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The effect of jumps into distant sites on carrier energy relaxation in a disordered hopping system

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Abstract. An analytic model of charge-carrier kinetics in a disordered hopping system accounting for the possibility of jumps to non-nearest hopping neighbours is formulated. The model is applied to the analysis of charge-carrier energy relaxation at both low and finite temperatures. Carrier jumps to distant hopping neighbours are shown to increase the depth of the carrier energy distribution at both low and finite temperatures, and to cause a shift of the effective transport level to deeper states at finite temperatures.

1. Introduction

Non-crystalline materials that can be considered as hopping networks are characterized by a strong disorder in both energy and position of hopping sites [1–4]. This makes it very difficult to solve the problem analytically or simulate the charge-carrier transport and recombination in such systems by starting from a one-particle master equation. Consequently, any analytic approach to this problem is normally based on a specific set of assumptions and/or simplifications. One of the most common simplifying assumptions is the restriction of carrier jumps from a given site to just its nearest hopping neighbour [2, 3]. The rate of carrier jumps, $\nu_j(r, E, E')$, from a site of energy E to another site of energy E' over the distance r is normally described by the Miller–Abrahams expression [5] as

$$\nu_j(r, E, E') = \nu_0 \exp(-2\gamma r) \times \begin{cases} \exp\left(-\dfrac{E - E'}{kT}\right) & E > E' \\ 1 & E < E' \end{cases} \tag{1}$$

where ν_0 is the attempt-to-jump frequency, γ the inverse localization radius, T the temperature, and k the Boltzmann constant. Occurrence of hopping transport implies a weak overlap of wave-functions of carriers localized at different sites and, therefore, the condition $\gamma r > 1$ is fulfilled for most pairs of hopping sites. In such a dilute system each hopping site will have just one nearest hopping neighbour, i.e. another hopping site whose hopping parameter u:

$$u = 2\gamma r + \begin{cases} \dfrac{E - E'}{kT} & E > E' \\ 0 & E < E' \end{cases} \tag{2}$$

has a minimum value amongst those of all available states. All other states have higher values of u and, given the exponential dependence of the jump rate on the hopping parameter, the rate of jumps to more distant neighbours is normally neglected in comparison with that to the

nearest neighbour. Although this simplification looks quite reasonable for a dilute hopping system, it might be too rough for a more condensed network.

In the present paper we develop an analytic method to account for carrier jumps from a given site to an arbitrary site in the neighbourhood. Both low- and finite-temperature conditions are considered. This method is applied to the problem of energy relaxation of charge carriers injected into a disordered hopping system. Comparing the energy distributions of localized carriers calculated with different numbers of hopping neighbours taken into consideration allows an estimate to be made of the relative contributions to the relaxation process of jumps to more distant sites. Analysis of carrier energy relaxation also reveals the effect of non-nearest-neighbour jumps on the energy position of the effective transport level [6].

2. Carrier jumps to distant hopping neighbours

Before an equilibrium energy distribution of carriers over hopping sites is established, most carriers are localized on currently metastable sites (MS), and the energy distribution of the carriers follows the energy distribution of the density of metastable states (DMS), $g_d(E, t)$ [7, 8]. A state is referred to as currently metastable if a carrier that arrived at this state at a time $t' < t$ has a high probability of still being in this state at a given time t. In other words, a state is metastable at a time t if it has no hopping neighbours accessible for carrier jumps within this time. At the initial time, $t = 0$, when carriers are excited all sites are metastable and the DMS is equal to the total density of states (DOS). At longer times, evolution of the DMS energy distribution is governed by the probability of carrier jumps from states of a given energy. In the following we consider a completely random spatial distribution of states and calculate the jump probability and, concomitantly, the DMS distribution, taking into account carrier jumps to all neighbouring sites. We start our consideration with the low-temperature conditions.

