Quantum theory of light-interstitial hopping

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The light-interstitial hopping process is reviewed by taking a statistical viewpoint of the lattice-trap integral. The validity of applying the central-limit theorem to the integral is tested by the Lindeberg-Feller and Liapounov conditions. Both are satisfied in the high-temperature limit. At low temperatures, the factor $\hbar\omega_D/E_a$ becomes decisive for the effectiveness of the closed-form Gaussian solution which shows a T^6 rate law below 0.1 of the Debye temperature. The conditions are used to investigate several systems.

INTRODUCTION

Recently, light-interstitial diffusion in solids has attracted considerable attention,[1-9] partially due to its nonclassical behavior at low temperatures. Such behavior requires quantum interpretations. Stoneham and Flynn[1] have applied the small-polaron theory[10,11] to successfully interpret the diffusion of light-interstitials in several systems.[2] Their method utilizes the adiabatic approximation in accounting for the hopping transition between two neighboring Wannier states, by-passing the conceptual difficulty of requiring the existence of a transition state in classical thermodynamic approaches.[12] In the Stoneham-Flynn method, discussion focuses on the lattice-trap integration. Their analysis, neglecting the diagonal transitions, yields a classical Arrhenius formula at high temperatures, with good agreement between the calculated activation energies and the experimental data, and a T^7 hopping rate at low temperatures.

At low temperatures, the tunneling process[1-7,13] of T^{-9} behavior has frequently been discussed, although an experiment has never revealed its existence. The tunneling process of an interstitial could be repressed, and thus become diagonal hopping, by the residual stresses induced by various crystal defects, including other interstitials. In fact, the term, "diagonal tunneling" could be misleading since there exists a coordinate transformation in configuration space accompanying the transition; that is, a screw symmetry is associated, in configuration space, with the defect movements. Thus the lattice trapping means more than an energy barrier. This complexity will be analyzed in a future report. We will here, therefore, only consider the hopping mechanism which arises from the Fermi golden-rule formulation used by Stoneham and Flynn, as well as others.

Recently, Teichler[8] and Lagos[9] have used a Gaussian formula to interpret the μ^+ diffusion data. However, these solutions lack a rigorous mathematic basis. In the following we will take a statistical viewpoint of the overlap integral, and discuss the validity of the Gaussian closed-form solution of the hopping process.

FORMULATION

In the framework of the Stoneham-Flynn method, the hopping rate between two nearest-neighbor Wannier states $|p,n\rangle$ and $|p',n'\rangle$ is written as

$$W_{pp'}=\left\langle \frac{2\pi}{\hbar}|J_{pp'}|^2\sum_{n_q'}\prod_q f_{pp'}(n_q',n_q)\delta(\hbar\tilde{\omega})\right\rangle_{\bar{n}_q} . \quad (1)$$

Here, $J_{pp'}$ is the interstitial transition matrix element between the two localized positions, $f_{pp'}$ is the overlap integral of the lattice part, the δ function ensures the conservation of energy of the processes, with $\tilde{\omega}=\sum_q \omega_q(n_q'-n_q)$, and $\langle\ \rangle_{\bar{n}_q}$ takes the thermal average over all modes. Explicitly, we have[14]

$$f_{pp'}(n_q,n_q)=1-(n_q+\tfrac{1}{2})\frac{\omega_q}{\hbar}(\Delta Q_q)^2+O((\Delta Q_q)^4) , \quad (2a)$$

$$f_{pp'}(n_q+1,n_q)=f_{pp'}(n_q,n_q+1)=\tfrac{1}{2}(n_q+1)\frac{\omega_q}{\hbar}(\Delta Q_q)^2+O((\Delta Q_q)^4) , \quad (2b)$$

$$f_{pp'}(n_q+2,n_q)=f_{pp'}(n_q,n_q+2)=O((\Delta Q_q)^4) , \quad (2c)$$

$$f_{pp'}(n_q+3,n_q)=f_{pp'}(n_q,n_q+3)=O((\Delta Q_q)^6) , \quad (2d)$$

etc. Here, ΔQ_q is the change of the mean displacement of mode q resulting from the jump which can be expressed as[15]

$$\Delta Q_q=\frac{i}{3}\left[\frac{M_0}{N}\right]^{1/2}\frac{\delta V}{\Omega}\frac{1+\nu}{1-\nu}(e^{-i\vec{q}\cdot\vec{d}}-1)\frac{1}{q}\frac{\sin(qr_0)}{qr_0} \quad (3)$$

