STATISTICAL DETERMINATION OF THE COEFFICIENT OF SELF-DIFFUSION IN A MONATOMIC MOLECULAR CRYSTAL

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Using the statistical theory of a crystal, we calculate the coefficient of self-diffusion in a monatomic molecular crystal for diffusion by the vacancy mechanism with a Lennard–Jones (6-12) potential. The results are compared to experiment for argon, krypton, and xenon.

Introduction. Diffusion processes in solids are primarily described using the theory of random walks [1] and various simplifying models (see [2, 3] for example). For a cubic crystal the coefficient of self-diffusion has the form [1]

$$D = kR^2/6, \tag{1}$$

where k is a frequency, R is the length of atomic jumps, equal to the distance between nearest neighbors on the cubic lattice.

The jump frequency k is calculated with the help of various models (see [3]). The most systematic approach for calculating k is based on statistical mechanics [4]. In [4] the results for k calculated according to the dynamical theory [5, 6] were compared to those based on equilibrium statistical mechanics [7], and it was shown that the results are equivalent. An equilibrium statistical mechanics method for calculating the coefficient of self-diffusion somewhat different from [7] was worked out in [4]. In this method, an expression [8] is used for the concentration of vacancies, which is obtained using approximations additional to those in the calculation of k.

In the present paper we calculate the coefficient of self-diffusion using the equilibrium statistical theory of a crystal with vacancies [9-14] which is based on the statistical method of conditional distributions [15]. Using this theory, we can calculate the jump frequency of an atom in the crystal without resorting to additional assumptions. A closed system of equations is obtained for the determination of k, and hence D. The theory requires only the interatomic potential.

Statistical Method. We consider a system of N identical particles in thermodynamic equilibrium in a volume V. Let the Hamiltonian function of the system be

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

Here $\mathbf{p}_\mu$, $\mathbf{q}_\mu$ are the momentum and coordinate, respectively, of atom μ, m is the mass of the atom, $\Phi(\mathbf{q}_\mu, \mathbf{q}_\nu)$ is the atomic interaction potential, and the prime on the sum means that the summation is carried out for $\mu \neq \nu$. The Gibbs distribution function for a system of N particles has the form (see [16])

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

where

$$Z_N = \int d\mathbf{p}_1 \ldots \int d\mathbf{p}_N \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \exp\{-\beta H_N\} \tag{4}$$

is the partition function, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, and T is the absolute temperature.

We divide the total volume V of the system into $M = N + N_0$ cells of volume $w_i = V/M$ $(i = 1, 2, \ldots, M)$. We consider only those states of the system where each cell is either

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empty or contains a single particle. Such a set of states, with the help of the integration of the Gibbs distribution (3) can be identified with a set of "partial" distribution functions [9], describing the probabilities of various states of groups of cells under the condition that the remaining cells are either empty or contain a single particle. We use the following notation for these functions: each function has indices denoting the number of the cell whose state this function describes: if the momentum and coordinate with indices corresponding to the given cell number appear as argument of the function, this means that the given cell contains a particle, if the function appears only with an index and not the corresponding arguments, this means that the cell is empty.

To illustrate the approach, we consider only the set of functions corresponding to states of single cells and pairs of cells: F_i, $F_i(\mathbf{p}_i, \mathbf{q}_i)$, F_{ij}, $F_{ij}(\mathbf{p}_i, \mathbf{q}_i)$, $F_{ij}(\mathbf{p}_i, \mathbf{q}_i, \mathbf{p}_j, \mathbf{q}_j)$. $F_i(\mathbf{p}_i, \mathbf{q}_i)$ is the probability density of observing an arbitrary particle near the point $\mathbf{q}_i \in \omega_i$ with momentum close to $\mathbf{p}_i$; F_{ij} is the probability that cells i and j are empty; $F_{ij}(\mathbf{p}_i, \mathbf{q}_i)$ is the probability of observing a particle near the point $\mathbf{q}_i \in \omega_i$ with momentum $\mathbf{p}_i$ and the cell j is empty; finally $F_{ij}(\mathbf{p}_i, \mathbf{q}_i, \mathbf{p}_j, \mathbf{q}_j)$ is the probability density of observing two particles near the points $\mathbf{q}_i \in \omega_i$ and $\mathbf{q}_j \in \omega_j$ with momenta near $\mathbf{p}_i$ and $\mathbf{p}_j$, respectively.