2.1. Low-temperature energy relaxation

At low temperatures only carrier jumps to deeper states are possible. The probability, $p_i(r, E)$, for a trap with energy E to have i deeper states at a distance less than r is determined by the Poisson distribution as

$$p_i(r, E) = \frac{\left[\frac{4}{3}\pi r^3 N_d(E)\right]^i}{i!} \exp\left[-\frac{4}{3}\pi r^3 N_d(E)\right] \tag{3}$$

where $N_d(E)$ is the total density of states with energy below E:

$$N_d(E) = \int_E^\infty \mathrm{d}E'\, g(E'). \tag{4}$$

These deeper states around a site with energy E can be ordered and numbered according to the distance from a given localized state to this site. The nearest state will be referred to as the first neighbour ($i = 1$), the next-nearest state will be the second neighbour ($i = 2$), etc. Using equation (3) one can easily obtain the probability density, $w_i(r, E)$, for a trap with the fixed energy E to have the ith neighbour at the distance r:

$$w_i(r, E) = 4\pi r^2 N_d(E) \frac{\left[\frac{4}{3}\pi r^3 N_d(E)\right]^{i-1}}{(i-1)!} \exp\left[-\frac{4}{3}\pi r^3 N_d(E)\right]. \tag{5}$$

The probability, $P(r, t)$, that a carrier does not make a jump from the trap into a localized state over the distance r up to the time t is also given by the Poisson distribution:

$$P(r, t) = \exp\left[-\nu_0 t \exp(-2\gamma r)\right]. \tag{6}$$

Combining equations (5) and (6) and integrating over coordinates yields the probability $P_i(E,t)$ that a carrier made no jumps from the state to the ith neighbour up to the time t:

$$P_i(E,t) = \frac{3\left[\frac{4}{3}\pi N_d(E)\right]^i}{(i-1)!}\int_0^\infty \mathrm{d}r\, r^{3i-1}\exp\left[-\frac{4}{3}\pi r^3 N_d(E) - \nu_0 t\exp(-2\gamma r)\right]. \tag{7}$$

A carrier remains in the metastable trap if it makes no jump to any neighbour. Since carrier jumps to different neighbours should be considered as independent events, the probability, $P(E,t)$, of finding a carrier at the time t still in a metastable trap at energy E is given by the product of all $P_i(E,t)$:

$$P(E,t) = \prod_{i=1}^\infty \frac{3\left[\frac{4}{3}\pi N_d(E)\right]^i}{(i-1)!}\int_0^\infty \mathrm{d}r\, r^{3i-1}\exp\left[-\frac{4}{3}\pi r^3 N_d(E) - \nu_0 t\exp(-2\gamma r)\right]. \tag{8}$$

Energy distributions of both the DMS and the density of carriers localized in hopping sites, $\rho(E,t)$, are determined by the function $P(E,t)$ as

$$g_d(E,t) = g(E)P(E,t) \qquad \rho(E) = \frac{N_0}{N_t}g(E)P(E,t) \tag{9}$$

where N_t is the total density of hopping sites and N_0 is the total density of carriers. Note that equation (8) can be rewritten using a dimensionless distance z, introduced by normalizing the distance r with respect to the localization radius, $z = 2\gamma r$, as

$$P(E,t) = \prod_{i=1}^\infty \frac{3}{(i-1)!}\left[\frac{\pi N_d(E)}{6\gamma^3}\right]^i\int_0^\infty \mathrm{d}z\, z^{3i-1}\exp\left[-\frac{\pi N_d(E)z^3}{6\gamma^3} - \nu_0 t\exp(-z)\right] \tag{10}$$

implying that the behaviour of the function $P(E,t)$ is governed by only two parameters: N_d/γ^3 and ν_0. At long times, $\nu_0 t \gg 1$, equation (10) can be simplified using the following approximation for the double-exponential term in the integrands of this equation:

$$\exp\left[-\nu_0 t\exp(-z)\right] \simeq \begin{cases} 0 & z < z_d(t) \\ 1 & z > z_d(t) \end{cases} \qquad z_d(t) = \ln(\nu_0 t). \tag{11}$$

Substituting equation (11) into equation (10) and integrating yields

$$P(E,t) = \prod_{i=1}^\infty \left\{1 - \exp\left[-\frac{\pi N_d(E)}{6\gamma^3}[\ln(\nu_0 t)]^3\right]\sum_{l=i}^\infty \frac{1}{l!}\left[\frac{\pi N_d(E)}{6\gamma^3}[\ln(\nu_0 t)]^3\right]^l\right\}. \tag{12}$$

