One-Dimensional Hopping Diffusion in a Coherent Phonon Field

Dror Lubin
Department of Nuclear Physics, The Weizmann Institute of Science, Rehovot 76 100, Israel

Isaac Goldhirsch
Department of Fluid Mechanics and Heat Transfer, Faculty of Engineering, Tel-Aviv University, Tel-Aviv 69 978, Israel
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A model of hopping diffusion, with tunneling as the hopping mechanism, is studied. In the presence of phonons, the size of the barrier, and hence the hopping rate, is time dependent. A closed expression for the diffusion coefficient in the single-phonon case is obtained. It is found that for systems with low conductivity, a properly chosen phonon can increase the conductivity by a large factor. Such a phonon can be forced upon the system externally. The analytical results are supplemented by numerical calculations.

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Phonon-assisted hopping conduction has been discussed by many authors.[1] In all investigations we are aware of, the dynamical role of the phonons is either to change the effective mass of the hopping electron or to supply it with sufficient energy needed to hop. In this paper we address another facet of the problem of phonon-assisted hopping: The phonon is considered as a coherent time-dependent lattice distortion, whose role is to change the effective potential barrier for hopping. Under suitable conditions, a classical picture of a time-dependent lattice distortion can be justified, and the electron dynamics can be analyzed using a master equation.

We consider hopping diffusion on a one-dimensional lattice, with lattice constant a, of sites separated by energy barriers of typical height E. The tunneling process is assumed to occur only between nearest-neighbor sites, and the hopping probability between sites i,j per unit time at time t is modeled by $p_{i,j}(t)=(\nu/2)\times\exp[-\lambda d_{i,j}(t)]$, where ν is a typical attempt frequency (possibly containing a thermal factor, which is space uniform), $d_{i,j}(t)$ is the distance at time t between the sites, and $\lambda=2(2mE)^{1/2}/\hbar$ is the inverse effective tunneling length (m is the electron mass). When the lattice is static, the diffusion coefficient D is simply $D=a^2\nu\times\exp(-\lambda a)\equiv D_0\exp(-\lambda a)$, and there is no net drift. Now, we introduce a single acoustic phonon of wave vector k, amplitude A, and phase ϕ, so that the position of site j deviates from its equilibrium position by $\Delta_j=A\times\cos(k[ja-ct]+\phi)$, where c is the sound velocity and t is the time. The distance between neighboring sites at time t is

$$d_{j,j\pm1}(t)=a-2A\sin\left(\frac{ka}{2}\right)\sin\left(k[ja-ct]+\phi\pm\frac{ka}{2}\right). \tag{1}$$

Defining $\mu\equiv 2\lambda A\sin(ka/2)$, the master equation describing the time evolution of $P_j(t)$, the occupation probability of site j at time t, reads

$$\frac{d}{dt}P_j(t)=\frac{\nu}{2}e^{-\lambda a}\sum_{\sigma=\pm1}e^{\mu\sin(k[ja-ct]+\phi+\sigma ka/2)}\times[P_{j+\sigma}(t)-P_j(t)]. \tag{2}$$

A condition for Eq. (2) to be valid is that the time required for the tunneling process to occur be short compared with the time in which $d(t)$ changes significantly. The tunneling time can be estimated roughly from the uncertainty principle as $t_t^{-1}\approx 2E/\hbar=\lambda^2\hbar/4m$. The phonon frequency is given by $t_p^{-1}=ck$. The requirement $t_t\ll t_p$ is satisfied if $4mck\ll\hbar\lambda^2$. The above condition can be modified by introducing the result of Ref. 2 for the value of the tunneling time, calculated for a time-dependent potential barrier. In our notation the result of Ref. 2 reads $t_t\approx 2ma/\lambda\hbar$. Consequently, $t_t\ll t_p$ means $(\lambda a/2)4mck\ll\hbar\lambda^2$. Typical values of λa are obviously not much larger than $O(1)$ and thus the naive consideration presented before leads to a sensible result. Using typical values for c, we find that even when k and λ are of the same order, the condition is satisfied. We note further that as λ increases, the above requirement is easier to satisfy. It follows that when the above condition holds, the distance between sites can be justifiably assumed to be constant during the tunneling event. We may thus use the static tunneling probability in the master equation.

The use of the master equation here should, in principle, be justified. Attempts to do so are well known.[3] Here we mention that a physically based condition would be a long enough residence time of an electron at a site, during which phase information is lost. This condition holds when the hopping rate is low, i.e., in a strongly insulating system, which is the case assumed below. Notice that the dephasing process is due to interactions with the phonon bath. The coherent phonon considered in this paper is an externally applied one, and is "independent" of the thermal ("internal") phonon gas.

