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Lattice-Kinetic Theory of the Self-Diffusion Coefficient for Simple Liquids

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With 1 Figure

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Summary

A kinetic theory of the self-diffusion coefficient D for a simple liquid is developed in terms of the correlated walk model with the possibility of a trap. A formula for the coefficient D is derived: $D = (1/6)q(1 + \delta)(1 - \delta)^{-1}a_0 v$, where a_0 and v represent the interparticle distance and the average migration speed respectively; δ (< 1) is the degree of dynamical correlation; the factor $q = \exp(-\epsilon_b/k_B T)$, where ϵ_b is the activation energy, represents the probability of a tagged molecule overcoming the energy barrier ϵ_b generated by its surrounding molecules. Comparison with the experimental results of Naghizadeh and Rice [J. Chem. Phys. 36, 2710 (1982)] for simple liquids yields that $\epsilon_b/k_B = 318\ 440\ 609$ K for Ar, Kr, Xe and $(1 + \delta)/(1 - \delta) = 5.8$. The obtained formula and the model presented may be used to analyze the diffusion data for various liquids as well as the foreign-atom or vacancy diffusion in a crystal.

1. Introduction

It is well known that the general features of transport phenomena of a gas can be understood in terms of a mean free path [1]. For a liquid, the concept of the mean free path for particles simply breaks down. Although a unified way of treating transport coefficients of both gases and liquids by means of the correlation function formula [2] is known, this method requires many steps of mathematical as well as physical approximations, and does not allow a direct, simple physical interpretation. One of the main purposes of the present study is to identify simple physical concepts for characterizing the self-diffusion coefficient of a simple (inert-gas-molecular) liquid. We will approach this problem by analyzing the experimental diffusion coefficient [3] by means of the corresponding-state principle [3, 4], identifying the central physical concepts and finally analyzing quantitatively the data in terms of the correlated walk model [5].

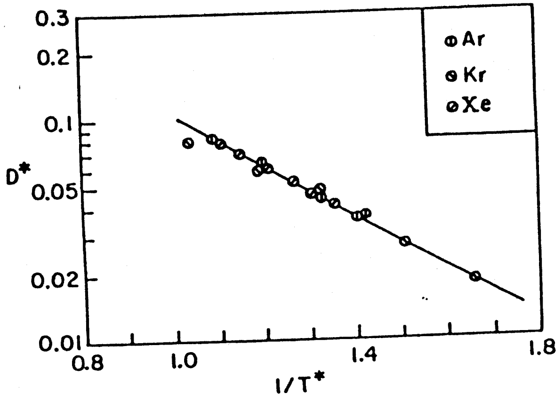

Fig. 1. The logarithm of the reduced self-diffusion coefficient $D^* \equiv Ds^{-1}m^{1/2}\epsilon^{-1/2}$ for simple liquids is plotted as a function of the inverse of the reduced temperature $T^* \equiv k_BT\epsilon^{-1}$, reproduced from ref. [6]; the experimental points are due to Naghizadeh and Rice [3]

The intermolecular interaction between inert-gas atoms (Ar, Kr, Xe) can be represented very well by the (6-12) Lennard-Jones potential with molecular-size parameter s and energy-depth parameter ϵ. Naghizadeh and Rice [3], and again Tham and Gubbins [6], showed that the measured self-diffusion coefficients $D^* \equiv D(m/\epsilon s^2)^{1/2}$ reduced in terms of s, ϵ, and m (mass), for simple fluids fall quite well on a single curve in the $D^* - T^* \equiv Tk_B/\epsilon$ plane in accordance with the law of corresponding states. This behavior is shown in Fig. 1. The temperature dependence is characterized by

$$D = \text{constant} \exp(-\epsilon_b/k_BT), \tag{1.1}$$

where ϵ_b is a constant possessing the dimension of energy. This may be interpreted as follows: Consider a reference (tagged) molecule in a liquid. This molecule moves a distance of a few Angstrom by overcoming the energy barrier ϵ_b generated by the surrounding molecules. By the Boltzmann factor argument, the probability of overcoming such an energy barrier will be proportional to $\exp(-\epsilon_b/k_BT)$. The diffusion coefficient is expected to be proportional to this probability and therefore should show the temperature-dependence as given by (1.1).