Equation (12) shows that the low-temperature occupational probability proves to be a *universal* function

$$P(y) = \prod_{i=1}^\infty \left[1 - \exp(-y)\sum_{l=i}^\infty \frac{y^l}{l!}\right] \tag{13}$$

of a *single* parameter

$$y = \frac{\pi N_d(E)}{6\gamma^3}[\ln(\nu_0 t)]^3 \tag{14}$$

that accounts for both the energy and time dependencies of the probability for a given localized state to be a metastable trap. The function $P(y)$ is plotted in figure 1 with different numbers of hopping neighbours taken into consideration. At $y \ll 1$, which corresponds to large energies and/or short times, the probability $P(y)$ is close to being independent of the number, i_{max}, of hopping neighbours taken into account. However, this number strongly affects the probability for a state to remain metastable at $y > 0.5$, i.e. at longer times and lower energies. Note that

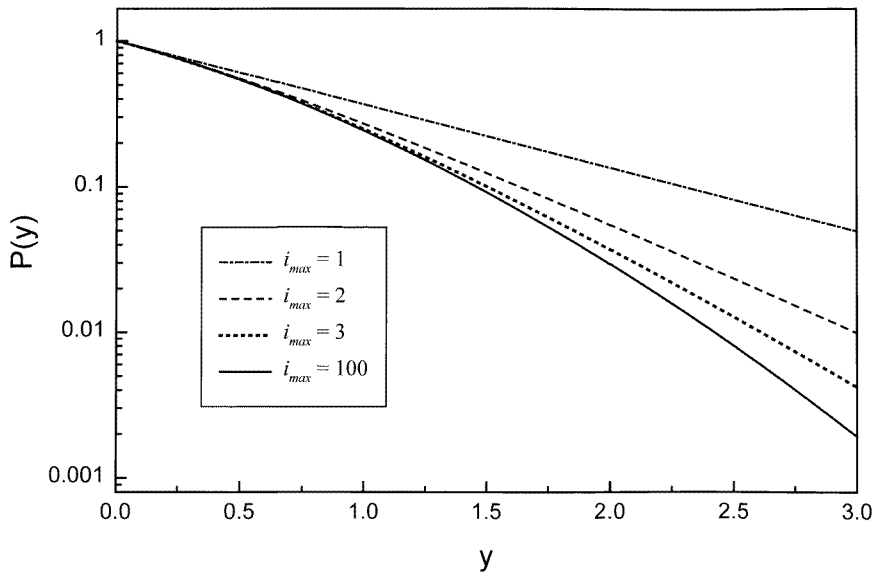

Figure 1. The localized-state occupational probability, P, as a function of the universal parameter y with different numbers of hopping neighbours taken into account.

the contribution to this probability of jumps to the second-nearest hopping neighbours is larger than the contribution of jumps to all other neighbours.

Energy relaxation of carriers in a disordered hopping system is often described by means of a time-dependent demarcation energy, $E_d(t)$, that splits the DOS distribution into currently shallow, $E < E_d(t)$, and currently deep, $E > E_d(t)$, states [6, 9]. A natural definition of such a demarcation energy, in terms of the probability defined above, is

$$P\,[E_d(t), t] = \frac{1}{2}. \tag{15}$$

Use of the parameter y allows rewriting equation (15) as

$$P(y_d) = \frac{1}{2} \tag{16}$$

where y_d is the value of y that relates the demarcation energy and the time as defined by equation (14). This y_d is again a *universal* parameter; it depends neither upon the DOS distribution nor upon the total density of hopping states. Solving equations (16) and (13) yields $y_d = \ln 2 = 0.693$ for $i_{max} = 1$, $y_d = 0.573$ for $i_{max} = 2$, $y_d = 0.559$ for $i_{max} = 3$, and $y_d = 0.557$ for $i_{max} = 100$.