In equilibrium statistical mechanics, the momentum and coordinate distributions are independent:

$$F_i(\mathbf{p}_i, \mathbf{q}_i) = F(\mathbf{p}_i) F_i(\mathbf{q}_i), \quad F_{ij}(\mathbf{p}_i, \mathbf{q}_i) = F(\mathbf{p}_i) F_{ij}(\mathbf{q}_i),$$
$$F_{ij}(\mathbf{p}_i, \mathbf{q}_i, \mathbf{p}_j, \mathbf{q}_j) = F(\mathbf{p}_i) F(\mathbf{p}_j) F_{ij}(\mathbf{q}_i, \mathbf{q}_j), \tag{5}$$

and

$$F(\mathbf{p}_i) = (\beta/2\pi m)^{3/2} \exp\{-\beta \mathbf{p}_i^2/(2m)\}. \tag{6}$$

It then follows that

$$\int d\mathbf{p}_i F_i(\mathbf{p}_i, \mathbf{q}_i) = F_i(\mathbf{q}_i), \quad \int d\mathbf{p}_i F_{ij}(\mathbf{p}_i, \mathbf{q}_i) = F_{ij}(\mathbf{q}_i),$$
$$\int d\mathbf{p}_i \int d\mathbf{p}_j F_{ij}(\mathbf{p}_i, \mathbf{q}_i, \mathbf{p}_j, \mathbf{q}_j) = F_{ij}(\mathbf{q}_i, \mathbf{q}_j). \tag{7}$$

The functions $F_i(\mathbf{q}_i)$, $F_{ij}(\mathbf{q}_i)$, $F_{ij}(\mathbf{q}_i, \mathbf{q}_j)$ give the distribution of particles in configuration space, and together with the functions F_i and F_{ij} they satisfy the following rigorous probability relations which follow from their definition

$$F_i + \int_i d\mathbf{q}_i F_i(\mathbf{q}_i) = 1, \quad F_i = F_{ij} + \int_j d\mathbf{q}_j F_{ij}(\mathbf{q}_j),$$
$$F_i(\mathbf{q}_i) = F_{ij}(\mathbf{q}_i) + \int_j d\mathbf{q}_j F_{ij}(\mathbf{q}_i, \mathbf{q}_j), \tag{8}$$

where the integration goes over the cell volume. This set of relations can be continued to include functions describing three, four, and higher numbers of cells. For the single-vacancy mechanism of self-diffusion with which we are principally concerned here, it is sufficient to use the above equations.

Using the mean force potentials of [15] and the pseudopotentials of [17, 18], the functions in (8) can be written in the form

$$F_i = (n_0/Q_0) \exp\{-\beta\varphi_i\}, \quad F_i(q_i) = (n/Q) \exp\{-\beta\varphi_i(\mathbf{q}_i)\},$$
$$F_{ij} = (n_0/Q_0)^2 \exp\{-\beta\varphi_{ij}\}, \quad F_{ij}(\mathbf{q}_i) = [n_0 n/(Q_0 Q)] \exp\{-\beta\varphi_{ij}(\mathbf{q}_i)\},$$
$$F_{ij}(\mathbf{q}_i, \mathbf{q}_j) = (n/Q)^2 \exp\{-\beta[\Phi(\mathbf{q}_i, \mathbf{q}_j) + \varphi_{ij}(\mathbf{q}_i, \mathbf{q}_j)]\}, \tag{9}$$
$$Q_0 = \exp\{-\beta\varphi_i\}, \quad Q = \int_i d\mathbf{q}_i \exp\{-\beta\varphi_i(\mathbf{q}_i)\}. \tag{10}$$

Here $n_0 = N_0/M$ is the concentration of empty calls, and $n = N/M$ is the concentration of particles. The quantity n_0 is determined from the extremum condition on the free energy

$$F = M\tilde{f} = -(M/\beta)[n_0 \ln(Q_0/n_0) + n \ln(Q/n)] \tag{11}$$

and has the form

$$n_0 = Q_0 \exp\{-\beta P w\}, \tag{12}$$

where the pressure is

$$P=-(\partial\tilde{f}/\partial w)_{\beta,n_0}. \tag{13}$$

Therefore, in order to get the thermodynamic properties of the system in terms of the free energy, one must know the quantities φ_i and $\varphi_i(\mathbf{q}_i)$.