In order to solve the master equation, Eq. (2), we first expand the exponent appearing in it to all orders in μ, obtaining

$$\frac{d}{dt}P_j(t)=\frac{\nu}{2}e^{-\lambda a}\sum_{\sigma=\pm 1}\sum_{n=0}^{\infty}\frac{\mu^n}{n!}\sin^n\left(k[ja-ct]+\phi+\frac{\sigma ka}{2}\right)[P_{j+\sigma}(t)-P_j(t)]\,, \tag{3}$$

and then express $\sin(x)$ as $(e^{ix}-e^{-ix})/2i$ and use the binomial expansion to get

$$\frac{d}{dt}P_j(t)=\frac{\nu}{2}e^{-\lambda a}\sum_{\sigma=\pm 1}\sum_{n=0}^{\infty}\left(\frac{\mu}{2i}\right)^n\frac{1}{n!}\sum_{l=0}^{n}\binom{n}{l}(-1)^l e^{i(k[ja-ct]+\phi+\sigma ka/2)(n-2l)}[P_{j+\sigma}(t)-P_j(t)]\,. \tag{4}$$

Now, we can perform a Fourier transform in space: $\tilde{P}(\theta,t)=\sum_{j=-\infty}^{j=+\infty}\exp(-i\theta j)P_j(t)$. The resulting equation is

$$\frac{d}{dt}\tilde{P}(\theta,t)=\frac{\nu}{2}e^{-\lambda a}\sum_{\sigma=\pm 1}\sum_{n=0}^{\infty}\left(\frac{\mu}{2i}\right)^n\frac{1}{n!}\times\sum_{l=0}^{n}\binom{n}{l}(-1)^l e^{i(-kct+\phi+\sigma ka/2)(n-2l)}(e^{i\sigma(\theta-ka[n-2l])}-1)\tilde{P}(\theta-ka[n-2l],t)\,. \tag{5}$$

Performing the summation over σ one obtains

$$\frac{d}{dt}\tilde{P}(\theta,t)=-2\nu e^{-\lambda a}\sum_{n=0}^{\infty}\left(\frac{\mu}{2i}\right)^n\frac{1}{n!}\times\sum_{l=0}^{n}\binom{n}{l}(-1)^l e^{i(-kct+\phi)(n-2l)}\sin\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}-\frac{ka}{2}[n-2l]\right)\tilde{P}(\theta-ka[n-2l],t)\,. \tag{6}$$

Finally, we Laplace transform in time, $\hat{P}(\theta,s)=\int_0^\infty dt\exp(-st)\tilde{P}(\theta,t)$, with the initial condition $P_j(0)=\delta_{j,0}$, to get the equation for $\hat{P}(\theta,s)$:

$$s\hat{P}(\theta,s)-1=-2\nu e^{-\lambda a}\sum_{n=0}^{\infty}\left(\frac{\mu}{2i}\right)^n\frac{1}{n!}\sum_{l=0}^{n}\binom{n}{l}(-1)^l e^{i\phi(n-2l)}\times\sin\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}-\frac{ka}{2}[n-2l]\right)\hat{P}(\theta-ka[n-2l],s+ikc[n-2l])\,. \tag{7}$$

In order to proceed, we assume that the solution is analytic in μ, so it can be expanded as

$$\hat{P}(\theta,s)=\sum_{m=0}^{\infty}\mu^m\hat{P}_m(\theta,s)\,. \tag{8}$$

Inserting the expansion (8) into Eq. (7) and equating equal powers of μ, we obtain the recursion relations

$$\begin{aligned}\hat{P}_0(\theta,s)&=\frac{1}{s-\nu(\cos\theta-1)e^{-\lambda a}}\,,\\ \hat{P}_m(\theta,s)&=-2\nu e^{-\lambda a}\sum_{n=1}^{m}\left(\frac{1}{2i}\right)^n\frac{1}{n!}\sum_{l=0}^{n}\binom{n}{l}(-1)^l e^{i\phi(n-2l)}\sin\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}-\frac{ka}{2}[n-2l]\right)\\ &\quad\times\frac{\hat{P}_{m-n}(\theta-ka[n-2l],s+ikc[n-2l])}{s-\nu(\cos\theta-1)e^{-\lambda a}}\,.\end{aligned} \tag{9}$$

