Unified Description of Charge-Carrier Mobilities in Disordered Semiconducting Polymers
无序半导体聚合物中电荷载流子迁移率的统一描述

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From a numerical solution of the master equation for hopping transport in a disordered energy landscape with a Gaussian density of states, we determine the dependence of the charge-carrier mobility on temperature, carrier density, and electric field. Experimental current-voltage characteristics in devices based on semiconducting polymers are excellently reproduced with this unified description of the mobility. At room temperature it is mainly the dependence on carrier density that plays an important role, whereas at low temperatures and high fields the electric field dependence becomes important. Omission in the past of the carrier-density dependence has led to an underestimation of the hopping distance and the width of the density of states in these polymers.

从具有高斯态密度的无序能量场中跳跃输运主方程的数值解，我们确定了电荷载流子迁移率对温度、载流子密度和电场的依赖关系。基于半导体聚合物的器件中的实验电流-电压特性可以用迁移率的统一描述很好地再现。在室温下，主要是对载流子密度的依赖性起着重要作用，而在低温和高场下，电场依赖性变得重要。过去对载流子密度依赖性的忽略导致了对这些聚合物中跳跃距离和态密度宽度的低估。

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Introduction.—The use of conjugated semiconducting polymers in light-emitting diodes (PLEDs) [1] and field-effect transistors (FETs) [2] has triggered intensive research into the optoelectronic and electrical transport properties of these materials [3,4]. Understanding their charge-carrier transport is of crucial importance to design and synthesize better materials and further improve device performances. One of the most important parameters determining performance is the mobility □ of the charge carriers. In particular, the dependence of □ on temperature T and electric field E has been extensively addressed in literature [5–8]. Charge transport in disordered polymers is regarded as a hopping process between localized sites, which are thought to consist of conjugated polymer chain segments. The variations in the on-site energies due to disorder are usually assumed to be Gaussian. Very recent direct measurements of the energy distribution in an electrochemically gated polymer transistor, indeed, showed a nearly Gaussian shape [9]. Monte Carlo simulations of hopping transport were performed by Bässler *et al.* for the case of a Gaussian disorder model (GDM), showing a non-Arrhenius temperature dependence □ exp $c\hat{}^2$, with c 0.44, $\hat{}$ □/k_BT, and □ the width of the

引言。—共轭半导体聚合物在发光二极管(pled)[1]和场效应晶体管(fet)[2]中的使用引发了对这些材料的光电和电传输特性的深入研究[3，4]。了解它们的电荷载流子传输对于设计和合成更好的材料以及进一步改善器件性能至关重要。决定性能的最重要参数之一是电荷载流子的迁移率μ。特别是，μ对温度T和电场E的依赖性在文献[5–8]中有广泛论述。无序聚合物中的电荷传输被认为是局域化位点之间的跳跃过程，局域化位点被认为是由共轭聚合物链段组成的。由于无序引起的现场能量的变化通常被假定为高斯分布。最近对电化学门控聚合物晶体管中能量分布的直接测量，确实显示了一种近似高斯形状[9]。Bässler等人对高斯无序模型(GDM)的情况进行了跳跃输运的蒙特卡罗模拟，显示了非阿伦尼乌斯温度依赖性μ exp cσ^2，c为0.44，σ^2/kBT，σ为的宽度

Gaussian, while a Poole-Frenkel □ exp e E behavior 高斯，而普尔-弗伦克尔μ exp e行为

was found, in a limited field range, for the dependence on the electric field [5,6]. However, as pointed out by Gartstein and Conwell [10], a spatially correlated potential for the charge carriers is needed to explain the Poole-Frenkel behavior in a wide region of field strengths. Several suggestions were put forward as a cause for this correlation, such as charge-dipole interactions [11,12] or thermal fluctuations in molecular geometries [13].

