

Conjecture on electron mobility in liquid hydrocarbons

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We propose that the mobility of electrons in liquid hydrocarbons can be explained by a physical model which implies that the medium is microscopically inhomogeneous with regard to electron transport. Rotational fluctuations result in high and low mobility regions. The effective medium theory is utilized to correlate all the available mobility data with V_0 , the energy of the quasifree electron in each liquid.

I. BACKGROUND

A series of theoretical studies^{1,2} on excess electron states in liquid rare gases has established a localization criterion which relates the energetic stability of the localized state to the energy V_0 of the quasifree electrons in that particular dense fluid. In media characterized by large positive V_0 (i.e., $V_0 = +1.0$ eV for liquid He and $V_0 = +0.5$ eV for liquid Ne), the excess electron is localized, being characterized by low ($\sim 10^{-2}$ cm² V⁻¹·sec⁻¹) electron mobility μ . On the other hand, in heavy rare gases Ar, Kr, and Xe where V_0 is negative ($V_0 = -0.33$ eV for liquid Ar), the excess electron is quasifree and exhibits high ($\mu \sim 5 \times 10^2 - 2 \times 10^3$ cm² V⁻¹·sec⁻¹) mobilities. These theoretical studies consider a microscopically homogeneous medium disregarding the role of density fluctuations which are, however, crucial for the elucidation of the problem of electron mobility in dense He gas.³

Studies of excess electrons in liquid hydrocarbons are extremely interesting in that they establish the nature of electron-medium interactions in complex nonpolar liquids. Minday, Schmidt, and Davis,⁴ Schmidt and Allen,⁵ and Freeman⁶ have recorded electron mobilities in a variety of liquid saturated hydrocarbons which exhibit a variation of three orders of magnitude (see Table I) for chemically and physically similar systems. Recently, V_0 values for these systems became available from the work of Holroyd and Allen,⁷ Holroyd⁸, and Schiller, Vass, and Mandics⁹ and are summarized in Table I.

Holroyd and Allen⁷ originally drew attention to a correlation between μ and V_0 in liquid hydrocarbons. From the available experimental data, it is apparent that the theoretical models applied to liquid rare gases have to be drastically modified since in the complex hydrocarbon solvents a gradual change of μ with V_0 is exhibited. Thus, the concepts of an excess electron interacting with a microscopically homogeneous medium are no longer applicable. Schmidt and Allen⁵ were the first to postulate that some sort of "fortuitous coincidence of rotational phases of neighboring molecules" results in temporary trapping sites. A simple approach to the problem is based on Frommhold's formula,¹⁰

$$\mu = \mu_F / (1 + \nu\tau), \quad (1)$$

which assumes that the quasifree electron mobility μ_F is reduced by the product of the lifetime of the electron τ in the traps, and the localization frequency ν . In this context, Davis *et al.*¹¹ have generalized the Cohen-Lekner mobility equations to account for scattering from anisotropic molecules. The role of fluctuations in determining the features of electron mobility in liquid hydrocarbons was recently emphasized by Schiller.¹² He considered a two carrier model, where electron localization via bubble formation occurs in certain regions characterized by low local medium energy. He invokes fluctuations of the local medium energy, characterized by the standard deviation of $C_v kT^2$, and attempts to calculate the fraction of trapped electrons. He then assumes that the medium is homogeneous with regard to electron transport and that the mobility is proportional to the fraction of the quasifree electrons.

In this article, we attempt to provide a semiquantitative theory of electron transport in liquid hydrocarbons in terms of electron transport in a microscopically inhomogeneous system.¹³⁻¹⁶ Electron mobility in liquid hydrocarbons is dominated by local rotational fluctuations, as originally suggested by Schmidt and Allen⁵ and by Schiller.¹² We propose that the medium can be described in terms of "transparent" regions characterized by high μ and "almost opaque" regions specified by low μ . The fraction of transparent allowed regions C will be determined from a phenomenological fluctuation theory for the electron-medium local potential. The electron mobility will then be related to C by a semiclassical effective medium theory resulting in a correlation between μ and V_0 .