The mean force potentials $\varphi_i(\mathbf{q}_i)$, $\varphi_{ij}(\mathbf{q}_i)$, $\varphi_{ij}(\mathbf{q}_i,\mathbf{q}_j)$ and the pseudopotentials φ_i and φ_{ij} are sums of the form

$$\varphi_i=\sum_{l\neq i}^{M}\varphi_{i,l},\quad \varphi_i(\mathbf{q}_i)=\sum_{l\neq i}^{M}\varphi_{i,l}(\mathbf{q}_i), \tag{14}$$

$$\begin{gathered}\varphi_{ij}=\sum_{l\neq i,j}^{M}\varphi_{ij,l},\quad \varphi_{ij}(\mathbf{q}_i)=\sum_{l\neq i,j}^{M}\varphi_{ij,l}(\mathbf{q}_i),\\ \varphi_{ij}(\mathbf{q}_i,\ \mathbf{q}_j)=\sum_{l\neq i,j}^{M}\varphi_{ij,l}(\mathbf{q}_i,\ \mathbf{q}_j).\end{gathered} \tag{15}$$

They satisfy the system of integral equations (8). However, the number of integral equations is less than the number of potentials and the system (8) is not closed. In order to close the system it is necessary to relate the potentials (15) determining the binary functions and the potentials (14) determining the singlet functions. The system can be closed by decomposing the potentials (15) into irreducible parts by using the expressions [17, 19]

$$\begin{gathered}\varphi_{ij,l}=\varphi_{i,l}+\varphi_{j,l}+\omega_{ij,l},\quad \varphi_{ij,l}(\mathbf{q}_i)=\varphi_{i,l}(\mathbf{q}_i)+\varphi_{j,l}+\omega_{ij,l}(\mathbf{q}_i),\\ \varphi_{ij,l}(\mathbf{q}_i,\ \mathbf{q}_j)=\varphi_{i,l}(\mathbf{q}_i)+\varphi_{j,l}(\mathbf{q}_j)+\omega_{ij,l}(\mathbf{q}_i,\ \mathbf{q}_j).\end{gathered} \tag{16}$$

The quantities ω are irreducible parts of the potentials. If we put

$$\omega_{ij,l}=\omega_{ij,l}(\mathbf{q}_i)=\omega_{ij,l}(\mathbf{q}_i,\ \mathbf{q}_j)=0, \tag{17}$$

which corresponds to neglecting three-particle correlations, then the binary functions are related to the singlet functions by

$$\begin{gathered}F_{ij}=\exp\{\beta[\varphi_{i,j}+\varphi_{j,i}]\}F_iF_j,\\ F_{ij}(\mathbf{q}_i)=\exp\{\beta[\varphi_{i,j}(\mathbf{q}_i)+\varphi_{j,i}]\}F_i(\mathbf{q}_i)F_j,\\ F_{ij}(\mathbf{q}_i,\ \mathbf{q}_j)=\exp\{\beta[\varphi_{i,j}(\mathbf{q}_i)+\varphi_{j,i}(\mathbf{q}_j)-\Phi(\mathbf{q}_i,\ \mathbf{q}_j)]\}F_i(\mathbf{q}_i)F_j(\mathbf{q}_j).\end{gathered} \tag{18}$$

A closed system of equations for the potentials can now be obtained by substituting (18) into the second and third of equations (8). We obtain

$$\exp\{-\beta\varphi_{i,j}\}=\exp\{\beta\varphi_{j,i}\}F_j+\int_{j}d\mathbf{q}_j\exp\{\beta\varphi_{j,i}(\mathbf{q}_j)\}F_j(\mathbf{q}_j), \tag{19}$$

$$\begin{gathered}\exp\{-\beta\varphi_{i,j}(\mathbf{q}_i)\}=\exp\{\beta\varphi_{j,i}\}F_j+\int_{j}d\mathbf{q}_j\exp\{\beta[\varphi_{j,i}(\mathbf{q}_j)\\ -\Phi(\mathbf{q}_i,\ \mathbf{q}_j)]\}F_j(\mathbf{q}_j),\end{gathered} \tag{20}$$

where the singlet functions are given by (9).

The solution of the system of integral equations (19), (20) gives all the functions (9), and through the free energy (11), the thermodynamics of the system.

In the treatment of a crystalline system, the cell of the theory is identified with the Wigner–Seitz cell, and the empty cells are interpreted as vacancies (Shottky defects).

The following function is of direct interest for the discussion below:

$$F_{ij}(\mathbf{p}_i,\ \mathbf{q}_i)=[\beta/(2\pi m)]^{3/2}\exp\{-\beta p_i^2/(2m)\}\exp\{\beta[\varphi_{i,j}(\mathbf{q}_i)+\varphi_{j,i}]\}F_i(\mathbf{q}_i)F_j. \tag{21}$$

By definition, this function is the probability density of observing a particle at the point $\mathbf{q}_i\in w_i$ with momentum $\mathbf{p}_i$ when cell j is empty (contains a vacancy) under the condition that all states of the remaining M − 2 cells are taken into account.

Jump Frequency and the Solution of the System of Integral Equations. Let cell i contain an atom and cell j be empty, and assume that these two cells are nearest neighbors on an fcc lattice. We choose a coordinate system with the origin at the center of cell i, the z axis along the line joining the centers of cells i and j, and the x and y axes perpendicular to the z axis.