in the continuum approximation. Here, M_0, Ω, and ν are the atomic mass, volume, and Poisson ratio of the solvent solid, δV and $\vec{d}$ are the dilatation and jump vector, respectively, of the diffusing interstitial, and r_0 is a core parameter equivalent to the starting of the lattice sum in evaluating ΔQ_q, and is usually taken as zero as an approximation. Note that ΔQ_q is of the order $N^{1/2}$, N being the number of active modes involved in the jump process. With mode independence and the linearity of the functions of n_q in Eqs. (2), when N is large, Eq. (1) can readily be transformed into the formula generally adapted by the previous reports.[1,10,11,14] However, we will take a dif-

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ferent viewpoint of the equation and try to analyze it by statistical methods.

By setting $s_q = n_q' - n_q$ and with suitable change of the sum and product sequences in Eq. (1), the overlap part of the equation can be alternatively written as[16]

$$F = \sum_{s_q=-\infty}^{+\infty} \prod_q \langle f_{pp'}(s_q, n_q)\rangle_{n_q} \delta(\hbar\tilde{\omega}) \ . \tag{4}$$

This formulation is exactly the same as presented in random-walk problems,[17] with random variables $\hbar\omega_q s_q$ and discrete probability distributions $\langle f_{pp'}(s_q, n_q)\rangle_{n_q}$. Here we are asking for the probability distribution of the sum variable $\hbar\tilde{\omega} = \sum_q \hbar\omega_q s_q$, subject to energy conservation as stated by $\delta(\hbar\tilde{\omega})$. The normalization of the total probability is automatically maintained, as manifested by Eqs. (2).

Owing to the discreteness of the probability distributions of Eqs. (2) and, more seriously, the finite variance of Eq. (4) as the number of modes become infinite, the convergence of Eq. (4) becomes complicated.[18] Since the general solution is not available, we will focus on the validity of the central-limit theorem, which will be applicable with restrictions to be discussed in the next section. However, let us first assume that the central-limit theorem is applicable. If it is, then the solution of Eq. (4) is a normal distribution, and the transition rate reads[16]

$$W_{pp'} = \frac{2\pi}{\hbar} |J_{pp'}|^2 \frac{1}{(2\pi\sigma^2)^{1/2}} \exp[-\tfrac{1}{2}(\mu/\sigma)^2] \ , \tag{5}$$

with the mean

$$\mu = \sum_q \frac{\omega_q^2}{2} (\Delta Q_q)^2 = 4E_a \ , \tag{6a}$$

$$E_a = \sum_q \tfrac{1}{2}\omega_q^2 (\Delta Q_q/2)^2 = \sum_q \epsilon_q \ , \tag{6b}$$

and the variance

$$\sigma^2 = \hbar \sum_q (\langle n_q\rangle + \tfrac{1}{2}) \omega_q^3 (\Delta Q_q)^2 \ . \tag{7}$$

Here, E_a is the lattice-trap energy. Notice that the diagonal hoppings are included in the solution. Defining an effective temperature T_e by

$$k_B T_e = \sigma^2/8E_a \ , \tag{8}$$

We then have

$$W_{pp'} = (\pi/4\hbar^2 E_a k_B T_e)^{1/2} |J_{pp'}|^2 \exp(-E_a/k_B T_e) \ . \tag{9}$$

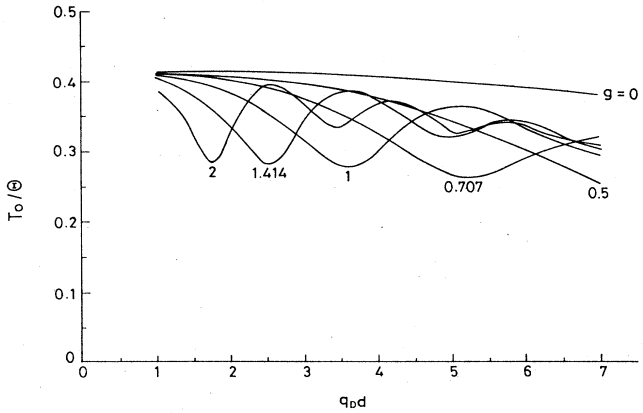

FIG. 1. Variation of the effective temperature at 0 K, T_0, as functions of the Debye wave vector q_D and the core distortion parameter $g = r_0/d$. d is the impurity jump distance and r_0 is defined in Eq. (3).

