materials [1], i.e., strength loss, so it is necessary to control the heat treatment to obtain the necessary quality.

The control task is an inverse treatment [2], and computerized solution requires regularization [3]. A similar problem has been considered in [4] for another powder-processing technique.