We will assume that the atom in cell i jumps over into the empty cell j if it reaches any point on the boundary S_{ij} between the cells and it will thus have a positive z-component of the momentum. We average over the states of the other cells. Then the jump frequency is given by the expression [4]

$$k=\sum_{j=1}^{z_1}\int_0^{\infty}(dp_i^z/m)\int_{-\infty}^{\infty}(dp_i^x/m)\int_{-\infty}^{\infty}(dp_i^y/m)(p_i^z/m)\int_{S_{ij}}d\mathbf{q}_iF_{ij}(\mathbf{p}_i,\ \mathbf{q}_i). \tag{22}$$

This expressions differs from the analogous result in [4] in that an isolated vacancy was actually considered in [4] and it was assumed that all surrounding cells contain particles, whereas according to (22), each of the M − 2 cells can have finite probabilities of being empty or containing a single particle. Thus all of the states of the crystal are taken into account in (22) for the jump frequency.

Using the explicit form of the function $F_{ij}(\mathbf{p}_i,\ \mathbf{q}_i)$ in (21), the integration with respect to momentum in (22) can be performed immediately, and we get

$$k=z_1(2\pi\beta m)^{-1/2}\exp\{\beta\varphi_{j,i}\}\ F_j\int_{S_{ij}}d\mathbf{q}_i\exp\{\beta\varphi_{i,j}(\mathbf{q}_i)\}\ F_i(\mathbf{q}_i). \tag{23}$$

In an infinite crystal, the probability that a given cell is empty does not depend on j and $F_j = n_0$ ($j = 1, 2,\dots,M$). Using this and the explicit form of the function $F_i(\mathbf{q}_i)$, (23) can be written in the form

$$k=z_1(2\pi\beta m)^{-1/2}n_0(1-n_0)\exp\{\beta\varphi_{j,i}\}\int_{S_{ij}}d\mathbf{q}_i\exp\{\beta[\varphi_{i,j}(\mathbf{q}_i)-\varphi_i(\mathbf{q}_i)]\}/\int_{w_i}d\mathbf{q}_i\exp\{-\beta\varphi_i(\mathbf{q}_i)\}. \tag{24}$$

This is also an expression for the jump frequency of an atom in an equilibrium crystal with a concentration of vacancies equal to n_0. The integrals in this expression can be calculated knowing the solution of the system of nonlinear integral equation (19), (20) which can be obtained, for example, by numerical methods [15]. Then the integrals can be done by approximate methods, in particular, by the method of Laplace, and then the jump frequency and self-diffusion coefficient can be described in the traditional terms of a "preexponential factor" and an "activation energy."

The evaluation of the integrals in (24) must be based, as noted above, on the solution of the system of integral equations (20).

As a first step to obtaining an approximate solution of this system, we use the fact that $n_0 \ll 1$ ($n_0 \sim 10^{-3}$ to 10^{-4} near the triple point), and therefore we can look for the solution as a series in n_0 and consider the zeroth approximation [10]. The system (20) then takes the form

$$\exp\{-\beta\varphi_{i,j}\}=\int_j d\mathbf{q}_j\exp\{\beta\varphi_{j,i}(\mathbf{q}_j)\}\ F_j(\mathbf{q}_j), \tag{25}$$

$$\exp\{-\beta\varphi_{i,j}(\mathbf{q}_i)\}=\int_j dq_j\exp\{\beta\ [\varphi_{j,i}(\mathbf{q}_j)-\Phi(\mathbf{q}_i,\ \mathbf{q}_j)]\}\ F_j(\mathbf{q}_j). \tag{26}$$

Equation (26) in this approximation reduces exactly to the equation for an ideal crystal with no vacancies. An asymptotic solution can be obtained using the fact that there are sharp maxima to the function $F_j(\mathbf{q}_j)$ at the lattice points.

We write the coordinate of an atom in cell j in the form $\mathbf{q}_j = \mathbf{n}_j + \mathbf{u}_j$, where $\mathbf{n}_j$ is the coordinate of the lattice point (center of the cell) and $\mathbf{u}_j$ is the deviation of the atom from the lattice point and we have $\mathbf{u}_j\in w_j$. Then application of the Laplace evaluation of the integral in (26) with the inclusion of the first two terms of the asymptotic series gives [20]

$$\varphi_{i,j}(\mathbf{q}_i)=\Phi(\mathbf{q}_i,\ \mathbf{n}_j)-\varphi_{j,i}(\mathbf{n}_j)-\beta^{-1}\ln\{1+(1/\sigma)$$
$$\times\{\Delta\varphi_{j,i}(\mathbf{n}_j)-\Phi''(\mathbf{q}_i,\ \mathbf{n}_j)-2\Phi'(\mathbf{q}_i,\ \mathbf{n}_j)/|\mathbf{q}_i-\mathbf{n}_j|+\beta\,[\nabla\varphi_{j,i}(\mathbf{n}_j)+\Phi'(\mathbf{q}_i,\ \mathbf{n}_j)(\mathbf{q}_i-\mathbf{n}_j)/|\mathbf{q}_i-\mathbf{n}_j|]^2\}\}. \tag{27}$$