II. ELECTRON TRANSPORT IN A MICROSCOPICALLY INHOMOGENEOUS MEDIUM

In recent theoretical studies of the electronic states and transport in disordered systems, Cohen has emphasized the crucial role of potential fluctuations,¹³ while Ziman¹⁴ has adopted a semiclassical picture of percolation of classical particles in a random potential, which was subsequently developed by Cohen and Sak,¹⁵ Cohen and Eggarter,³ and Kirkpatrick.¹⁶

We shall adopt a similar semiclassical approach and envision the medium to be divided into cells of volume L^3 , and treat the local relative orientations and, thus,

TABLE I. Experimental data on electrons in liquid hydrocarbons.^a

Liquid	μ cm ² V ⁻¹ ·sec ⁻¹	T °K	E _A kcal/mole	V ₀ eV
Methane	300 ^b	120		
Tetramethylsilane	90 ^c	296		-0.61, ^b -0.62, ⁱ -0.55 ⁱ
Neopentane	55 ^c	296		-0.43, ^b -0.43 ⁱ , -0.35 ⁱ
	67 ^d	296	0.5	
	50 ^e	296	0.5	
2, 2, 4, 4-Tetramethylpentane	37.5 ^e	347	1.48	(-0.33) ^k
2, 2, 5, 5-Tetramethylhexane	17.4 ^e	371	1.1	(-0.28) ^k
2, 2-Dimethylbutane	12.6 ^c	290	1.2	-0.24, ^b -0.15 ⁱ
2, 2, 3, 3-Tetramethylpentane	8.5 ^e	373	1.46	(-0.21) ^k
2, 2, 4-Trimethylpentane	7 ^e	-0.15, ^b -0.18, ⁱ -0.14 ⁱ
2-Methyl-2-butene	2.4 ^f	281	2.0	(-0.19) ^k
2-Methylpropane	1.42 ^b	236	3.0	(-0.18) ^k
Cyclopentane	1.1 ^c	296	...	-0.18, ^b -0.28, ⁱ -0.17 ⁱ
Cyclohexane	0.67 ^e	329	3.0	(-0.15) ^k
	0.48 ^e	296		
	0.38 ^e	298		
Benzene	0.6 ^f	298	...	-0.14 ⁱ
Toluene	0.54 ^d	298	...	-0.22 ⁱ
Propane	0.4 ^e	208	2.6	(-0.13) ^k
n-Butane	0.4 ^e	296	...	(-0.13) ^k
n-Pentane	0.075 ^f	298	...	+0.02, ^b -0.01, ⁱ +0.04 ⁱ
	0.16	296		
n-Hexane	0.09 ^f	307	4.06	0.09, ^b 0.04, ⁱ 0.0, ⁱ 0.16 ⁱ
	0.118 ^e	307	4.82	
2-Methylpentane	-0.14 ⁱ
2-Methylpentane	+0.01, ^b 0.0, ⁱ -0.14 ⁱ
2, 3-Dimethylbutane	-0.10 ⁱ
Methylcyclohexane	+0.14 ^b
n-Decane	+0.22 ^b

^a All data are for saturated hydrocarbons, except benzene and toluene, which were also included.

^b P. G. Fuochi and G. R. Freeman, *J. Chem. Phys.* **56**, 2333 (1972).

^c W. F. Schmidt and A. O. Allen, *J. Chem. Phys.* **50**, 5037 (1969); **52**, 4788 (1970).

^d R. M. Minday, L. D. Schmidt, and H. T. Davis, *J. Phys. Chem.* **76**, 442 (1972).

^e J. Dodelet and G. R. Freeman, *Can. J. Chem.* (to be published).

^f R. M. Minday, L. D. Schmidt, and H. T. Davis, *J. Chem. Phys.* **50**, 1473 (1969); **54**, 3112 (1971).

^g R. G. Brown (unpublished) quoted by H. T. Davis in *Electrons in Fluids—Proceedings of Colloque Weyl III*, edited by J. Jortner and N. R. Kestner (Springer, Berlin, to be published).

^h R. A. Holroyd, *J. Chem. Phys.* (to be published).

ⁱ R. A. Holroyd and M. Allen, *J. Chem. Phys.* **54**, 5014 (1971).

^j R. A. Holroyd, B. K. Dietrich, and H. A. Schwartz, *J. Phys. Chem.* (to be published).

^k Interpolated value based on the present mobility theory.