The idea of interpreting the diffusion in a liquid in terms of an *activation energy* ϵ_b was proposed a long time ago by Eyring [7] and others [4, 8]. In fact, the experimental data for the self-diffusion coefficients of various liquids including CH_4, *n*-pentane, *n*-heptane, benzene, ethanol and water [9] can be represented by the exponential temperature dependence of the type (1.1). Despite such extensive evidence, the idea of an activation energy has not always been accepted by all the researchers [3]. This situation may be contrasted with the case of the impurity-atom (or vacancy) diffusion in a crystal, where a similar exponential temperature-dependence

$$D_{\text{impurity}} \propto \exp(-\epsilon_a/k_BT), \tag{1.2}$$

where ϵ_a is an energy parameter, is universally observed [10]. Here, the activation energy ϵ_a can be regarded as a constant characteristic of a particular kind of migrating molecule (or vacancy) and the host crystal. In contrast, the energy parameter ϵ_b for the liquid must be considered as a *mean* energy barrier generated by the *moving* molecules, and therefore may depend on the temperature and pressure. In this respect, the ϵ_b is similar to the mean free path for a gas; it happens to be nearly temperature-independent for simple liquids.

In the present work, we will develop a correlated walk model with the possibility of a trap and substantiate the formula (1.1) in a clear manner. In addition, we will demonstrate special importance of the dynamical correlation to account for the magnitude of the diffusion coefficient.

2. Summary of Experimental Data

Naghizadeh and Rice [3] took measurements of self-diffusion coefficients in liquids Ar, Kr, and Xe. Their data and the corresponding-state principle analysis are represented in Fig. 1. The approximate temperature range in which the measurements were taken is shown in Tab. 1.

Table 1

	Temperature range (K)
Ar	85–108
Kr	100–160
Xe	160–200

We see from Fig. 1 that the self-diffusion coefficients all fit the same equation

$$\ln D^* = d_0 - d_1(T^*)^{-1}, \tag{2.1}$$

where

$$d_0 = 0.403, \qquad d_1 = 2.65. \tag{2.2}$$

Using Eqs. (2.1) and (2.2), we can express the coefficient D in the following form

$$D = s(\epsilon/m)^{1/2} \exp(d_0) \times \exp(-d_1/k_BT) \tag{2.3}$$

or

$$D = \text{constant} \times \exp(-\epsilon_b/k_BT), \tag{2.4}$$

where ϵ_b is a constant possessing the dimension of energy.

The potential parameters (s, ϵ) and atomic weights for Ar, Kr, and Xe are listed in Tab. 2.

Table 2

	s (Å)	ϵ/k_B (K)	Atomic weight
Ar	3.45	119.8	39.944
Kr	3.70	166.1	83.80
Xe	4.03	229.8	131.30

Using these data and (2.3), we can represent the self-diffusion coefficients as follows:

$$D_{Ar} = 8.1 \times 10^{-8} \times \exp(-318K/T)\ \mathrm{m^2s^{-1}}, \tag{2.5a}$$

$$D_{Kr} = 7.1 \times 10^{-8} \times \exp(-440K/T)\ \mathrm{m^2s^{-1}}, \tag{2.5b}$$

$$D_{Xe} = 7.3 \times 10^{-8} \times \exp(-609K/T)\ \mathrm{m^2s^{-1}}. \tag{2.5c}$$

We note that the exponential factors are considerably smaller than one in the actual experimental temperature range. We will come back to this point later in Sect. 5.

3. The Correlated Walks on a Simple Cubic Lattice

The correlated walk model, which was introduced first by Goldstein [11], is an extension of the more familiar random walk model [12]. Recently, we have applied the former model to various physical problems [5, 13].

The correlated walks in three dimensions may be set up as follows. Let us consider a simple cubic lattice. A walker, by assumption, moves on the lattice with the rule that he may proceed in the same direction as that of the previous step with probability α, reverse with probability β, turn at right angles with probability γ or stay at the same site with probability σ with the normalization condition

$$\alpha + \beta + 4\gamma + \sigma = 1, \tag{3.1}$$

where the factor 4 is due to the fact that there are four orthogonal directions to any direction of the previous step. The stationary walker may stay at the same site with probability σ' or restart in any of the six directions with probability μ with the normalization condition

$$\sigma' + 6\mu = 1. \tag{3.2}$$

Note that the step probabilities are *correlated* in contradistinction to the case of the random walks. The feature that the walker can stop, stay and restart, makes it suitable for discussions of the migrating molecules in the liquid.