In order to calcualte the derivatives of $\varphi_{j,i}(\mathbf{q}_j)$ on the right-hand side of this relation, we differentiate the potential $\varphi_{i,j}(\mathbf{q}_i)$ the necessary number of times and then put $\mathbf{q}_i = \mathbf{n}_i$. We then obtain the system of transcendental equations

$$\varphi_{i,j}(\mathbf{n}_i)=[\Phi(n_{ij})-\beta^{-1}\ln(1-\Gamma_{ij})]/2, \tag{28}$$

$$g_{i,j}=[2\beta\Phi''(n_{ij})\,g_{i,j}-\Phi_3(n_{ij})]/[2\beta\sigma(1-\Gamma_{ij})], \tag{29}$$

$$\Delta\varphi_{i,j}(\mathbf{n}_i) = \Delta\Phi(n_{ij}) + \beta g_{i,j}^2 + [\Phi_4(n_{ij}) - 2\beta(K_{ij} + g_{i,j}\Phi_3(n_{ij}))]/[2\beta\sigma(1-\Gamma_{ij})]. \tag{30}$$

Here Δ is the Laplacian, $n_{ij} = |\mathbf{n}_j - \mathbf{n}_i|$,

$$\Gamma_{ij} = [\Delta\Phi(n_{ij}) - \Delta\varphi_{i,j}(\mathbf{n}_i) - \beta g_{i,j}^2]/(2\sigma); \ \sigma = \sum_{j\neq i}^{M} \Delta\varphi_{i,j}(\mathbf{n}_i) =$$

$$= \sum_{l=1}^{\infty}(z_l/3)\Delta\varphi_l; \ g_{i,j} = k_{i,j} + \Phi'(n_{ij}); \ k_{i,j} = |\nabla\varphi_{i,j}(\mathbf{n}_i)|; \tag{31}$$

$$\Phi_3(n_{ij}) = \Phi'''(n_{ij}) + 2[\Phi''(n_{ij}) - \Phi'(n_{ij})/n_{ij}]/n_{ij},$$

$$\Phi_4(n_{ij}) = \Phi^{(4)}(n_{ij}) + 4\Phi'''(n_{ij})/n_{ij}; \ K_{ij} = [\Phi''(n_{ij})]^2 + 2[\Phi'(n_{ij})/n_{ij}]^2, \tag{32}$$

where we use $\Delta\varphi_l$ to denote $\Delta\varphi_{i,j}(n_i)$ when cell j is located on the coordinate sphere l with respect to cell i. Finally z_l is the coordination number.

Evaluating the integral in (25) to the same accuracy, we obtain the following expression for the pseudopotential $\varphi_{i,j}$

$$\varphi_{i,j} = -\Phi(n_{ij})/2 + \beta^{-1}\ln\{(1-\Gamma_{ij})^{1/2}/[1 + (\Delta\varphi_{i,j}(\mathbf{n}_i) + \beta k_{i,j}^2)/(2\sigma)]\}. \tag{33}$$

Then for the integral in the denominator of (24) we have

$$\int_i d\mathbf{q}_i \exp\{-\beta\varphi_i(\mathbf{q}_i)\} = [2\pi/(\beta\sigma)]^{3/2}\exp\{-\beta\varphi_i(\mathbf{n}_i)\}. \tag{34}$$

We now consider the evaluation of the surface integral in (24). Here we use the fact that an explicit form of the integrand is known; it is given by (27). Analysis of the behavior of this function on the surface where the integral is to be evaluated (the boundary between the cells) shows that the function $\varphi_i(\mathbf{q}_i) - \varphi_{i,j}(\mathbf{q}_i)$ has a minimum at the point $\mathbf{s}_i = (\mathbf{n}_i - \mathbf{n}_j)/2$. This point lies midway between the centers of cells i and j. In our coordinate system, this point is given by $\mathbf{s}_i = \mathbf{s}_i(0, 0, R/2)$. The minimum of the function $\varphi_i(\mathbf{q}_i) - \varphi_{i,j}(\mathbf{q}_i)$ corresponds to the maximum of the integrand, and this we can use the Laplace method to evaluate the surface integral. We then obtain

$$\int_{S_{ij}} dq_i^x dq_i^y \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) - \varphi_i(\mathbf{q}_i)]\} = [2\pi/(\beta\sigma_s)]\exp\{\beta[\varphi_{i,j}(\mathbf{s}_i) - \varphi_i(\mathbf{s}_i)]\}, \tag{35}$$

where

$$\sigma_s = (1/2)(\nabla_{ix}^2 + \nabla_{iy}^2)[\varphi_i(\mathbf{s}_i) - \varphi_{i,j}(\mathbf{s}_i)]. \tag{36}$$