^l R. Schiller, Sz. Vass, and J. Mandics, *J. Phys. Chem.* (to be published).

the potential V in each cell as a random quantity. The effective local potentials of each of the cells,

$$V = V(\mathbf{x}, \mathbf{\Omega}, E), \quad (2)$$

are determined by the positions \mathbf{x} and by the orientations $\mathbf{\Omega}$ of the molecules within the sampling length L . The sampling length for local potential fluctuations depends on the energy E of the electron.³ The variational calculations of Halperin and Lax¹⁷ suggest that $L(E) \propto |E - \bar{V}|^{-1/2}$, where \bar{V} is the (energy dependent) average potential. Thus, any effective cell potential is, in general, energy dependent. The distribution of the potentials

(for each energy E) is assumed to be Gaussian about an average \bar{V} being characterized by the standard deviation ξ :

$$P(V) = (2\pi\xi^2)^{-1/2} \exp[-(V - \bar{V})^2/2\xi^2]. \quad (3)$$

For each energy, we now divide the medium into two types of regions: the allowed regions in which the mobility is high $\mu = \mu_0 \sim 100$ cm² V⁻¹·sec⁻¹, and the prohibited regions where the mobility is low $\mu = \mu_1 \sim 10^{-1}$ cm² V⁻¹·sec⁻¹. The allowed transparent regions are defined by the condition that the electron energy is

higher than the effective potential of these cells, i.e.,

$$E \geq V(\mathbf{x}, \Omega, E), \quad (4a)$$

while the forbidden almost opaque regions are defined by the condition:

$$E \leq V(\mathbf{x}, \Omega, E). \quad (4b)$$

The fraction of allowed volume $C(E)$ at a given energy E is

$$C(E) = (2\pi\xi^2)^{-1/2} \int_{-\infty}^E \exp\left[-\frac{(V-\bar{V})^2}{2\xi^2}\right] dV. \quad (5)$$

In view of our ignorance of the details of local rotational fluctuations, we cannot proceed to calculate the mobility from the density of states.³ Rather, several drastic approximations will be introduced at this point. First, we consider a constant average electron energy $\langle E \rangle$ for all liquid hydrocarbons, setting $V = V(\langle E \rangle)$, $\bar{V} = \bar{V}(\langle E \rangle)$, and $C(\langle E \rangle) = C$ in Eq. (5). Second, we assume that the average potential \bar{V} (at energy $\langle E \rangle$) is simply related to the experimental energy V_0 of the quasifree electron state by the simple linear equation

$$\bar{V} = \alpha + V_0, \quad (6)$$

where α is constant for all hydrocarbons. A justification for Eq. (6) may be obtained by considering the potential V in a given cell in the spirit of the Wigner Seitz model.^{1,2} V consists of a short range repulsive contribution V_a , an electronic polarization term U_p , and an electrostatic interaction term U_d of the C-H dipoles, so that a cell potential is $V = V_a + U_p + U_d$, while the average potential is $\bar{V} = \bar{V}_a + \bar{U}_p + \bar{U}_d$. Now, provided that the contributions \bar{U}_p and \bar{U}_d are constants^{1,2} then the experimental quasifree electron energy monitors the average properties of the medium and $V_0 = T + \bar{U}_p + \bar{U}_d$, where T is the kinetic energy contribution.^{1,2} Thus $\bar{V} = (\bar{V}_a - T) + V_0$. Assuming that the repulsive contributions are identical for different hydrocarbon solvents we have Eq. (6) with $\alpha = (\bar{V}_a - T)$.

At this low level of sophistication, the fraction of allowed volume is

$$\begin{aligned} C &= (2\pi\xi^2)^{-1/2} \int_{-\infty}^{\langle E \rangle} \exp\left[-\frac{(V-V_0-\alpha)^2}{2\xi^2}\right] dV, \\ &= (2\pi)^{-1/2} \int_{-\infty}^{(E-\alpha)/\xi} \exp\left(-\frac{t^2}{2}\right) dt, \end{aligned} \quad (7)$$

where $E_t = \langle E \rangle - \alpha$ is an effective cut off energy parameter, which we take to be the same for all liquid hydrocarbons.