In an earlier work [5], we calculated the mean square displacement for this model exactly (see ref. [5], Eq. (3.9)). By examining its asymptotic behavior for a long time, we can compute the diffusion coefficient D for the model. The result is given by (ref. [5], Eq. (5.4))

$$D = \frac{1}{6}\,\frac{1+\delta}{1-\delta}\,\frac{1-\sigma'}{1+\sigma-\sigma'}\,\frac{a^2}{\tau}, \tag{3.3}$$

where

$$\delta \equiv \alpha - \beta; \tag{3.4}$$

and a and τ represent respectively the lattice constant and the unit jump time. This expression (3.3) was obtained after lengthy calculation with the aid of generating function techniques [5]. One can obtain the same result (3.3) much more simply by Taylor-expanding the recurrence equations for the arrival probabilities. This method is briefly discussed in the Appendix.

4. Simulation of the Molecular Motion

a) *Lattice*

Any molecule in a liquid moves in a continuous space. In our lattice model, we approximate this motion by the motion of a particle on a simple cubic lattice. We may choose the lattice constant a to be the molecular size parameter s:

$$a = s. \tag{4.1}$$

For a simple liquid, the interparticle distance is approximately equal to s. This unit a is much smaller than the distance in which the mass density, the current density, etc., are measured. This allows us to define and discuss the diffusion in our lattice model.

b) *Unit Time and Step Probabilities*

Let us imagine a liquid with one tagged (radio-activated) molecule and follow the motion of this molecule. At any instant, the molecule may be nearly stationary within the fluctuating cage generated by its neighboring molecules or may be moving out of the cage and into a new location. Let us choose a typical time τ in which it travels the distance a when it is in motion. Let us now perform the following gedanken-experiment. We use a super-camera and take one picture per unit time τ (with the exposure time τ). After taking 1000 shots, we look at our pictures and count how many times the molecule moved a distance of the order a, how many times it moved forward, turned and reversed, how many times it was at rest. The result of this examination will give us the set of values for the step probabilities $(\alpha, \beta, \gamma, \sigma, \sigma', \mu)$. Note that the step probabilities so determined depend on the choice of the unit time τ. If the time τ is too large, the molecule moves a distance far greater than a. If it is too small, the molecule cannot move the distance a (within the time τ). The practical choice of the unit time will be discussed in the next section, where we analyze the experimental data.

5. Analysis and Discussions

Earlier in Sect. 3, we noted an expression for the self-diffusion coefficient D as given in (3.3). Let us re-express it in the form

$$D = \frac{1}{6}\,\frac{1+\delta}{1-\delta}\,\frac{1}{1+\sigma(1-\sigma')^{-1}}\left(\frac{a}{\tau}\right)a. \tag{5.1}$$

As explained in Subsection 4a, we may assume that

$$\begin{aligned} a \text{ (lattice constant)} &= \text{interparticle distance} \\ &= s \text{ (molecular size parameter)}. \end{aligned} \tag{5.2}$$

The ratio a/τ, which represents the jump speed in the model, can be identified as the *microscopic migration speed* v as explained in Subsection 4b

$$a/\tau \text{ (jump speed)} = v \text{ (microscopic migration speed)}. \tag{5.3}$$

Let us now look at the factor $[1+\sigma(1-\sigma')^{-1}]^{-1}$. We expand $[1-\sigma']^{-1}$ in a series, and obtain

$$1+\sigma(1-\sigma')^{-1} = 1+\sigma+\sigma\sigma'+\sigma\sigma'^2+\cdots. \tag{5.4}$$

We may now interpret those terms on the right-hand side as relative probabilities in the following manner:

If the walker arrives at a site it must move out of it with zero, one, two, ..., units (τ) of time. The relative probabilities corresponding to

these events are represented by the terms on the right-hand side. We may normalize the sum of these probabilities to unity. Then, the factor

$$\frac{1}{1+\sigma(1-\sigma')^{-1}} \equiv q \tag{5.5}$$

represents exactly the probability that the walker moves in and out without stopping, that is, the probability of finding the molecule in the state of migration. This number q can also be regarded as the ratio of the number of migrating molecules to the number of stationary molecules. To migrate the molecule must overcome the energy barrier ϵ_b generated by the surrounding molecules. From the Boltzmann factor arguments, this number q can then be represented by $\exp(-\epsilon_b/k_BT)$. Thus, we find the equivalence

$$q \equiv \frac{1}{1+\sigma(1-\sigma')^{-1}} \sim \exp(-\epsilon_b/k_BT). \tag{5.6}$$

We can alternatively interpret the factor $[1+\sigma(1-\sigma')^{-1}]^{-1}$ as the ratio of the travel time τ in which the molecule migrates the distance a with no stopping to the effective migration time $\tau + t_0$ with inclusion of the "trap" time t_0

$$q \equiv \frac{1}{1+\sigma(1-\sigma')^{-1}} = \frac{\tau}{\tau+t_0}\,. \tag{5.7}$$

Note that the trapping possibility effectively reduces the diffusion coefficient D by the ratio q.

The molecule in motion after overcoming the energy barrier in general should have a relatively large momentum compared with the molecule trapped in the cage. The molecule in such an activated state may proceed a few steps in the same direction rather than proceed in a zig-zag manner or stop. Such correlation of successive steps will make the diffusion coefficient greater than otherwise. This effect is represented by the factor $(1+\delta)/(1-\delta)$ in formula (5.1).

We are now ready to analyze the experimental data. For definiteness, let us take the case of argon, in which case the self-diffusion coefficient D is given by (2.5a).

First we look at the temperature-dependent exponential factor. Using (5.6) and comparing it with (2.5a), we obtain

$$\epsilon_b/k_B \equiv T_b = 318\ \text{K}. \tag{5.8}$$

In the experimental temperature range (85–108 K), the exponential factor

$$\exp(-318\ \text{K}/T) \sim \frac{\tau}{\tau+t_0} \tag{5.9}$$

is much smaller than unity. This indicates the reasonableness of our interpretation that the factor $\exp(-\epsilon_b/k_BT)$ represents the fraction of the number of migrating molecules over the total number. It also means that the actual trap time t_0 is much greater than the transit time without stopping, τ.

Second, we will examine the prefactor. From (4.1) or (5.2), we may choose

$$a = s = 3.54 \text{ Å}. \tag{5.10}$$

For the average migration speed a/τ, we may take the thermal speed $(3k_BT'/M)^{1/2}$ with the temperature T' corresponding to the midpoint of the temperature range in Fig. 1, $T^* = 0.80$:

$$a/\tau = (3k_BT'/M)^{1/2} = (2.4\epsilon/M)^{1/2} = 245 \text{ ms}^{-1}. \tag{5.11}$$

Substituting (5.8)–(5.10) into (5.1), we obtain

$$D_{\text{Ar}} = \frac{1+\delta}{1-\delta}(1.40 \times 10^{-8}) \exp(-318 \text{ K}/T) \text{ m}^2\text{s}^{-1}. \tag{5.12}$$

Notice that this expression is fairly close to (2.5a). If we further choose

$$\frac{1+\delta}{1-\delta} = 5.8, \tag{5.13}$$

we then get a numerical agreement between (2.5a) and (5.12).

Solving Eq. (5.13), we obtain

$$\delta \equiv \alpha - \beta = 0.71, \tag{5.14}$$

which implies a large degree of correlation in the forward direction. Alternatively, we may interpret this situation as follows. In the random walk limit ($\delta = 0$, $\sigma = 0$), expression (5.1) for the diffusion coefficient is reduced to

$$D_{\text{random walk}} = \frac{1}{6}\left(\frac{a}{\tau}\right)a. \tag{5.15}$$

Comparison with (5.1) indicates that the correlation of steps lengthens the unit step a by the factor $(1+\delta)/(1-\delta)$. In other words, if we define the "effective" unit step-length (lattice constant) by

$$\frac{1+\delta}{1-\delta}a \equiv a^*, \tag{5.16}$$

and assume random walks on the new lattice, we can get the same diffusion coefficient except for the effect of the trapping represented by $[1 + \sigma(1-\sigma')^{-1}]^{-1}$.