The second derivatives of the potentials at $\mathbf{s}_i$ appearing here can be evaluated directly by differentiating expression (27).

Coefficient of Self-Diffusion. Comparison of Calculated and Experimental Results. Using our result for the jump frequency (24) we can write

$$k = \nu\exp\{-\beta E\}, \tag{37}$$

where the so-called effective frequency is

$$\nu = z_1(\sigma/m)^{1/2}(\sigma/2\pi\sigma_s), \tag{38}$$

and

$$E = \varphi_j + Pw + [\varphi_i(\mathbf{s}_i) - \varphi_i(\mathbf{n}_i)] - [\varphi_{i,j}(\mathbf{s}_i) + \varphi_{j,i}] \tag{39}$$

is a quantity with the dimensions of energy. We analyze the terms in this expression:

$$g_v = \varphi_j + Pw, \tag{40}$$

the Gibbs potential for the formation of vacancies, and

$$E_m = \varphi_i(\mathbf{s}_i) - \varphi_i(\mathbf{n}_i) \tag{41}$$

can be interpreted as a vacancy migration energy; it is the difference of the mean force potentials $\varphi_i(\mathbf{q}_i)$ acting on an atom in cell i at the boundary of the cells (at the saddle-point $\mathbf{s}_i$) and at the lattice point $\mathbf{n}_i$. The quantity E_m, as can be seen by comparing with the rigorous expression for the free energy (11), cannot be given a thermodynamic interpretation, as in the theory of absolute reaction rates [21].

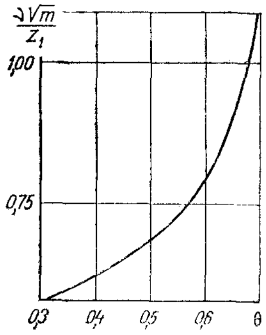

Fig. 1

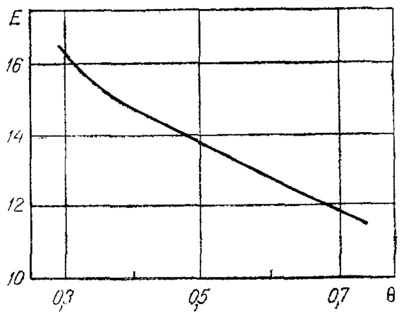

Fig. 2

Fig. 1. Dependence of the effective frequency on temperature [calculated from Eq. (38)] for P = 0.

Fig. 2. Dependence of the diffusion activation energy on temperature [calculated from Eq. (39)] for P = 0.

The quantity

$$\Delta E_m = \varphi_{i,j}(\mathbf{s}_i) + \varphi_{j,i} \tag{42}$$

is a correction to the migration energy due to atom-vacancy correlations. Indeed, the function $F_{ij}(\mathbf{q}_i)$, determining this correlation, can be represented in the form

$$F_{ij}(\mathbf{q}_i) = [1 + g_{ij}(\mathbf{q}_i)]\, F_i(\mathbf{q}_i)\, F_j, \tag{43}$$

where

$$g_{ij}(\mathbf{q}_i) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i) + \varphi_{j,i}]\} - 1 \tag{44}$$

is a factor characterizing the atom-vacancy correlations (not to be confused with the correlation coefficient f, describing the degree of independence of the migration of an atom; see below). If $g_{ij}(\mathbf{q}_i)$ is zero at the saddle-point

$$g_{ij}(\mathbf{s}_i) = 0, \tag{45}$$

then

$$F_{ij}(\mathbf{s}_i) = F_i(\mathbf{s}_i)\, F_j. \tag{46}$$

This means that the probability of simultaneously observing an atom at the point s_i and a vacancy in cell j is equal to the product of the corresponding singlet probabilities. But it then follows at once from (45) and (46) that $\Delta E_m = 0$. Thus, ΔE_m does represent a correlation correction to the migration activation energy.