We now proceed to relate the mobility to C . Invoking semiclassical arguments, we realize that the mobility should not be simply proportional to C . Consider a situation in which all of the allowed regions were clustered in one part of the medium. The contribution of this area to the mobility would be negligible since the quasifree electron could never traverse the entire

medium. Thus, we must only consider those contiguous regions which span the material from one side to the other if we want the contribution of the high mobility. All other regions will yield only low mobility contributions. The value of C (denoted by C^*) above which macroscopic extended channels open throughout the material is called the critical percolation limit.¹⁸ This value C^* is estimated as 0.2 to 0.3 for specific three dimensional lattice models.¹⁸ Following related studies of disordered systems¹⁸ we choose $C^* \sim 0.2$.

To evaluate mobility in a microscopically inhomogeneous system we utilize the semiclassical effective medium theory of Bruggeman¹⁸ and Landauer¹⁹ which was recently revived by Kirkpatrick.¹⁶ The final result applied to our problem is^{16,19,20}

$$f = \mu/\mu_0 = a + [a^2 + (x/2)]^{1/2}, \quad (8)$$

$$a = \frac{1}{2} \left[\left(\frac{3}{2}C - \frac{1}{2} \right) (1-x) + (x/2) \right], \quad (9)$$

and

$$x = \mu_1/\mu_0. \quad (10)$$

For low x values ($x < 10^{-2}$), f is independent of x for $0.4 < C < 1$, the mobility being characterized by the simple expression

$$\mu = \mu_0 \left(\frac{3}{2}C - \frac{1}{2} \right); \quad C > 0.4. \quad (11)$$

For $C < 0.4$, μ exhibits a sharp drop reaching the value of μ_1 at $C = 0$.

Note added in proof: The effective medium theory (Refs. 16, 19, and 20) was derived for the electrical conductivity rather than for the mobility. Cohen and Jortner (unpublished) have derived Eqs. (8)–(10) from an effective medium theory for the diffusion coefficient.

This theory was very successful in the elucidation of metal–nonmetal transition in one and two component disordered systems.^{20,21} We shall now apply it to the problem at hand.

III. ELECTRON MOBILITIES IN LIQUID HYDROCARBONS

We now propose to apply the inhomogeneous model to electron transport in liquid hydrocarbons. We envision rotational local fluctuations to determine the “allowed” and the “forbidden” low mobility regions. The cells characterized by a low local potential (relative to $\langle E \rangle$) provide the high mobility region. On the other hand, for certain relative orientations of the C–H bonds on neighboring molecules, the electron may find a ready made trap. These traps are likely those postulated by Schmidt and Allen⁵ and by Davis *et al.*,⁴ rather than electron cavities such as encountered in liquid rare gases,^{1,2} which involve large radial distortions.

The actual electron mobility in a particular hydrocarbon will be determined by the allowed volume frac-

tion which from Eq. (7) is

$$C = \frac{1}{2} + \frac{1}{2} \operatorname{erf}[(V_0 - E_t)/\sqrt{2}\xi], \quad (V_0 - E_t) < 0;$$

$$C = \frac{1}{2} - \frac{1}{2} \operatorname{erf}[(V_0 - E_t)/\sqrt{2}\xi], \quad (V_0 - E_t) > 0 \quad (12)$$

We subsequently relate the mobility to C via Eqs. (8)–(10). Equations (8)–(12) result, now, in an approximate transport theory in liquid hydrocarbons which relates μ to V_0 .

Utilizing the experimental data in Table I, the four parameters E_t , ξ , μ_0 , and x were fitted. In the high mobility systems, where $C > 0.4$ and $f > 0.1$, μ is independent of x . By selecting $\mu_0 = 100 \text{ cm}^2 \text{ V}^{-1} \cdot \text{sec}^{-1}$ as a typical value, we have then determined $\xi = 0.26 \text{ eV}$ and $E_t = -0.27 \text{ eV}$ from the fit of the three highest mobility data. This establishes the relation between μ and C over the entire range. The mobility data for $C < 0.4$ were then fit with $x = 6 \times 10^{-4}$, since for low x values extensive numerical calculations^{20,21} indicate that $\mu(C=0.15)/\mu(C=0)$ is about 2.