The value 5.8 obtained for $(1+\delta)/(1-\delta)$ depends on the choice of the migration speed. A molecule which overcomes the energy barrier may have a higher kinetic energy than the thermal energy and therefore may move with a greater speed than that which we chose in (5.11). Consideration of this effect may bring down the value 5.8 toward unity, say, by a few tens of percentage.

In summary, we have the following picture for the diffusion. At a given time, most particles are trapped within their molecular cages. The ratio of the number of migrating molecules to the total number of molecules is given by $\exp(-\epsilon_b/k_BT)$. The few that move migrate only a distance of the order of a few interparticle distances with cooperation of the neighboring molecules.

The present theory may be used to analyze the diffusion data for various liquids. We have examined many data of the self-diffusion coefficients for CH_4, H_2O, *n*-pentane, *n*-heptane, benzene, ethanol, sulfer (2 phases), etc. [9]. All these liquids exhibit the exponential temperature dependence indicative of a trap-and-go process in spite of the fact that some of these molecules are far from spherical. We will report these investigations in separate papers.

Tham and Gubbins [6] observed that the reduced thermal conductivity data for simple liquids fall on a single curve when plotted in reduced units in accordance with the corresponding-state principle, but their temperature dependence is quite different and far from the exponential temperature dependence observed for the diffusion data. In fact the thermal conductivity decreases as the temperature is raised. This somewhat unexpected temperature dependence may be understood if we assume that the heat conduction of a liquid can be accounted for mainly by transport of energy by phonons just as in the case of the heat conductivity in a solid. We plan to investigate this problem and report it in the near future.

The viscosity of a liquid decreases almost exponentially as the temperature is raised. This is an even harder problem to resolve. To find central concepts associated with each of the different transport coefficients will be an important initial step toward the complete understanding of the multi-faceted transport phenomena in liquids.

The level of description presented in the present work is semi-microscopic. In fact, we have not attempted to determine the values of the parameters (ϵ_b, δ) from the basic Hamiltonian of the system. Several attempts at describing the diffusion in liquids from first principles have been made [8]. Some of these were examined by Naghizadeh and Rice [3] critically and in an enlightening manner. A complete microscopic theory which may be compared with experiments is yet to be developed in the future.

Appendix
Derivation of Formula (3.3) for the Diffusion Coefficient

Let us first consider a one-dimensional correlated walk with the possibility of a trap. The unit step length and jump time are denoted by a and τ. In this case, there is no possibility of the walker turning at 90° ($\gamma = 0$). The step probabilities, then, are normalized by

$$\alpha + \beta + \sigma = 1, \tag{A.1}$$

$$2\mu + \sigma' = 1. \tag{A.2}$$

The probability that the walker arrives at the (discrete) site $x \equiv Na$ at the (discrete) time $t \equiv N\tau$ with the right (left) step will be denoted by $P_1(x,t)$ ($P_2(x,t)$). The probability that the walker stays stationary at the time t is denoted by $P_0(x,t)$. These probabilities of arrival, P_j, with the directions $j = 0, 1$, or 2, satisfy the following recurrence relations

$$P_1(x,t) = \alpha P_1(x-a, t-\tau) + \beta P_2(x-a, t-\tau) + \mu P_0(x-a, t-\tau), \tag{A.3}$$

$$P_2(x,t) = \beta P_1(x+a, t-\tau) + \alpha P_2(x+a, t-\tau) + \mu P_0(x+a, t-\tau), \tag{A.4}$$

$$P_0(x,t) = \sigma P_1(x, t-\tau) + \sigma P_2(x, t-\tau) + \sigma' P_0(x, t-\tau). \tag{A.5}$$

The sum

$$P(x,t) \equiv P_1(x,t) + P_2(x,t) + P_0(x,t) \tag{A.6}$$

represents the probability that the walker finds himself at the site x at the time t. In the limits in which the position is measured in infinitesimal lengths a, and the time is measured in infinitesimal intervals τ, the probability distribution function $p(x,t)$ defined by

$$\begin{aligned} p(x,t)a &= \text{the probability of finding the walker in} \\ &\quad (x - \tfrac{1}{2}a, x + \tfrac{1}{2}a) \text{ at the time } t \\ &= P(x,t), \end{aligned} \tag{A.7}$$

can be regarded as a continuous function of x and t, and this $p(x,t)$ is expected to obey the diffusion equation

$$\frac{\partial p(x,t)}{\partial t} = D\,\frac{\partial^2 p(x,t)}{\partial x^2}, \tag{A.8}$$

where the constant D represents the diffusion coefficient.