Using the notation $n^{(j)}\equiv\sum_{i=1}^{j}n_i$, $l^{(j)}\equiv\sum_{i=1}^{j}l_i$, and $s_{n,l}\equiv s+ikc[n-2l]-\nu\{\cos(\theta-ka[n-2l])-1\}e^{-\lambda a}$, Eq. (9) can be iterated repeatedly to obtain a closed expression:

$$\hat{P}_m(\theta,s)=\sum_{n_1=1}^{m}\sum_{l_1=0}^{n_1}\cdots\sum_{n_p=1}^{m-n^{(p-1)}}\sum_{l_p=0}^{n_p}(-2\nu e^{-\lambda a})^p\left(\frac{1}{2i}\right)^m\left(\prod_{j=1}^{p}\frac{1}{l_j!(n_j-l_j)!}\right)(-1)^{l^{(p)}}e^{i\phi(m-2l^{(p)})}\frac{\sin(\frac{1}{2}\theta)}{s_{0,0}}\times\left(\prod_{j=1}^{p-1}\frac{\sin^2(\frac{1}{2}\theta-\frac{1}{2}ka[n^{(j)}-2l^{(j)}])}{s_{n^{(j)},l^{(j)}}}\right)\frac{\sin(\frac{1}{2}\theta-\frac{1}{2}ka[m-2l^{(p)}])}{s_{m,l^{(p)}}}\,, \tag{10}$$

where we sum over all the partitions $n_1,n_2,\ldots,n_p$ such that $n^{(p)}=m$.

In order to find the diffusion coefficient D and the drift velocity V we must first compute the average displacement and average-squared displacement,

$$\langle x(t)\rangle = a\sum_{j=-\infty}^{+\infty} jP_j(t) = ia\frac{d}{d\theta}\tilde{P}(\theta,t)\Big|_{\theta=0}, \quad \langle x^2(t)\rangle = a^2\sum_{j=-\infty}^{+\infty} j^2P_j(t) = -a^2\frac{d^2}{d\theta^2}\tilde{P}(\theta,t)\Big|_{\theta=0}, \tag{11}$$

and then use

$$V=\lim_{t\to\infty}\frac{1}{t}\langle x(t)\rangle, \quad D=\lim_{t\to\infty}\frac{1}{t}[\langle x^2(t)\rangle-\langle x(t)\rangle^2]. \tag{12}$$

It follows that we have to consider in Eq. (10) only terms that grow at least linearly in time at $\theta=0$. Since each term is a product of factors of the form $1/(s+\alpha_j)$, there will be such a contribution only from terms with at least two vanishing α_j's, which requires $n^{(j)}=2l^{(j)}$ for some $1\le j\le p$. However, if this condition is satisfied for some $j<p$, the relevant term is of the form $\sin^3(\theta/2)f(\theta)$, and both its first and second derivatives with respect to θ vanish at $\theta=0$. It is therefore necessary that $m=2l^{(p)}$, in which case the term whose contribution is linear in t is of the form $\sin^2(\theta/2)f(\theta)$, and while its first derivative still vanishes at $\theta=0$, the second derivative with respect to θ at $\theta=0$ is $f(0)/2$. It follows that there is no net drift in the system. As for the diffusion, we note that the only contribution which grows linearly in time has a factor t arising from the terms proportional to $1/s^2$, and each other factor of $1/(s+\alpha_j)$ contributes a factor $1/\alpha_j$ to D. The conclusion is that the contribution of order μ^m, D_m, to the diffusion coefficient, as obtained from $\hat{P}_m$, is

$$D_m=-\frac{a^2}{2}\sum_{n_1=1}^{m}\sum_{l_1=0}^{n_1}\cdots\sum_{n_p=1}^{m-n^{(p-1)}}\sum_{l_p=0}^{n_p}(-2ve^{-\lambda a})^p(\tfrac{1}{2})^m\left(\prod_{j=1}^{p}\frac{1}{l_j!(n_j-l_j)!}\right)$$
$$\times\left(\prod_{j=1}^{p-1}\frac{\sin^2(\frac{1}{2}ka[n^{(j)}-2l^{(j)}])}{ikc[n^{(j)}-2l^{(j)}]-v\{\cos(ka[n^{(j)}-2l^{(j)}])-1\}e^{-\lambda a}}\right), \tag{13}$$

where $m=2l^{(p)}$. Finally, we can perform some algebraic manipulations on Eq. (13) before we use the expansion (8) to obtain our final result for the diffusion coefficient:

$$D=D_0e^{-\lambda a}\sum_{m=0}^{\infty}\left[\lambda A\sin\left(\frac{ka}{2}\right)\right]^{2m}\left[\sum_{n_1=1}^{2m}\sum_{l_1=0}^{n_1}\cdots\sum_{n_p=1}^{2m-n^{(p-1)}}\sum_{l_p=0}^{n_p}\left(\prod_{j=1}^{p}\frac{1}{l_j!(n_j-l_j)!}\right)\right.$$
$$\left.\times\left(\prod_{j=1}^{p-1}\frac{-4\sin^4(\frac{1}{2}ka[n^{(j)}-2l^{(j)}])}{k^2c^2[n^{(j)}-2l^{(j)}]^2v^{-2}e^{2\lambda a}+4\sin^4(\frac{1}{2}ka[n^{(j)}-2l^{(j)}])}\right)\right], \tag{14}$$

with $l^{(p)}=m$.

Using the notation $f_j\equiv-4\sin^4(jka/2)/[4\sin^4(jka/2)+j^2k^2c^2v^{-2}e^{2\lambda a}]$, the expansion of D to the first three orders in μ is

$$D\cong D_0e^{-\lambda a}\{1+(1+2f_1)[\lambda A\sin(ka/2)]^2+\tfrac{1}{4}(1+8f_1+2f_2+8f_1f_2+12f_1^2+8f_1^2f_2)[\lambda A\sin(ka/2)]^4\}. \tag{15}$$

Equation (14) is an exact closed expression for the diffusion constant D. It is, however, a rather complicated one, and so we consider some limiting cases in which it can be simplified. When λa is large, or ka is small, all the f_j's are negligible, and for every m in the summation, only the term with $p=1$ contributes significantly. The sum in Eq. (14), with $p=1$ terms only, can be identified as that which defines the modified Bessel function. We therefore have that for small wave vectors, or for strongly insulating systems,

$$D\cong D_0e^{-\lambda a}I_0(2\lambda A\sin(ka/2)), \tag{16}$$

where I_0 is the modified Bessel function of the first kind. It is interesting to note that Eq. (16) could have been obtained from a mean-field calculation. It follows from the value of p_{ij} that $\langle p_{ij}\rangle$, defined as the time average of $p_{ij}(t)$ over a period of the phonon, yields an effective (time-independent) hopping rate that corresponds to the diffusion constant obtained in Eq. (16). When λa is not large (or ka is not very small), the mean-field result does not hold, and we should use Eq. (15), which indeed describes the numerical results with high accuracy.

Since I_0 increases exponentially as a function of its argument, when the latter is at least $O(1)$, it follows that when $\lambda a\gg 1$ (strongly insulating system) the phonon strongly increases the diffusion coefficient:

$$D\propto D_0\exp\left\{-\lambda a\left[1-\frac{2A}{a}\sin\left(\frac{ka}{2}\right)\right]\right\}. \tag{17}$$

The amplitude A is limited by the requirement that neighboring atoms do not cross each other: $A/a<1/2|\sin(ka/2)|$. In the extreme case, when the latter relation is an equality, the resulting diffusion is similar to what is obtained for $\lambda a=0$ (i.e., a conductor). However, such a case can only be approached but not obtained in practice. It is seen therefore that in systems which are

very bad conductors, the diffusion can be significantly enhanced by exciting mechanically an appropriate phonon. We reiterate that as λ increases the use of the master equation is better justified.

It is also important to note that when the phonon is excited mechanically in a real system, it is possible to force it to be along some lattice axis. In that case, the one-dimensional analysis applies to the conductivity measured along that axis, even when the system is three dimensional.

We bear in mind that in deriving the expression (14) for the diffusion coefficient we had to make one assumption, namely, that P is an analytic function of μ. To check the validity of that assumption we compared the prediction of Eq. (14) with the result obtained by numerical integration of the master equation (2). It turns out that it is very difficult to integrate Eq. (2) over long enough times and still achieve the accuracy required to verify Eq. (14). To solve this problem, we developed a method that enables us to compute numerically the diffusion coefficient to very high precision, and with relatively small computation time.

