of electrons, ions, and excited atoms with ground-state atoms, and the electron yields due to ions, excited atoms, and photons are known. At present the only gas for which this information is available is helium. Even in the case of helium, our knowledge of such processes as molecular ion formation from highly excited atoms and the net yield of electrons from cathode surfaces is unsatisfactory and constitutes a possible source of significant error in our calculation.

Our conclusion that the net effect of resonance radiation can be described in much the same manner as the effect of delayed nonresonance photons is one more example of the fact that the transport of resonance radiation cannot be treated properly using conventional diffusion theory. Thus, the time constant characteristic of the resonance radiation, $1/A_I$, varies as the square root of the electrode separation and is independent of gas density while the time constant characteristic of conventional diffusion, Nd^2/D_a, is directly proportional to the gas density and to the square of the electrode separation.

Two outstanding features of the analysis presented in this paper are the complexity of the problem and the fact that none of the processes found to control the current buildup in helium are the simple processes involving atomic ions, atomic metastables, and nonresonance photons usually considered in the analysis of experimental data. Examination of available data as to ion and excited atom behavior in neon and argon suggests that the existence of four closely-spaced metastable and resonance states would lead to more complicated calculations than for helium. The calculations are not expected to be significantly simpler in the molecular gases except possibly in the case of hydrogen where there are no metastable molecules[15] and where the time required for the destruction of metastable atoms and for an H_2^+ ion to be converted into an H_3^+ ion[43] is believed to be very short.

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[43] Eyering, Hirshfelder, and Taylor, J. Chem. Phys. 4, 479 (1936).

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Dynamical Theory of Diffusion in Crystals*

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Corrections to a previous paper by the second author are presented. A calculation leading to the simplification of the pair correlation functions is also presented.

THE purpose of this brief paper is twofold: to correct some errors in a previous article,[1] and to extend the utility of the theory by demonstrating a great simplification of the pair correlation function. It is to be emphasized at the outset that the errors in no way alter the physical arguments advanced by Rice or the final formulation of the diffusion coefficient.

We proceed by remarking that the dynamical theory presented previously is based on the Einstein relation

$$\mathfrak{D}=\tfrac{1}{2}\Gamma(\Delta x)^2, \tag{1}$$

with Γ the frequency of atomic jumps and Δx the length of a jump. Equation (1) is conveniently rewritten in the form

$$\mathfrak{D}=[(\Delta x)^2/2]\sum_{\text{n.n.}}\varphi\tilde{P}(\{\delta\}), \tag{2}$$

with φ the site fraction of vacancies, and $\tilde{P}(\{\delta\})$ the frequency of occurrence of a configuration in which the migrating atom has large amplitude of vibration properly oriented and there is a properly phased motion of the surrounding atoms. The summation is to be taken over all atoms that can jump into the vacancy. This usually consists of just the nearest neighbors and has been so indicated by n.n. Following the arguments

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[1] S. A. Rice, Phys. Rev. 112, 804 (1958).

presented by Rice[1] $\tilde{P}(\{\delta\})$ is given by

$$\tilde{P}(\{\delta\}) \propto \int \Gamma_1 \frac{P^{(h)}(q_1 \cdots q_h)}{e^{-U_0/kT}} \prod_{j=1}^{h} \delta(q_j - q_{j0}) dq_j, \quad (3)$$

with Γ_1 the frequency with which the migrating atom, treated as independent, attains the critical configuration and where $P^{(h)}$ is the joint probability of finding particles 1, $\cdots$, h within the ranges $dq_1 \cdots dq_h$ about $q_1 \cdots q_h$. The factor $\exp(-U_0/kT)$ arises from the requirement that the jump frequency be conditioned on $q_1 = q_0$. Finally, the factor $\prod_{j=1}^{h} \delta(q_j - q_{j0})$ arises from the assumption that there is a negligible contribution from all configurations with values of $q_j > q_{j0}$, since the state wherein $q_j = q_{j0}$ is already one which occurs with low probability. The joint probability $P^{(h)}$ is related to the probability density $\tilde{P}^{(h)}$ defined in Eq. (R-20)[2] by

$$P^{(h)} = v^h \tilde{P}^{(h)}, \quad (4)$$

with v a free volume to be determined subsequently. Note that a factor v^h is missing in the first form of Eq. (R-32).

