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Temperature- and field-dependent conductivity in disordered materials

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We present a model to describe electrical transport in disordered materials. Solving the rate equation by the Green function technique and taking into account the electric field effect on the effective dimension of the transport path, we obtain a different law for the conductivity field dependence. This law could be confounded with the Poole-Frenkel law in the range of field, corresponding to the experimental observations in organic materials and conjugated polymers. We show that this behavior is a common feature of all disordered systems. We find a field-induced crossover on the temperature dependence of the conductivity.

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I. INTRODUCTION

Several works have been devoted these past three decades to the transport characteristics in the high electrical field regime in disordered materials. Observations have shown strong nonlinearities in the field dependences of the conductivity in disordered systems, such as amorphous semiconductor,[1–3] amorphous carbon,[4] doped polymers,[5–13] and conjugated polymers.[14,15] Understanding the carrier transport properties in these materials is important for all electronic applications. The absence of long-range order in these materials leads to the localization of the electronic states and it results in a transport of charge carriers via hopping mechanism.

An intense activity has been devoted to the field dependence of the conductivity in disordered organic materials and conjugated polymers caused by the discovery of polymeric field-effect transistors and light-emitting diodes.[16,17] Time-of-flight measurements show that the electric-field dependence of the conductivity is described by the Poole-Frenkel law $\ln \sigma \propto \sqrt{E}$ in a wide range of field strengths.[5–10] In order to explain these behaviors, three important models have been discussed in the literature: the Gaussian disorder model (GDM),[11] the correlated disorder model (CDM),[12,13] and the geometry fluctuation model (GFM).[14,15] In the CDM, it is assumed that energy distributions for spatially close sites are correlated with the long-range interaction between the charged carriers and the dipole moments of the molecular dopants. In the GDM, such correlations are neglected. GDM and CDM models hold in the materials with permanent dipole moments, which is not the case for most conjugated polymers. In the GFM, the thermal fluctuations in the molecular geometry modify the energy levels of localized states. This model is valid for systems without permanent dipole moments. Several works have recently been devoted to the dependence of the charge-carrier mobility on the temperature, on the carrier density, and on the electric field.[18–21] Since Poole-Frenkel behavior has been observed in the disordered materials with and without permanent dipole moment and seems to be universal, an alternative mechanism is necessary to explain this universality. In this work we propose a model, in which the effect of the applied electric field modifies the electronic transport path, and study the predictions of this model for the field and temperature dependence of the conductivity. We show in this paper that Poole-Frenkel behavior is a common feature for all disordered materials.

The paper is organized as follows. In Sec. II, we introduce our model. In Sec. III, we present the analytical results for the dc conductivity in the moderate- and high-field regimes. Section IV is devoted to one-dimensional analytical and numerical results for constant, Gaussian, and exponential density of states. We summarize our conclusions in Sec. V.

II. THEORY

We consider a finite array of N localized states which are randomly distributed in position and energy. Each site is assumed to be occupied by no more than one electron; i.e., there is only one energy level (localized state) available to it at this site.

The time evolution of the site occupational probability, called the rate equation,[22] is given by

$$\frac{d\rho_i(t)}{dt} = -\sum_j \{w_{ij}\rho_i(t)[1-\rho_j(t)] - w_{ji}\rho_j(t)[1-\rho_i(t)]\}, \tag{1}$$

where w_{ij} is the transition rate between the sites i and j.

In this form, the rate equation is nonlinear and is very difficult to handle. For this reason, two linearization methods were developed, by Butcher[24] in the low-field regime and by Bourbie[25] in the moderate- and high-field regimes. These methods give for the frequency-dependent conductivity,

$$\sigma(\omega) = -\frac{\omega^2 e^2}{6\Omega k_B T}\left\langle \sum_{ij} F_i R_{ij}^2 G_{ij}(\omega) \right\rangle. \tag{2}$$

The bracket denotes a configurational average, R_{ij}^2 is the squared distance separating the sites i and j, e the electronic charge, Ω the volume of the system, k_B the Boltzmann constant, and T the temperature of the system. Note that $F_i = f_i(1-f_i)$, with f_i being the thermal equilibrium distribution (Fermi-Dirac distribution), $G_{ij}(\omega)$ is the Green function corresponding to the linearized rate equation

$$G_{ij}(\omega) = \frac{1}{i\omega - \Gamma_{ij}}, \tag{3}$$

where Γ_{ij} is analogous matrix elements of a tight-binding Hamiltonian

$$\Gamma_{ij} = \tilde{\Gamma}_{ij}(1-\delta_{ij}) - \delta_{ij}\sum_{l\neq i}\tilde{\Gamma}_{il}$$

with $\tilde{\Gamma}_{ij}=W_{ij}/F_i$ and $W_{ij}=W_{ji}=f_i(1-f_j)w_{ij}$.