At high temperatures, $z_q = k_B T/\hbar\omega_q \gg 1$, and

$$\langle n_q\rangle + \tfrac{1}{2} = z_q + \tfrac{1}{12} z_q^3 - \tfrac{1}{720} z_q^4 + \tfrac{1}{30240} z_q^5 - \cdots \simeq z_q \ . \tag{10}$$

Combining Eqs. (8)–(10), Eq. (9) becomes the classical form obtained by Stoneham and Flynn. The expansion of Eq. (10) indicates that T_e deviates from the true temperature only about 4% at the Debye temperature Θ. At the extreme low temperature, T_e approaches a constant T_0 defined as

$$k_B T_0 = \sum_q \hbar\omega_q^3 (\Delta Q_q)^2/16E_a \ . \tag{11}$$

For the Debye solids, T_0 is close to 40% of Θ, as shown in Fig. 1.

Equation (9) is the same as obtained by Lagos.[9] In fact, his treatment of the conventional lattice-trap integral is just an alternative version of the central-limit solution, and like here, requires the more rigorous mathematic treatment to be carried out below.

APPLICABILITY OF CENTRAL-LIMIT THEOREM

We will try to utilize the Liapounov theorem as well as the Lindenberg-Feller theorem[19] to test the validity of Eq. (5). Both theorems are suitable for discrete probability distributions.

We define a "normed" random variable

TABLE I. Values of η_0 at various temperatures calculated according to Eq. (16).

System	Θ (K)	E_a (eV)	η_0 $T/\Theta=3$	$=2$	$=1$	$=\frac{1}{2}$	$=0$
H:Ta (bcc)	262	0.18[a]	0.042	0.062	0.12	0.23	0.31
H:Nb (bcc)	241	0.15[a]	0.044	0.065	0.13	0.24	0.33
H:Fe (bcc)	477	0.06[a]	0.097	0.15	0.29	0.54	0.73
N:Fe (bcc)	477	0.55[a]	0.032	0.048	0.095	0.18	0.24
μ^+:Cu (fcc)	343	0.109[b]	0.061	0.091	0.18	0.34	0.46
			$T_e = 1.01T$	$=1.021T$	$1.042T$	$=1.17T$	$\sim 0.4\Theta$

[a]Stoneham and Flynn, Ref. 1.
[b]From Lagos, Ref. 9.

$$x_q=(\hbar\omega_q s_q-8\epsilon_q)/\sigma \tag{12}$$

for mode q. The sum variable $S=\sum_q x_q$ will converge in distribution to the unit normal Φ, (1) if the third absolute moment,

$$\Gamma_N=\sum_q\sum_{x_q}|x_q|^3 f(x_q)\to 0 \quad \text{(Liapounov)}\,, \tag{13}$$

as $N\to\infty$, provided that the random variables are "holospoudic";[19] (2) or if, and only if,

$$B_N=\sum_q\sum_{x_q>\eta}|x_q|^2 f(x_q)\to 0 \quad \text{(Lindeberg-Feller)}\,, \tag{14}$$

as $N\to\infty$, η is an arbitrary positive number. Holospoudicity, which is the negligibility of the individual terms in S compared to S itself, is included in Eq. (14). Therefore, the condition (14) is stronger than Eq. (13), which could break down if only a few strong interactive local modes are associated with the hopping interstitial impurity. In the continuum approximation, Eqs. (2) and (3) ensure that the random process is holospoudic.

From Eqs. (12), as $N\to\infty$, $\epsilon_q\to 0$ and

$$\max_q\{|x_q|\}=\hbar\omega_D/(8k_BT_eE_a)^{1/2}<\eta \tag{15}$$

as $T\to\infty$. Hence the Lindeberg-Feller condition is strictly satisfied. The Gaussian is the exact solution for high-temperature hopping. The same result can be proved from the Liapounov condition. At low temperatures, condition (13) is approximately true if $|x_q|\ll 1$, the standard deviation of the unit normal Φ. In our language, this means, in the upper bound,