We illustrate the temporal evolution of the DMS for an exponential:

$$g(E) = \frac{N_t}{E_0} \exp\left(-\frac{E}{E_0}\right) \tag{17}$$

and for a modified Gaussian DOS distribution:

$$g(E) = 2\frac{N_t}{E_0}\frac{E}{E_0} \exp\left(-\frac{E^2}{E_0^2}\right) \tag{18}$$

which are typical for inorganic and organic disordered materials, respectively. In both cases N_t is the total density of states and E_0 the characteristic energy of a distribution. Substituting

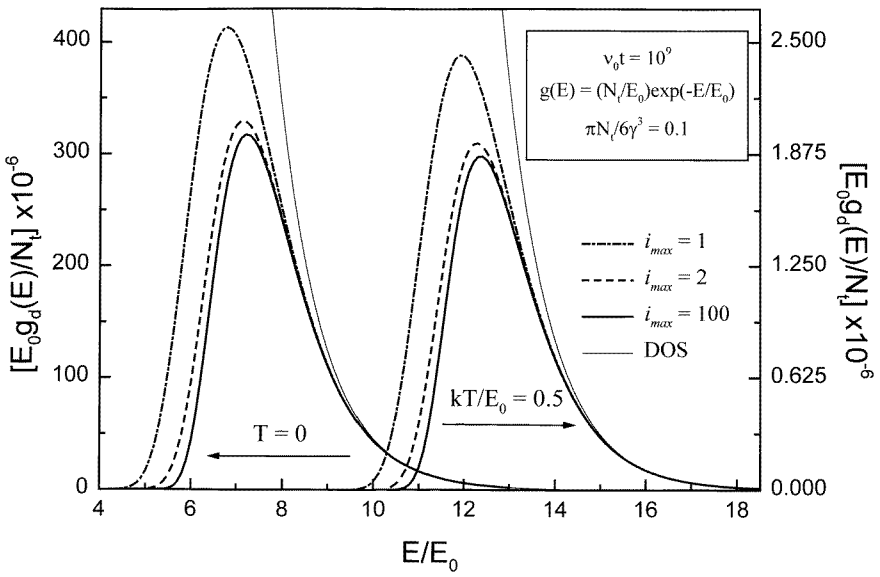

Figure 2. Comparison of energy distributions of the density of occupied metastable states at low and at finite temperatures for hopping systems with an exponential DOS function at $\nu_0 t = 10^9$. The DMS distributions are calculated for the values of i_{max} indicated.

equations (17) and (18) into equations (4) and (14) yields the following time dependencies of the demarcation energy:

$$E_d(t) = E_0 \ln\left(\frac{\pi N_t}{6 y_d \gamma^3}\right) + 3E_0 \ln\left[\ln(\nu_0 t)\right] \tag{19}$$

for the exponential DOS distribution and

$$E_d(t) = E_0 \sqrt{\ln\left(\frac{\pi N_t}{6 y_d \gamma^3}\right) + 3 \ln\left[\ln(\nu_0 t)\right]} \tag{20}$$

for the modified Gaussian DOS function. For an exponential DOS distribution, jumps to distant hopping neighbours change the value of a downward shift of the demarcation energy [6, 10] which is formed within the initial time domain of relaxation, $\nu_0 t \sim 1$, and remains constant afterwards. For a Gaussian DOS distribution the density of deeper states, available for carrier downward jumps, decreases with energy much faster than for an exponential DOS function. Therefore, the additional shift of the demarcation energy decreases with time and the effect of distant jumps is less important for such DOS functions. Energy distributions of the DMS, presented in figure 2 for a selection of i_{max}-values, are calculated from equations (13) and (14) for the exponential DOS distribution. Beyond the nearest-neighbour hops, contributions of jumps to the second-nearest neighbours ($i = 2$) are dominant, with the result that the curves plotted with $i_{max} = 2$ are very similar to those with $i_{max} = 100$. Comparison of the curves calculated for different numbers i_{max} proves that distant jumps of carriers mostly affect the density of carriers above the demarcation energy with the latter being shifted to deeper states. This downward shift, governed by the value of γ, is established early in the relaxation process and it either remains constant at longer times as predicted by equation (19) for the exponential DOS distribution or decreases with time as described by equation (20) for the modified Gaussian DOS function.