Consider now the displacements q_1 and q_2. In the $3N$ dimensional cartesian coordinate system (we neglect the 6 translation and rotation coordinates of the crystal as a rigid body) these represent displacements of atoms 1 and 2 in specified directions along unit coordinate axes. We have[3]

$$\tilde{P}^{(2)}(q_1 q_2) = \tilde{P}^{(1)}(q_1) \tilde{P}^{(1)}(q_2) g_{12}^{(2)} = \frac{\int e^{-U/kT} dq_3 \cdots dq_{3N}}{\int e^{-U/kT} dq_1 \cdots dq_{3N}}, \quad (5)$$

where

$$2U = \sum_{i,j=3} a_{ij} q_i q_j + 2 \sum_{i=3} a_{1i} q_1 q_i + 2 \sum_{j=3} a_{2j} q_2 q_j + a_{1,} q_1^2 + 2 a_{12} q_1 q_2 + a_{22} q_2^2, \quad (6)$$

which may be rewritten (note the factors of 2)

$$2U = \sum_{i=3} m \omega_i'^2 Q_i^2 + 2 \sum_{l,i=3} a_{1i} q_{1l} R_{il} Q_l + 2 \sum_{l',j=3} a_{2j} q_2 R_{jl'} Q_{l'} + a_{11} q_1^2 + 2 a_{12} q_1 q_2 + a_{22} q_2^2, \quad (7)$$

where ω_i' is the ith eigenfrequency of the crystal when the two degrees of freedom are constrained, Q_i is the corresponding normal mode and R_{il} is a component of the modal matrix $\mathbf{R}$. By completing the square

$$\tilde{P}^{(2)}(q_1, q_2) = \left[\prod_{\mu=3}^{3N} (2\pi kT/m\omega_\mu'^2)^{\frac{1}{2}} \Big/ \prod_{\mu=1}^{3N} (2\pi kT/m\omega_\mu^2)^{\frac{1}{2}} \right] \times \exp\left[\frac{1}{2kT} \sum_{\mu=3}^{3N} \frac{L_\mu^2}{m\omega_\mu'^2} \right] \times \exp[-(1/2kT)(a_{11} q_1^2 + 2 a_{12} q_1 q_2 + a_{22} q_2^2)], \quad (8)$$

with ω_μ the angular frequency of the μth mode when there are no constraints. We have here used the fact that the determinant of the transformation matrix has the value unity. Moreover, L_μ is related to the normal eigenvector R_{il}, corresponding to column i of the transformation matrix by [note the factor of $\sqrt{2}$ difference from (R-31)]

$$L_\mu = \sum_{i=3}^{3N} (a_{1i} q_1 + a_{2i} q_2) R_{i\mu}. \quad (9)$$

Consider now the sum

$$\sum_{\mu=3}^{3N} \frac{L_\mu^2}{m\omega_\mu'^2} = \sum_{\mu=3} \sum_{l,m=3} (a_{1l} q_1 + a_{2l} q_2)(a_{1m} q_1 + a_{2m} q_2) \frac{R_{l\mu} R_{m\mu}}{m\omega_\mu'^2} = \sum_{l,m=3} (a_{1l} q_1 + a_{2l} q_2)(a_{1m} q_1 + a_{2m} q_2) \sum_{\mu=3} \frac{R_{l\mu} R_{m\mu}}{m\omega_\mu'^2}. \quad (10)$$

By the definition of the modal matrix,[4]

$$\mathbf{R}^{-1} \boldsymbol{\beta} \mathbf{R} = \boldsymbol{\kappa}, \quad (11)$$

with $\boldsymbol{\beta}$ the matrix of the coefficients a_{ij}, $i, j \neq 1, 2$ and $\boldsymbol{\kappa}$ the matrix of the eigenfrequencies. Noting that $\boldsymbol{\beta}^{-1} = \mathbf{R} \boldsymbol{\kappa}^{-1} \mathbf{R}^{-1}$, we have

$$(\beta^{-1})_{ij} = \sum_{\mu=3} \frac{R_{i\mu} R_{j\mu}}{m\omega_\mu'^2}. \quad (12)$$

The substitution of (12) into (10) leads to three terms, the first of which is

$$q_1^2 \Big[a_{11} - \sum_{l,m \neq 1,2} \beta_{lm}^{-1} a_{1l} a_{1m} \Big] = (q_1^2/|\beta|)(a_{11}|\beta| - \sum_{l,m \neq 1,2} a_{1l} B_{lm} a_{1m}), \quad (13)$$

with B_{lm} the cofactor of β_{lm}. The right-hand side of (13) may be rewritten as $q_1^2(|\beta'|/|\beta|)$ with $\beta_{ij}' = a_{ij}$, $i, j \neq 2$. Proceeding in a similar manner the other

[2] Equations prefixed by R refer to reference 1.

[3] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, New York, 1956).