$$\hbar\omega_D/\sigma=\eta_0\ll 1\,, \tag{16}$$

or, equivalently,

$$\frac{T_e}{\Theta}=\frac{\hbar\omega_D}{8\eta_0^2E_a}\,, \tag{17}$$

a condition close to that obtained by Lagos.[9] Here, η_0 is a positive number. For the Gaussian solution to be effective in describing the low-temperature diffusion behavior, we see that it requires a solid with a large lattice trapping E_a and a small Debye temperature. Table I shows the calculated η_0 at various temperatures for a few systems. It is obvious that N:α-iron should follow the Gaussian behavior to the lowest value of the ratio T/Θ among those listed. However, due to the low Debye temperatures, H:Ta or H:Nb could possibly follow the Gaussian behavior to the lowest actual temperatures. As indicated by the table, since T_e deviates less than 4% from T at the Debye temperature of solids, it can be said quite generally that the Gaussian solution can describe the diffusion behavior appropriately above the Debye temperature. For H:Fe this corresponds to a value of 0.29 for η_0. In comparison, the N:Fe system should maintain a Gaussian behavior close to absolute zero, and for H:Ta or H:Nb, to quite low temperatures. However, judging from Lagos's fitting for the μ^+:Cu system, the effective η_0 value could be as high as 0.4. Then the Gaussian would fit all of the above three systems down to the neighborhood of 0 K.

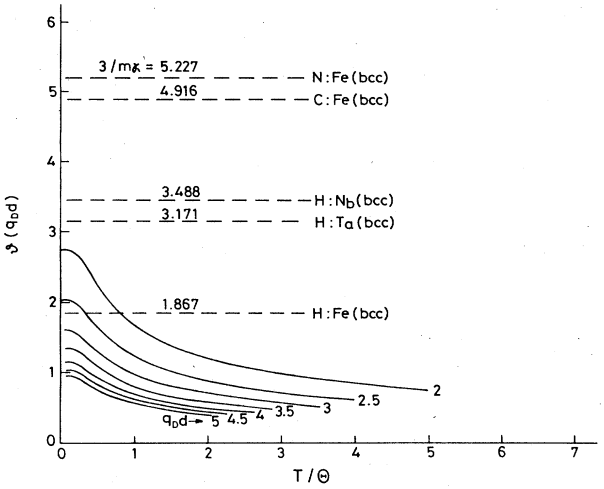

FIG. 2. Plots of $\mathscr{F}$ (curved solid lines) and $3/m\kappa$ (straight dashed lines) appearing on both sides of Eq. (20) for listed systems (octahedral-octahedral jump). Note that $\mathscr{F}$ depends sensitively on the Debye wave vector. For bcc and fcc crystals, q_Dd corresponds to $\sim$2.5 and $\sim$4.4, respectively.

We can also test the solution with the Liapounov condition. For Debye solids, this reads

$$\Gamma_N=m\kappa\mathscr{F}(q_Dd)$$

where

$$\kappa=\frac{6\pi}{a}\frac{\Omega}{\delta V}\frac{1-\nu}{1+\nu}\left[\frac{1}{K_BM_0\Theta}\right]^{1/2}, \tag{18}$$

$$\mathscr{F}(q_Dd)=\left\{\sqrt{y}\int_0^y dz\left[\left[\frac{1}{\exp(\beta z)-1}+\frac{1}{2}\right]z^4\left[1-\frac{\sin z}{z}\right]\right]\right\}\Big/\left\{\int_0^y dz\left[\left[\frac{1}{\exp(\beta z)-1}+\frac{1}{2}\right]z^3\left[1-\frac{\sin z}{z}\right]\right]^{3/2}\right\}. \tag{19}$$

Here, $y=q_Dd$ and $\beta=\hbar v/k_BTd$, v is the velocity of sound, and we have set $r_0=0$ in Eq. (3). For octahedral-octahedral hopping, m takes a value of 1 for bcc crystals and $2^{1/4}$ for fcc crystals. Since the characteristic function of the true distribution is bound by $\frac{1}{2}t^2+\Lambda\Gamma_N|t|^3$, $|\Lambda|\le\frac{1}{6}$,[19] this is to say that the Liapounov condition is followed approximately in conservative estimation by

$$\mathscr{F}\ll 3/m\kappa|t|\,. \tag{20}$$

Taking $|t|=1$, Fig. 2 shows the calculations for various systems, having the similar tendency indicated in Table I. Note that Γ_N is sensitive to the Debye wave vector q_D. For bcc systems, $q_Dd\simeq 2.5$,[1] and for fcc systems $q_Dd\simeq 4.4$. The fcc systems have smaller $\mathscr{F}$ value, but this factor is offset somewhat by the factor m.