The method applies when ka is a rational fraction of 2π. If $ka=(m/n)2\pi$, with m,n integers, Eq. (2) can be separated into a system of n equations:

$$\frac{d}{dt}P_{jn+l}(t)=\frac{\nu}{2}e^{-\lambda a}\sum_{\sigma=\pm 1}e^{\mu\sin(k[la-ct]+\phi+\sigma ka/2)}\times[P_{nj+l+\sigma}(t)-P_{nj+l}(t)], \tag{18}$$

for $l=1,2,\ldots,n$. The coefficients in the system (18) do not depend on j; therefore if we define an "n-step" Fourier transform in space, $\tilde{P}^{(l)}(\theta,t)=\sum_{j=-\infty}^{j=+\infty}\exp(-i\theta\times[nj+l])P_{nj+l}(t)$, we obtain the system of equations

$$\frac{d}{dt}\tilde{P}^{(l)}(\theta,t)=\frac{\nu}{2}e^{-\lambda a}\times\sum_{\sigma=\pm 1}e^{\mu\sin(k[la-ct]+\phi+\sigma ka/2)}\times[e^{i\sigma\theta}\tilde{P}^{(l+\sigma)}(\theta,t)-\tilde{P}^{(l)}(\theta,t)], \tag{19}$$

where l is defined mod(n). The system of equations (19) has two advantages: It is a finite, small (when n is small) system, and the coefficients are periodic in time. It therefore suffices to integrate a small number of equations over a finite range of time (one period) in order to obtain the behavior of the system at arbitrarily large time using Floquet's theorem. One has to integrate Eqs. (19) with n initial conditions that form a basis, and thus obtain the matrix that transforms the state of the system to its state after one period of the phonon oscillation has elapsed. The long-time behavior of the system is determined by the leading eigenvalue of that matrix. This procedure is repeated for several values of θ near $\theta=0$ and from these results one can evaluate the derivatives at $\theta=0$.

We remark that the straightforward integration of Eq. (2) indicates that D is a continuous function of k; therefore the restriction to rational fractions is not limiting the validity of the results. The computation was carried out for many values of the parameters, the results always being in full agreement with the analytic calculation.

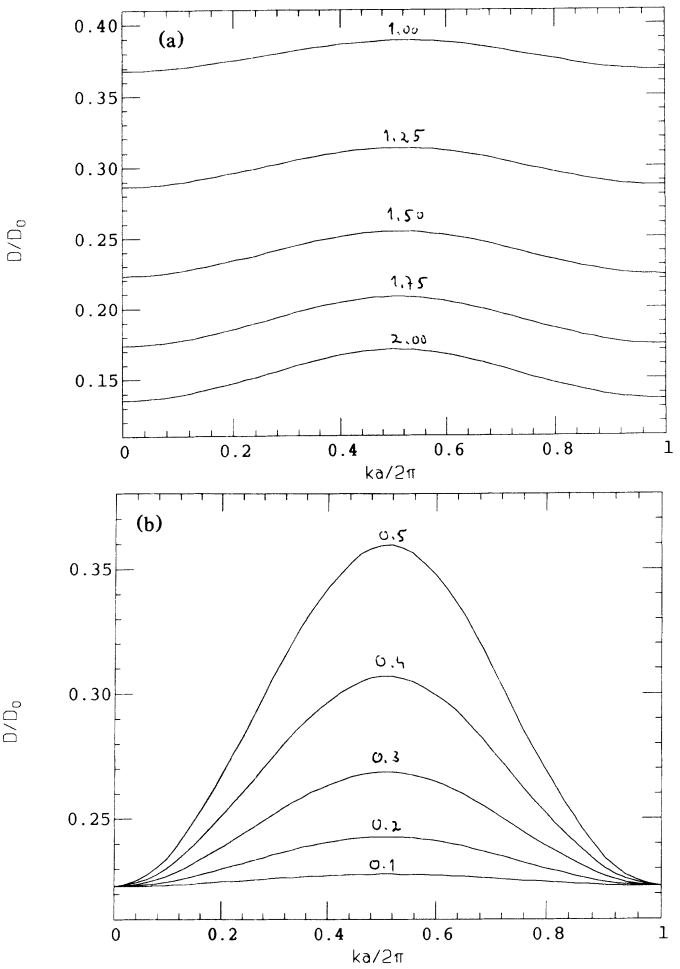

FIG. 1. The diffusion coefficient D/D_0 as a function of ka. (a) $4A=a$. The values of λa are 1.00,1.25,...,2.00 and are indicated on the plot. (b) $\lambda a=1.5$. The values of A/a are 0.1,0.2,...,0.5, and are indicated on the plot. See text for definitions of the parameters.

Typical results are given in Fig. 1. The diffusion coefficient D (measured in units of D_0) is plotted versus $ka/2\pi$ over the entire zone. In Fig. 1(a) we plot several values of λa, while A/a is kept fixed ($=0.25$). As λa is increased, the magnitude of D decreases, but its sensitivity to ka increases. In Fig. 1(b) λa is kept equal to 1.5, while A/a is varied. Again the sensitivity to ka increases with A. In both cases the numerical and analytical results are indistinguishable.

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