The mobility versus V_0 curve calculated for different solvents is displayed in Fig. 1. Also shown on the top scale is the fraction of allowed volume. The fit to the experimental data is quite good, supporting the present semiclassical description of electron mobility in hydro-

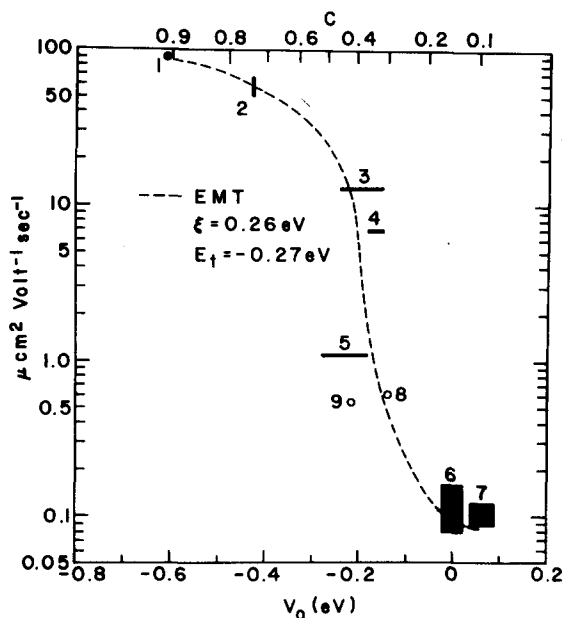


FIG. 1. Electron mobility in liquid hydrocarbons as a function of V_0 , and the allowed volume fraction available to the quasifree electron $C(E)$. Dashed line—Theoretical curve with $E_t = -0.27 \text{ eV}$, $\xi = 0.255 \text{ eV}$, $\mu_0 = 100 \text{ cm}^2 \text{ V}^{-1} \cdot \text{sec}^{-1}$, and $x = 6 \times 10^{-4}$. Experimental points for saturated hydrocarbons: (1) Tetramethylsilane, (2) neopentane, (3) 2,2-dimethylbutane, (4) 2,2,4-trimethylpentane, (5) cyclopentane, (6) *n*-pentane, and (7) *n*-hexane. We have also included two data points for aromatic hydrocarbons: (8) benzene and (9) toluene, where negative ion states could contribute to the mobility. (References to the original data are given in Table I.)

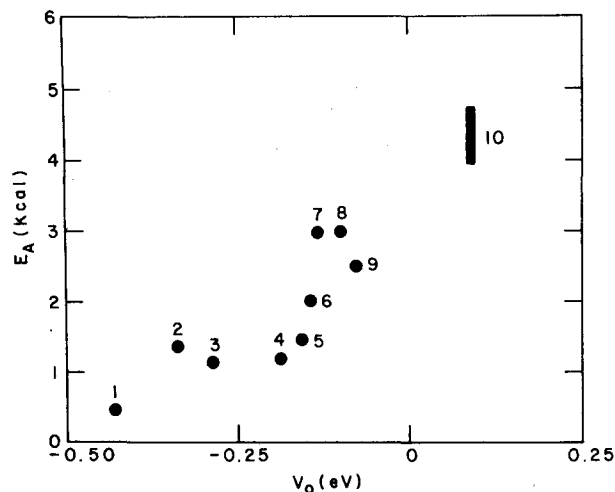


FIG. 2. Activation energy of electron mobility in liquid hydrocarbons as a function of V_0 . All V_0 values except for points 1, 4, and 10 are based on the validity of Fig. 1 since the experimental values of V_0 have not been measured. Experimental points: (1) neopentane, (2) 2,2,4,4-tetramethylpentane, (3) 2,2,5,5-tetramethylpentane, (4) 2,2-dimethylbutane, (5) 2,2,3,3-tetramethylpentane, (6) 2-methyl-2-butene, (7) 2-methylpropane, (8) cyclohexane, (9) propane, and (10) *n*-hexane. (References to the original data are given in Table I.)

carbons as being dominated by fluctuations and, subsequently, by percolation effects. When $C > C^*$, open extended channels exist throughout the liquid, while, for systems characterized by $C < C^*$, electron transport is due to contributions from the low mobility regions. More measurements will be needed in the range $V_0 = -0.3$ to $V_0 = -0.1 \text{ eV}$ where $C = 0.4$ – 0.2 , the vicinity of the percolation threshold.