2.2. Energy relaxation at finite temperatures

At a finite temperature both upward and downward carrier jumps are possible and the jump rate depends upon both the distance between hopping sites and the energy difference between them as described by equation (1). Under these conditions it is convenient to arrange hopping neighbours of a given site of energy E according to increasing value of their hopping parameters. A state that has the smallest hopping parameter will be referred to as the first neighbour ($i = 1$), a state that has the second-smallest one will be called the second neighbour ($i = 2$), etc. Using equation (2) one can write the average number of hopping neighbours, $n(u, E)$, whose hopping parameters are less than u, around a state of energy E, as

$$n(u, E) = \frac{\pi u^3}{6\gamma^3}\left[\int_E^\infty \mathrm{d}E'\, g(E') + \int_{E-kTu}^{E} \mathrm{d}E'\, g(E')\left(1 - \frac{E - E'}{kTu}\right)^3\right]. \tag{21}$$

The probability to find i hopping neighbours with hopping parameters less than u around this state, $p_i(u, E)$, is then described by the Poisson distribution of probabilities

$$p_i(u, E) = \frac{[n(u, E)]^i}{i!}\exp\left[-n(u, E)\right]. \tag{22}$$

Repeating for the case of finite temperature the procedure that was used in section 2.1 to derive equation (10) from equation (3), one obtains

$$P(E, t) = \prod_{i=1}^{\infty}\frac{1}{(i-1)!}\int_0^\infty \mathrm{d}u\, \frac{\partial n(u, E)}{\partial u}\,[n(u, E)]^{i-1}\exp\left[-n(u, E) - \nu_0 t\exp(-u)\right]. \tag{23}$$

Equation (23) allows a simplification similar to what has been done in equation (10). Using equation (11), with u replacing z, in the integrands of equation (23) yields

$$P(E, t) = \prod_{i=1}^{\infty}\left(1 - \exp\left\{-n\left[\ln(\nu_0 t), E\right]\right\}\sum_{l=i}^{\infty}\frac{1}{l!}\left\{n\left[\ln(\nu_0 t, E)\right]\right\}^l\right). \tag{24}$$

Equation (24) also has the universal form of equation (13) with the variable y being now associated with the density of hopping neighbours accessible for carrier jumps at finite temperatures:

$$y = n\left[\ln(\nu_0 t), E\right] = \frac{\pi}{6\gamma^3}\left[\ln(\nu_0 t)\right]^3\left[\int_E^\infty \mathrm{d}E'\, g(E') + \int_{E-kT\ln(\nu_0 t)}^{E}\mathrm{d}E'\, g(E')\left(1 - \frac{E - E'}{kT\ln(\nu_0 t)}\right)^3\right]. \tag{25}$$

The effect of carrier jumps to distant hopping neighbours on the energy relaxation at finite temperatures is illustrated in figures 2 and 3. Figure 2 compares energy distributions of localized carriers calculated at $T = 0$ and at a finite temperature. Although increasing temperature enhances the relaxation, the effect of distant jumps is much less sensitive to the temperature, with the result that the additional downward shift is practically temperature independent. This additional shift is still formed at short times of relaxation and remains constant at longer times as is again shown in figure 3. In other words, taking more hopping neighbours into consideration leads to a time-independent downward shift of the demarcation energy and to a lower density of MS traps remaining around and above $E_d(t)$.

Since carrier jumps to distant neighbours play an important role only at relatively short times, they may lead to a faster drift and diffusion only within a limited initial time interval after the pulse of non-equilibrium carrier generation. At longer times, most carriers make jumps to nearest hopping neighbours, and hops to distant ones no longer contribute significantly to