在有限的磁场范围内，发现了对电场的依赖性[5，6]。然而，正如Gartstein和Conwell [10]所指出的，需要电荷载流子的空间相关电势来解释在较宽的场强范围内的Poole- Frenkel行为。提出了几个建议作为这种相关性的原因，如电荷-偶极相互作用[11，12]或分子几何结构中的热波动[13]。

Recently, it was realized that the importance of another parameter had been overlooked: the charge-carrier density p [14,15]. Experiments on hole-only diodes and FETs,

最近，人们意识到另一个参数的重要性被忽略了：电荷载流子密度p [14，15]。关于空穴二极管和场效应晶体管的实验，

with the same polymer as active material, showed that □ can differ up to 3 orders of magnitude between the diode and the FET [15]. It was demonstrated that the only way to explain this huge difference is by taking a strong dependence of the mobility on p into account. More recent experiments suggested that at room temperature it is sufficient to take only the p dependence of □ into account, but that at low temperatures it is still necessary to assume an E dependence [16]. Experimentally, it is hard to separate the influences of E and p on □, since under a higher electric field more carriers will be injected. In Ref. [16] the p dependence of □ was taken equal to an empirical form, consisting of an algebraic contribution $p^{T_0/T\ 1}$, derived by Vissenberg and Matters for the high-density regime [17], plus a density-independent contribution, determined from the current-voltage characteristics of hole-only diodes at low voltages. The failure of this empirical form to reproduce the experimental current-voltage characteristics at low temperatures and high voltages was attributed to an unknown dependence of □ on E. The purpose of this Letter is to establish a unified theoretical description of the full T, p, and E dependence of □, and to critically compare the results with experiments.

使用相同的聚合物作为活性材料，表明二极管和FET之间的μ可以相差3个数量级[15]。证明了解释这种巨大差异的唯一方法是考虑迁移率对p的强烈依赖性。最近的实验表明，在室温下，只考虑μ的p相关性就足够了，但是在低温下，仍然有必要假设E相关性[16]。实验上，很难区分E和p对μ的影响，因为在更高的电场下，会注入更多的载流子。参考文献。[16]μ 的p 相关性等于一个经验形式，包括由Vissenberg推导出的代数贡献pT0 /T 1和高密度区的物质[17]，加上密度无关贡献，由低压下空穴二极管的电流- 电压特性确定。这种经验形式未能再现低温和高压下的实验电流-电压特性是由于μ对E的未知依赖性。这封信的目的是建立μ的完整T、p和E依赖性的统一理论描述，并严格地将结果与实验进行比较。

Theory.—We determine the mobility □ unambiguously from a numerical solution of the master equation represent-ing hopping of charge carriers on a lattice of sites:

理论。—我们从主方程的数值解明确地确定迁移率μ，主方程表示电荷载流子在点阵上的跳跃:

$$\sum_{j\neq i}\sum_{j\in G_i}\left[W_{ij}p_i(1-p_j)-W_{ji}p_j(1-p_i)\right]=0, \qquad (1)$$

Here p_i is the probability that site i is occupied by a charge and W_{ij} is the transition rate for hopping from site i to j. The factors $1-p_i$ account, in a mean-field approximation, for the fact that only one carrier can occupy a site, due to the high Coulomb penalty for the presence of two or more carriers. We consider hopping as a thermally assisted tun-

这里pi是位置I被电荷占据的概率，Wij是从位置I跳跃到j的跃迁速率。在平均场近似中，因子1 pi考虑到只有一个载流子可以占据一个位置的事实，这是由于两个或更多载流子的存在的高库仑惩罚。我们认为跳跃是一种热辅助调谐

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neling process and assume coupling to a system of acoustical phonons, which, in line with earlier work, leads to transition rates of the form [18]

奈林过程，并假设耦合到一个声学声子系统，这与早期的工作，导致跃迁率的形式[18]

□ exp 2□R □ s, s], s s ,
exp 2αR β s 的 , 的,

Results.—In Fig. 1 we display the p dependence of □ for different temperatures. This dependence shows a striking similarity to the p dependence found by Tanase *et al.* [15,16]. The numerical data of Fig. 1 can be rather well

结果。—在图1中，我们显示了不同温度下μ的p相关性。这种依赖性显示出与Tanase等人[15，16]发现的p依赖性惊人的相似性。图1的数字数据可能相当好

W_{ij} 0 ij j i ij j 我
W_{ij} 0

described by the following parametrization scheme [20]:
由以下参数化方案[20]描述：

j i j 我 (2)