What is new in our picture is the treatment of electron mobility in microscopically inhomogeneous liquid hydrocarbons in terms of the effective medium theory. This approach drastically differs from the conventional two carrier model. To demonstrate this point we consider the relation of the present theory to Frommhold's¹⁰ formula, Eq. (1). Utilizing Eqs. (8)–(10) we get

$$\nu\tau = f^{-1} - 1. \quad (13)$$

For high values of mobility, Eq. (11) yields, for low x ,

$$\nu\tau = 3(1-C)/(3C-1), \quad 1 > C > 0.4, \quad (14)$$

while for $C < 0.4$, $\nu\tau$ depends in a complicated manner both on C and on x . In contrast, the simple two carrier model of Schiller^{9,12} yields $\nu\tau = (1-C)/C$, for all C .

Some further support for the validity of the physical picture advanced by us is obtained from a preliminary analysis of the available activation energies $E_A = (d \ln \mu / dT) kT^2$ displayed in Fig. 2, where in cases where V_0 was not measured it was estimated from the μ vs V_0 relation of Fig. 1. The E_A vs V_0 data exhibit low activation energies for low V_0 , as well as an indication of a

minimum around $V_0 = -0.25$ eV, and a maximum in E_A around $V_0 = -0.12$ eV.

Although the experimental data are preliminary, we shall now attempt to rationalize them in terms of the effective medium theory. The activation energy is attributed to the temperature dependence of the allowed volume C , and of the mobility ratio x , so that^{20,21}

$$E_A = E_A^1 + kT^2(\partial \ln f / \partial x)(dx/dT) + (\partial \ln f / \partial C)(\partial C / \partial T), \quad (15)$$

where $E_A^1 \approx 0$ is the activation energy at $C=1$. The partial derivatives in Eq. (15) are obtained from Eqs. (8)–(10) in the form^{20–22}

$$\partial \ln f / \partial x = (f+1)/4f(f-a), \quad (16)$$

$$\partial \ln f / \partial C = 3/4(f-a). \quad (17)$$

The first partial derivative Eq. (16) exhibits a monotone increase over the whole C range, being negligible for $C > 0.35$ and reaching an asymptotic value of x^{-1} around the percolation probability for $C \lesssim 0.25$. The second contribution (17) exhibits a maximum at $C=0.33$, and then decreases towards $C=0$. The temperature coefficients in Eq. (15) can be roughly estimated. Assigning the T dependence of C to the parameter ξ (and thus neglecting a possible temperature dependence of E_i) we get

$$dC/dT \approx (|V_0 - E_i|/2\sqrt{2}\xi^2) \times \exp[-(V_0 - E_i)^2/2\xi^2](d\xi/dT), \quad (18)$$

while the second coefficient is approximated from the activation energy E_A^0 at low $C \rightarrow 0$:

$$dx/dT \approx x(E_A^0/kT^2). \quad (19)$$

As rough guesses, we assume that $\xi \propto T$ so that $d\xi/dT \approx$

$\xi/T \sim 8 \times 10^{-4}$ eV deg⁻¹, while $E_A^0 = 4$ kcal/mole is taken to be the experimental value for n -hexane so that $dx/dT \approx 1.3 \times 10^{-5}$ deg⁻¹. Thus, dx/dT is constant for all C , while dC/dT varies slowly in the regions $C = 0.9-0.6$ and $C = 0.4-0.1$, and, at $C = 0.5$, $dC/dT = 0$. From these qualitative considerations, we conclude the following:

(a) As both derivatives (16) and (17) and the temperature coefficients (18) and (19) are positive, then $(d \ln \mu / dT) > 0$ and the activation energy is positive throughout the whole C range.

(b) The temperature dependence of x contributes only for systems corresponding to the low $C \leq 0.3$ region.

(c) For systems corresponding to $C > 0.3$ the major contribution originates from the temperature dependence of C (or of ξ).

(d) Equations (17) and (18) predict a minimum in E_A for $C = 0.5$, i.e., around $V_0 \approx -0.27$ eV which is not inconsistent with the experimental data.

(e) A maximum in E_A vs C should be observed around $C = 0.33$, i.e., $V_0 \approx -0.15$ eV, which is consistent with the sparse data in Fig. 2. The predicted maximum in E_A vs C , just above the percolation threshold, is of considerable interest.

We hope that these speculations will stimulate further experimental work in this interesting field.

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