DISCUSSION

The central-limit theorem can be applied to solve the lattice-trap integral for the light-interstitial hopping process when the process is holospoudic and the Lindeberg-Feller condition holds. This statement is true for high-temperature hopping and when linear elasticity is applicable for the impure solid. At low temperatures the Lindeberg-Feller condition holds approximately for small $\hbar\omega_D/E_a$ values.

The normalization of the distribution to Φ allows us to make comparison among various systems. By comparing our calculated data and Lagos's fitting, it seems that a value of $\eta_0 \simeq 0.4$ should be an acceptable level for using the central-limit solution. Hence, N:Fe is the best candidate, followed by H:Ta or H:Nb, and then μ^+:Cu. For the H:Fe system in Table I, the Gaussian approximation should be used only with care in the low-temperature regime.

The advantage of our treatment is not limited only to the fact that diagonal hopping is included. In principle, it is applicable to crystals of various phonon dispersions. Additionally, the approximations of Eqs. (2) are not necessary if there is a reasonable value of N which allows the statistical method to be applied. When there exist a few strong active local modes, holospoudicity breaks down, and only the Lindeberg-Feller condition is useful. If the local modes have frequencies ω_l higher than ω_D, then the Lindeberg-Feller condition is still applicable with ω_D replaced by ω_l. This means that the effective regime of the solution is raised to higher temperatures, as manifested by Eq. (17). However, when the local-mode frequencies are lower than ω_D, the effectiveness of the Gaussian solution becomes better, in the framework of the Stoneham-Flynn theory. As Eq. (14) indicates, the same thing happens when the lattice-distortion spectrum ΔQ_q has a negligible high-frequency part. In evaluating various moments of $(\Delta Q_q)^2$ in the above equations, it is obvious that the high frequency modes are weighted most heavily. As manifested by the characteristics of the Fourier transformation, the high-frequency ΔQ_q are primarily due to core distortions, where solids are discrete and nonlinear. This fact could cause considerable errors in evaluating the related parameters. Therefore, core considerations must be taken into account if a more accurate calculation is required. As shown by Fig. 1, T_0 is decreased when a certain core part is removed in evaluating ΔQ_q, resulting in a larger η_0.

For the Debye solids at temperatures below 0.1Θ, the Gaussian solution shows a T^6 hopping behavior which is written as

$$W_{pp'} \cong W_0 \left[1 + A \left[\frac{T}{\Theta} \right]^6 \right], \tag{21}$$

$$A = 0.425 \left[\frac{\delta V}{\Omega} \right]^2 \left[\frac{1+\nu}{1-\nu} \right]^2 M_0 d^2 \omega_D^2 \times \left[\frac{\Theta}{T_0} \right] \left[\frac{1}{k_B T_0} - \frac{1}{2E_a} \right]. \tag{22}$$

The rate can either deviate positively or negatively from the zero-point rate W_0, depending on the relative magnitudes of $2E_a$ and kT_0. However, since $T_0 \simeq 0.4\Theta$, a negative deviation requires $\hbar\omega_D > 5E_a$, which should not be observed in most cases. In fact, E_a is a fictitious quantity composed of minute lattice adjustments of various phonon modes, no barrier, and hence no tunneling to each mode, and the temperature always assists the hopping process. Since W_0 essentially arises from the coherent fluctuation in the zero-point motion implied in our stochastic solution, the above behavior has the sense of phase coincidence as manifested in classical dynamic theory.[20,21] Owing to the approximation discussed above, a question remains regarding T^6 behavior at low temperatures. For T^6 behavior the diagonal hopping should be more important than the two-phonon processes which lead to a T^7 law, as treated by Stoneham and Flynn.

In the problem dealing with color-center absorption,[14,16] it is quite possible that, at low temperatures, the Gaussian cannot fit the absorption band shape in general. This is because of the high frequency of the optical phonons existing in those crystals.

CONCLUSION

The effectiveness of the central-limit behavior of light-interstitial hopping can be tested by the Lindeberg-Feller and Liapounov conditions. The factor $\hbar\omega_D/E_a$ determines the validity of the Gaussian closed-form solution, which indicates a T^6 rate law close to absolute zero. Core distortion could be important in testing the condition. This implies that the Debye model could cause some error in the estimation. Our statistical method has the advantage of wider applicability, for example, to those solids with various phonon dispersions or with high-order ΔQ_q in Eq. (2), and it can also be applied to the concentration-related hopping processes as well as other phenomena.

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