Therefore, the self-diffusion coefficient of vacancies can be written in the form

$$D = (\nu R^2/6)\exp\{-\beta E\}, \tag{47}$$

where

$$E = g_v + E_m - \Delta E_m. \tag{48}$$

In comparing the calcualted self-diffusion coefficient with experiment, it must be noted that the self-diffusion coefficient of vacancies is not actually measured in experiment, but that of tracer atoms D*, and this is related to D via the correlation coefficient

$$D^* = fD. \tag{49}$$

For an fcc lattice, f = 0.78146 [2].

The numerical calculations were performed for a crystal of particles interacting with the Lennard–Jones (6-12) potential:

$$\Phi(r) = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6]. \tag{50}$$

All energies expressed in units of the potential well depth ε, lengths in units of r_0, volumes in units of r_0^3, pressures in units of ε/r_0^3. The quantities $\nu\sqrt{m}/z_1$, E, $\ln\sqrt{m}D^*$ were calculated (Figs. 1 through 4). In this way, the computational results are dimensionless and valid for all r_0 and ε.

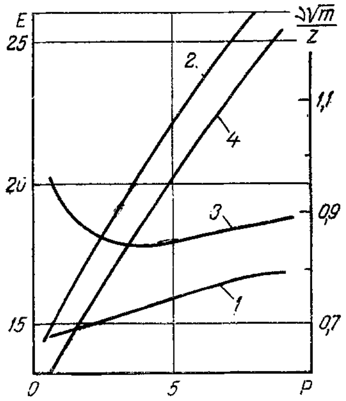

Fig. 3

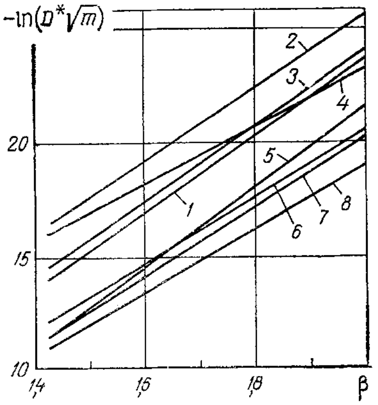

Fig. 4

Fig. 3. Dependence of the frequency and diffusion activation energy on pressure for $\theta = 0.5$ (curves 1 and 2) and $\theta = 0.7$ (curves 3 and 4).

Fig. 4. Dependence of the coefficient of self-diffusion on the reciprocal of the temperature: 1) calculated according to (47); the other curves are experimental; 2) Ar [22]; 3) Xe [23]; 4, 7) Ar [24]; 5) Ar [25]; 6) Kr [26]; 8) Kr [27].

We see from Fig. 1 that the dependence of ν on T is nonlinear.

In the region $\theta \geqslant 0.4$, the energy depends almost linearly on temperature (Fig. 2), which supports cutting off an expansion of the energy in a series in the temperature at the linear term [4]. However, at low temperatures other terms in the expansion must be taken into account.

In Fig. 4 we show the measurements of the self-diffusion coefficient in the rare gas crystals [22-27]; the experimental values are shown in reduced units $r_0(\varepsilon/m)^{1/2}$ as a function of the reciprocal of the temperature. Curve 1 in Fig. 4 was calculated according to (47) and shows a weak convexity. The experimental results for the self-diffusion coefficient were analyzed with the help of the Arrhenius formula

$$D = D_0 \exp\{-\beta H\}, \qquad (51)$$

where D_0 and H are constants independent of the temperature, and chosen such that the experimental data best approximates a straight line when plotted using the variables $\ln D$ and β. Although in these variables the results from (47) display a nearly linear dependence, calculations of ν and E (Figs. 1 and 2) show that they cannot be considered as constants independent of temperature.

LITERATURE CITED

1. S. Chandrasekar, Stochastic Problems in Physics and Astronomy [Russian translation], IL, Moscow (1947).
2. J. Manning, Kinetics of the Diffusion of Atoms in Crystals [Russian translation], Mir, Moscow (1971).
3. B. S. Bokshtein, S. Z. Bokshtein, and A. A. Zhukhovitskii, Thermodynamics and Kinetics of Diffusion in Solids [in Russian], Metallurgiya, Moscow (1974).
4. H. R. Glyde, "Rate processes in solids," Rev. Mod. Phys., 39, No. 2, 373-382 (1967).
5. S. A. Rice, "Dynamical theory of diffusion in crystals," Phys. Rev., 112, No. 3, 804-811 (1958).
6. O. P. Manley, "A method of evaluating diffusion coefficients in crystals," J. Phys. Chem. Solids, 13, Nos. 3/4, 244-250 (1960).
7. G. H. Vineyard, "Frequency factors and isotope effects in solid state rate processes," J. Phys. Chem. Solids, 3, Nos. 1/2, 121-127 (1957).
8. H. R. Glyde, "Vacancies in argon," J. Phys. Chem. Solids, 27, No. 10, 1659-1665 (1966).
9. E. T. Brook-Levinson and V. V. Belov, "Statistical method for the description of the equilibrium properties of materials at arbitrary values of the density," Dokl. Akad. Nauk BSSR, 24, No. 9, 805-808 (1980).