A way of deriving Eq. (A.8) and obtaining an expression for the diffusion coefficient is as follows. Let us introduce

$$P_{12}(x,t) \equiv P_1(x,t) + P_2(x,t). \tag{A.9}$$

Using (A.1)–(A.4) and re-arranging terms, we obtain

$$\begin{aligned} &\mu[P_0(x+a, t-\tau) + P_0(x-a, t-\tau)] + (1-\sigma')(\beta-\alpha)P_0(x, t-2\tau) \\ &\quad + \alpha[P_{12}(x+a, t-\tau) + P_{12}(x-a, t-\tau)] \\ &\quad + (1-\sigma)(\beta-\alpha)P_{12}(x, t-2\tau) - P_{12}(x,t) = 0. \end{aligned} \tag{A.10}$$

From (A.3), we directly get

$$P_{12}(x, t-\tau) = \frac{1}{\sigma}\,[P_0(x,t) - \sigma' P_0(x, t-\tau)]. \tag{A.11}$$

Introducing this expression in Eq. (A.10), we can get an equation for P_0 alone:

$$\begin{aligned} &P_0(x, t+\tau) - \alpha[P_0(x-a,t) + P_0(x+a,t)] - \sigma' P_0(x,t) \\ &\quad + \tfrac{1}{2}[\sigma'(1+\delta) - \alpha][P_0(x-a, t-\tau) + P_0(x+a, t-\tau)] \\ &\quad + (\alpha+\beta)\,\delta P_0(x, t-\tau) + \delta(\sigma - \sigma')P_0(x, t-2\tau) = 0; \\ &\qquad (\delta \equiv \alpha - \beta). \end{aligned} \tag{A.12}$$

We now take the continuum limit, and introduce the distribution function $p_0(x,t)$ as indicated in (A.7). This function p_0 satisfies the same equation as Eq. (A.12) for the probability P_0 (since this equation is linear). We now expand Eq. (A.12) for p_0 with respect to small a and τ. Terms of the lowest order and those of the order a vanish identically. First nontrivial terms occur in the orders a^2 and τ, and they can be represented by

$$\frac{1}{2}(1-\sigma')(1+\delta)\,\frac{\partial^2 p_0}{\partial x^2}\,a^2 = (1+\sigma-\sigma')(1-\delta)\,\frac{\partial p_0}{\partial t}\,\tau, \tag{A.13}$$

which can be converted into the form of the diffusion equation (A.8)

$$\frac{\partial p_0}{\partial t} = D\,\frac{\partial^2 p_0}{\partial x^2} \tag{A.14}$$

with

$$D = \frac{1}{2}\,\frac{1+\delta}{1-\delta}\,\frac{1-\sigma'}{1+\sigma-\sigma'}\,\frac{a^2}{\tau}. \tag{A.15}$$

We see in (A.14) that the "staying" probability distribution function, $p_0(x,t)$, obeys the desired diffusion equation. In fact, the full and partial probability distribution functions (p, p_1, p_2) all satisfy the same diffusion equation in the continuum limit; these distribution functions are different by constant factors, and are related as follows:

$$\begin{aligned} p_0(x,t) &= \frac{\sigma'}{1+\sigma-\sigma'}\,p(x,t), \\ p_1(x,t) = p_2(x,t) &= \frac{1-\sigma}{2(1+\sigma-\sigma')}\,p(x,t). \end{aligned} \tag{A.16}$$

These can be derived from the definition equation (A.6) and (A.11).

The diffusion coefficient D for a three dimensional walk can be obtained in a similar manner. The result is simply one third of expression (A.15):

$$D = \frac{1}{6}\frac{1+\delta}{1-\delta}\frac{1-\sigma'}{1+\sigma-\sigma'}\frac{a^2}{\tau} \quad \text{(3 dimensions).} \qquad \text{(A.17)}$$

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