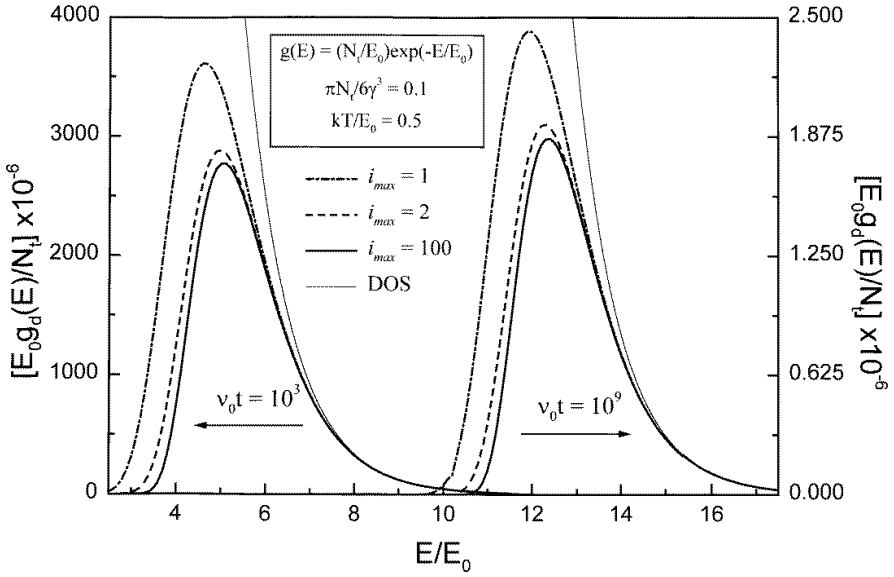

Figure 3. Energy distributions of the density of metastable states at a finite temperature for hopping systems with an exponential DOS function for two different times. The DMS distributions are calculated for the values of i_{max} indicated.

the transport characteristics. Therefore, carrier jumps to distant neighbours may affect time dependencies of the carrier-packet mean position and the packet spreading at short times, while at longer times this effect is limited to the appearance of simple numerical factors. The authors plan to consider this problem quantitatively in the future.

Most carriers start energy relaxation by making downward jumps and, therefore, the effect of distant hopping neighbours at short times is similar to that under the low-temperature conditions. At longer times, carriers trapped by currently deep traps will be released mostly due to upward jumps to shallower states and, correspondingly, the value of the demarcation parameter y_d is controlled by the second, temperature-dependent, term on the right-hand side of equation (25). Evaluation of this term for an exponential DOS distribution and use of equation (16) yields the following expression for the long-time asymptote of the demarcation energy at finite temperatures:

$$E_d(t) = E_0 \ln\left[\frac{3N_t}{\gamma^3 y_d}\left(\frac{E_0}{kT}\right)^3\right] + kT\ln(\nu_0 t). \tag{26}$$

This result implies the occurrence of an effective transport level that plays the role of the mobility edge in a hopping system [6]. The energy position of the transport level shifts down to deeper states as the number of allowed hopping neighbours increases. At finite temperatures, the time dependence of the demarcation energy is much less sensitive to the DOS distribution than at low temperatures. Since the main contribution to the second integral in equation (25) comes from energies close to the lower bound of integration, this integral can be estimated as

$$\int_{E-kT\ln(\nu_0 t)}^{E} \mathrm{d}E'\, g(E')\left(1-\frac{E-E'}{kT\ln(\nu_0 t)}\right)^3 \simeq E_0 g\left[E - kT\ln(\nu_0 t) - E_s\right] \tag{27}$$

where E_s is the energy difference between the lower bound of integration and the maximum of the integrand. Using this approximation in equations (25) and (16) yields a demarcation

energy which contains a time-independent E_t, which is the energy of the transport level: $E_d(t) = E_t + kT\ln(\nu_0 t)$. At finite temperatures it is the energy of the transport level rather than the form of the $E_d(t)$ function that depends upon the specific choice of DOS distribution.

All of the above results are obtained under the assumption of completely uncorrelated and random energies and positions of localized states. However, there are experimental facts that imply an important role of correlation between energies and positions of nearby hopping neighbours in processes of carrier transport and recombination [11–13]. These correlations normally manifest themselves as long-range potential fluctuations in addition to the short-range energy disorder. Such correlations may also affect the energy relaxation of excited carriers. Under such conditions, 'homogeneous' carrier thermalization within a disordered system of hopping sites is accompanied by carrier flow from regions of higher potential energy down into areas of lower energy within the potential landscape, with the result that the equilibrium distribution of carriers will be mesoscopically non-uniform. Investigations along these lines are being undertaken by the present authors.

3. Conclusions

Jumps to distant hopping neighbours increase the rate of carrier energy relaxation moderately in a positionally and energetically disordered hopping system. At low temperatures, this increase is manifested as an additional time-independent downward shift of the carrier energy distribution in systems with exponential energy distributions of the DOS. If the DOS decreases with energy faster than an exponential function, the additional downward shift formed within the initial time domain of relaxation decreases and becomes less important at longer times. At finite temperatures, distant-neighbour jumps affect the energy of the effective transport level, which shifts to deeper states with increasing number of hopping neighbours available for carrier jumps. In general, the results of the present study prove that models which neglect carrier jumps to distant neighbours in disordered hopping systems will be sufficiently accurate for most purposes.

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