(2)

$\square_0 \exp \quad 2\square R_{ij}]$, $s_j < s_i$, $\square T, p \quad \square_0 T \ \exp^{\,1} \ \hat{} \square^2 \quad \hat{} \ 2pa^3 \ \hat{\theta}]$, (3a)

exp 2αRij, sj < si,

μ T, p μ0 T exp 1 σ ˆ 2 σ ˆ
2pa3 ð], (3a)

where □ 1/k_BT, $□_0$ is an intrinsic rate, R_{ij} $\mathbf{R}_j$ $\mathbf{R}_i$ is the distance between sites i and j, □ is the inverse localization length of the localized wave functions under

其中，β 1/kBT，ν0是固有速率Rij 人教版
Ri是点I和j之间的距离，α是下定域波函数的逆定域长度

$□_0$ T $□_0 c_1$ exp $\frac{2}{2} c_2 □^2]$, (3b)
μ0 T μ0c1 exp c2σ ˆ 2], (3b)

ð 2 ð 2 ln □² □ ln ln 4

consideration, and s_i is the on-site energy of site i. The energy differences in Eq. (2) are supposed to contain a contribution eER_{ijx} due to an electric field E in the x direction (e is the charge of the carriers). In the absence of an electric field the occupational probabilities are given by the Fermi-Dirac distribution.

考虑，si为现场I的现场能量。(2)被认为包含由于x方向上的电场E(E是载流子的电荷)而产生的贡献eERijx。在没有电场的情况下，占据几率由费米-狄拉克分布给出。

We solve Eq. (1) by an iteration procedure similar to that suggested by Yu *et al.* [13]. For simplicity we take a regular cubic lattice with lattice constant a. For the inverse localization length we take $\gamma = 10/a$, a typical value for the relevant polymers [15] (we checked that varying γ predominantly changes the prefactor of the mobility). Our method allows for variable-range hopping [19], but for the parameter range studied here it was sufficient to consider hopping to a maximum distance of $3a$. We apply

我们求解Eq。(1)通过类似于Yu等人[13]建议的迭代程序。为简单起见，我们采用晶格常数为a的规则立方晶格。对于逆局域化长度，我们采用$\alpha = 10/a$，这是相关聚合物的典型值[15](我们检查了改变α主要改变迁移率的前因子)。我们的方法允许可变范围跳跃[19],但是对于这里研究的参数范围，它足以满足

侧面跳跃到3a的最大距离。我们申请

with $c_1 = 1.8 \times 10^{-9}$ and $c_2 = 0.42$. This parametrization is, in particular, satisfactory for not too high densities.

与c1 1.8 10 9和c2 0.42 。这种参数化特别适用于不太高的密度。

Because of particle-hole symmetry □ T, p □ T, a 3 因为粒子-空穴对称性μ T，p μ T，a 3 p , so the parametrization obviously fails at densities approaching a 3/2. In the limit of vanishing densities, we recover the □ exp c□2 temperature dependence found by Bässler *et al.* [5,6].

因此，在密度接近a 3/2. 时，参数化显然会失败在消失密度的极限下，我们恢复了巴斯勒等人[5，6]发现的μ exp cσ ˆ 2温度依赖性。

In Fig. 2 we display the E dependence of □ for different temperatures at a low and a high density, typical for periodic boundary conditions and the site energies without

周期边界条件和无边界条件下的位置能量

LEDs and FETs, respectively. We find that the E dependence can be approximately modeled by a *density-independent* pre- factor ƒ T, E :

在图2 中，我们分别显示了led 和fet 在低密度和高密度下不同温度下μ 的E 相关性。我们发现，e的依赖关系可以近似模拟一个密度无关的前因子*f* T，E ：

□ T, p, E ≈ □ T, pƒ T, E . (4) The prefactor can be rather well parametrized by

μ T，p，E ≈ μ T，p *f* T，E .(4)前因子可以通过下式很好地参数化