10. E. T. Brook-Levinson and A. V. Zakharov, "Statistical theory of vacancies in an equilibrium crystal," Dokl. Akad. Nauk BSSR, No. 6, 514-517 (1981).
11. E. T. Brook-Levinson and A. V. Zakharov, "Statistical thermodynamics of Shottky defects in molecular and ionic crystals," Inzh.-Fiz. Zh., 44, No. 2, 244-250 (1983).
12. V. V. Belov and E. T. Brook-Levinson, "Clusters of vacancies in crystals: Statistical description," Izv. Akad. Nauk BSSR, Ser. Fiz.-Mat. Nauk, No. 6, 91-97 (1983).
13. E. T. Brook-Levinson and O. D. Chernetsov, "Vacancy correlation factor and small clusters of vacancies in an equilibrium crystal," Phys. Lett., 91A, No. 4, 171-173 (1982).
14. E. T. Brook-Levinson and O. D. Chernetsov, "Statistical theory of vacancy interactions in heavy rare gas crystals," Fiz. Nizk. Temp., 10, No. 5, 576-584 (1984).
15. L. A. Rott, Statistical Theory of Molecular Systems [in Russian], Nauka, Moscow (1979).
16. Yu. L. Klimontovich, Statistical Physics [in Russian], Nauka, Moscow (1983).
17. E. T. Brook-Levinson, "Self-consistent statistical theory of vacancies in an equilibrium crystal without using the minimum condition on the thermodynamic potential," Dokl. Akad. Nauk BSSR, 25, No. 12, 1085-1088 (1981).
18. E. T. Brook-Levinson and V. V. Belov, Statistical Theory of Equilibrium Systems at Arbitrary Densities [in Russian], Minsk (1983) (Preprint No. 3, Inst. of Heat and Mass Transfer, Academy of Sciences of the BSSR).
19. V. V. Belov and E. T. Brook-Levinson, "A statistical-mechanical explanation of crystal line structure of the heavier rare gas solids," Phys. Lett., 80A, No. 4, 314-316 (1980).
20. E. T. Brook-Levinson and V. V. Belov, "Statistical theory of thermodynamic and structural properties of molecular crystals," Inzh.-Fiz. Zh., 40, No. 1, 126-133 (1980).
21. S. Glesston, K. Leider, and G. Airing, Theory of Absolute Reaction Rates [Russian translation], IL, Moscow (1948).
22. E. H. C. Parker, H. R. Glyde, and B. L. Smith, "Self-diffusion in solid argon," Phys. Rev., 176, No. 3, 1107-1110 (1968).
23. W. M. Yen and R. E. Norberg, "Nuclear magnetic resonance of Xe^{129} in solid and liquid xenon," Phys. Rev., 131, No. 1, 269-275 (1963).
24. A. Berne, G. Boato, and M. De Paz, "Experiments on solid argon," Nuovo Cimento, 46B, No. 2, 182-209 (1966).
25. A. Berne, G. Boato, and M. De Paz, "Self-diffusion coefficient in solid argon," Nuovo Cimento, 24, No. 6, 1179-1181 (1962).
26. D. G. Cowgill and R. E. Norberg, "Pulsed NMR studies of self-diffusion and defect structure in liquid and solid krypton," Phys. Rev. B, 13, No. 7, 2773-2781 (1976).
27. A. V. Chadwick and J. A. Morrison, "Self-diffusion in solid krypton," Phys. Rev. B, 1, No. 6, 2748-2753 (1970).

CARBON COMBUSTION IN CYLINDRICAL CHANNELS WITH EDDY WASHING OF THE WALL

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The article presents the experimentally determined dependences of carbon combustion on the wall of a model of a cyclone chamber and of the air excess number at the outlet from the model on a number of design and regime factors.

It is known [1, 2] that the combustion process of a carbon channel is the most interesting problem (the so-called "internal" problem) in studying heterogeneous combustion of carbon; its importance does not only concern the development of the theory of this process, it also has a direct bearing on the operation of real heating and technological installations. Of special interest is the investigation of the regularities of the burning of carbon in a cylindrical channel with rotary (cyclone) motion of the stream. In this case there is full analogy with the process occurring in cyclone furnaces where part of the fuel is burned after separation on the chamber wall [3]. If we take into account the known features of the interaction of the separating particles with the slag film covering the furnace wall [4] and

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