[4] See for example F. B. Hildebrand, *Methods of Applied Mathematics* (Prentice-Hall, Inc., Englewood Cliffs, 1952).

terms may be evaluated. The final result is

$$\tilde{P}^{(2)}(q_1q_2)=\left(\prod_{\mu=1}^{3N}\omega_\mu\Big/\prod_{\mu=3}^{3N}\omega_\mu'\right)\frac{m}{2\pi kT}\times\exp\left\{-\frac{1}{kT}\left[\frac{\alpha_1^2}{\alpha_1'^2}U_1+\frac{\alpha_2^2}{\alpha_2'^2}U_2+\frac{2\alpha_1\alpha_2}{\sum\alpha_{1s}'\alpha_{2s}'}(U_1U_2)^{\frac{1}{2}}\right]\right\} \quad (14)$$

where

$$\alpha_j^2=\textstyle\sum_k\alpha_{jk}^2,\quad U_j=q_{j0}^2/\sum_k\alpha_{jk}^2,\qquad \alpha_j'^2=\sum_k\alpha_{jk}'^2, \quad (15)$$

with the coefficients α_{jk} being the weight of the kth normal mode contribution to the displacement q_j. Similarly, α_{jk}' is the weight of the kth normal mode contributing to the displacement q_j when the degree of freedom corresponding to q_k is constrained. Note that as the distance between the atoms whose displacements are q_1 and q_2 increases, $\alpha_i^2/\alpha_i'^2\to 1$, $\alpha_1\alpha_2/\sum\alpha_{1s}'\alpha_{2s}'\to 0$ and therefore

$$\lim_{R_{12}\to\infty}\tilde{P}^{(2)}(q_1,q_2)=\frac{1}{\pi\langle q^2\rangle}\exp[-(1/kT)(U_1+U_2)], \quad (16)$$

where $\langle q^2\rangle$ is the mean square displacement and we have used the fact that the ratio of the product of the frequencies is, to a good approximation, the product of the two highest frequencies in the crystal. The mean square displacement is to be evaluated for these high frequencies from

$$\langle q_\mu^2\rangle=2kT/m\omega_\mu^2. \quad (17)$$

We are now ready to turn to the critical question of normalization. By the definition in Eq. (5) {note the $v^{\frac{3}{2}}$ and the change in sign of the L_μ^2 term when compared to (R-30) as well as the factor $\exp[(U_1+U_2)/kT]$}

$$g_{12}^{(2)}=v^{\frac{3}{2}}\left[\prod_{\mu=3}^{3N}(2\pi kT/m\omega_\mu'^2)^{\frac{1}{2}}\Big/\prod_{\mu=1}^{3N}(2\pi kT/m\omega_\mu^2)^{\frac{1}{2}}\right]\times\exp\left[\frac{1}{2kT}\sum\frac{L_\mu^2}{m\omega_\mu'^2}\right]\exp[(U_1+U_2)/kT]\times\exp[-(1/2kT)(a_{11}q_1^2+2a_{12}q_1q_2+a_{22}q_2^2)]. \quad (18)$$

To calculate the free volume v we use the condition

$$\lim_{R_{12}\to\infty}g_{12}^{(2)}=1, \quad (19)$$

so that

$$\tilde{P}^{(1)}(q_i)=e^{-U_i/kT}/(\pi\langle q^2\rangle)^{\frac{1}{2}}, \quad (20)$$

and

$$v=(\pi\langle q^2\rangle)^{\frac{3}{2}}. \quad (21)$$

It is pertinent at this point to make some further comments about the assumptions involved in the theory proposed by Rice.[1] First note that the jump of an atom into a neighboring vacancy may be accomplished not only when the shell atoms have exactly the critical amplitude, but also when this amplitude is exceeded. If the critical configuration is already improbable, the integration over even more improbable states should give a negligible contribution. Just this point is being investigated in detail by one of us[5] (OPM) and will be published along with an alternative formulation which appears to lead to results equivalent to the first presentation.[1] Second, note that Eq. (8) would appear to eliminate the necessity of considering the pair correlation functions. In a formal sense this is true since $g_{12}^{(2)}$ is defined in terms of $P^{(2)}$ by Eq. (5). However, as in the theory of fluids, there are advantages to considering the motion of atoms at first as independent and then correcting for the correlation. This is particularly useful when model considerations are used as is shown in a separate publication.[6] The decomposition into independent probabilities multiplied by a correlation function is, of course, just the decomposition of Eq. (5). Finally, we note that none of the corrections have modified the physical arguments advanced by Rice[1] but only the details of the calculation of $g_{12}^{(2)}$. The reduction of the pair correlation function exhibited in Eq. (18) should greatly facilitate numerical computation.

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[5] O. P. Manley (to be published).
[6] Corneliussen, Lawson, Nachtrieb, and Rice (to be published).