The propagator $G_{ij}(\omega)$ has been determined by two methods: the renormalized perturbative expansion developed by Movaghar and Schirmacher[26] and the diagrammatic method proposed by Gouchanour *et al.*[27] and Bourbie.[28] In the mean-field approximation, the two methods give the same expression for the conductivity,[26,28]

$$\sigma(\omega) = \frac{e^2\langle F(\varepsilon)\rangle N}{6\Omega k_B T}\left\langle \int d\mathbf{R}\frac{R^2\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}{1+G_1^{\varepsilon}(\omega)\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}\right\rangle, \tag{4}$$

where

$$G_1^{\varepsilon}(\omega) = \left(i\omega + \int d\varepsilon d\mathbf{R} N(\varepsilon')g(\mathbf{R})\frac{\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}{1+G_1^{\varepsilon}(\omega)\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}\right)^{-1} \tag{5}$$

with $N(\varepsilon)$ being the density of states, $g(\mathbf{R})$ the pair correlation function, $\tilde{\Gamma}_{ij}=\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})$, and $F(\varepsilon)=f(\varepsilon)[1-f(\varepsilon)]$ with $f(\varepsilon)$ being the Fermi-Dirac distribution. The configurational average $\langle F(\varepsilon)\rangle$ is given by

$$\langle F(\varepsilon)\rangle = n_c(1-n_c),$$

where n_c is the average of carriers per site.

In the random approximation $[g(\mathbf{R})=1]$, the conductivity (4) can be written as

$$\sigma(\omega) = \frac{e^2\langle F(\varepsilon)\rangle N\langle R^2(\omega)\rangle}{6\Omega k_B T}\int d\varepsilon N(\varepsilon)\left[\frac{1}{G_1^{\varepsilon}(\omega)} - i\omega\right], \tag{6}$$

where $\langle R^2(\omega)\rangle$ is the average of squared hopping distance:

$$\langle R^2(\omega)\rangle = \left\langle \int d\mathbf{R}\frac{R^2\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}{1+G_1^{\varepsilon}(\omega)\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}\right\rangle \times \left\langle \int d\mathbf{R}\frac{\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}{1+G_1^{\varepsilon}(\omega)\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R})}\right\rangle^{-1}.$$

The relation (6) is identical to the formula of Sher and Lax[29] for the frequency-dependent conductivity although it has been derived from a rather different formalism.

III. dc CONDUCTIVITY

For the dc conductivity ($\omega=0$), the conductivity becomes inversely proportional to a generalized dwelling time $\tau = G_1^{\varepsilon}(0)$, which characterizes the mean time that a carrier stays at site i. The averaged local Green function $G_1^{\varepsilon}(0)$ is given by Eq. (5). The dc conductivity can be determined analytically in the case of hopping with exponentially varying rates.

The hopping rate from site i to site j separated by the distance $\mathbf{R}$ and the energy Δ is given by

$$\tilde{\Gamma}(\varepsilon,\varepsilon',\mathbf{R}) = \begin{cases} \exp\{-2\alpha R - \beta(\Delta - e\mathbf{E}\mathbf{R})\} & \text{if } \Delta > e\mathbf{E}\cdot\mathbf{R} \\ \nu_0 \exp\{-2\alpha R\} & \text{if } \Delta < e\mathbf{E}\cdot\mathbf{R}, \end{cases} \tag{7}$$

where $\Delta=\varepsilon_j-\varepsilon_i$, $1/\alpha$ is the localization length, ν_0 the characteristic frequency of phonons, $\beta=1/k_BT$, and E the electric field.

When supposing that $G_1^{\varepsilon}(0)$ is independent of ε, then

$$[G_1^{\varepsilon}(0)]^{-1} = \nu_0 e^{-\lambda}, \tag{8}$$

with λ being a parameter to determine.

Taking into account Eqs. (7) and (8), and using the fact that $G_1^{\varepsilon}(0) \gg 1$, in the strongly localized systems, the relation (5) for ($\omega=0$) leads to a characteristic equation available for different densities of states,

$$\gamma_d \int_0^{\lambda/\beta} d\varepsilon N(\varepsilon)(\lambda - \beta\varepsilon)^d = 1, \tag{9}$$

with d being the effective spatial dimension for the hopping electrons.

The temperature, the field, and the dimension effects are contained in the function γ_d

$$\gamma_d = \begin{cases} \displaystyle\int_0^{\theta_0} d\theta \frac{(2\pi \sin\theta)^{d-2}}{(2\alpha - \beta eE\cos\theta)^d} & \text{for } d=2,3 \\ \displaystyle\frac{1}{(2\alpha - \beta eE)} & \text{for } d=1, \end{cases} \tag{10}$$

where θ_0 is the maximum angle of hopping (angle between the vectors $\mathbf{E}$ and $\mathbf{R}$).

In our previous paper,[28] we have distinguished three regimes: the isotropic hopping regime ($\theta_0=\pi$) corresponding to the low-field domain, the directed hopping regime ($\theta_0 = \pi/2$) relevant to the intermediate-field domain, and the one-dimensional hopping regime ($\theta_0=0$) associated with the high-field domain. In these regimes, the conductivity varies like,[23] $\ln\sigma \propto E^2$ in the isotropic regime, $\ln\sigma \propto E$ in the directed regime, and $\ln\sigma \propto E^{1/2}$ in the one-dimensional regime,

Equation (9) can be solved for different densities of states. Illustrations are reported for three distinct components of the density of states: a constant, an exponential, and a Gaussian variation with different dimensions.

Taking into account Eqs. (6) and (9) for a constant density of states $N(\varepsilon)=N_0$, we obtain the well-known expression

$$\sigma(\omega=0) = \sigma_d \exp\left\{-\left[\frac{T_d(E)}{T}\right]^{1/(d+1)}\right\}, \tag{11}$$

where

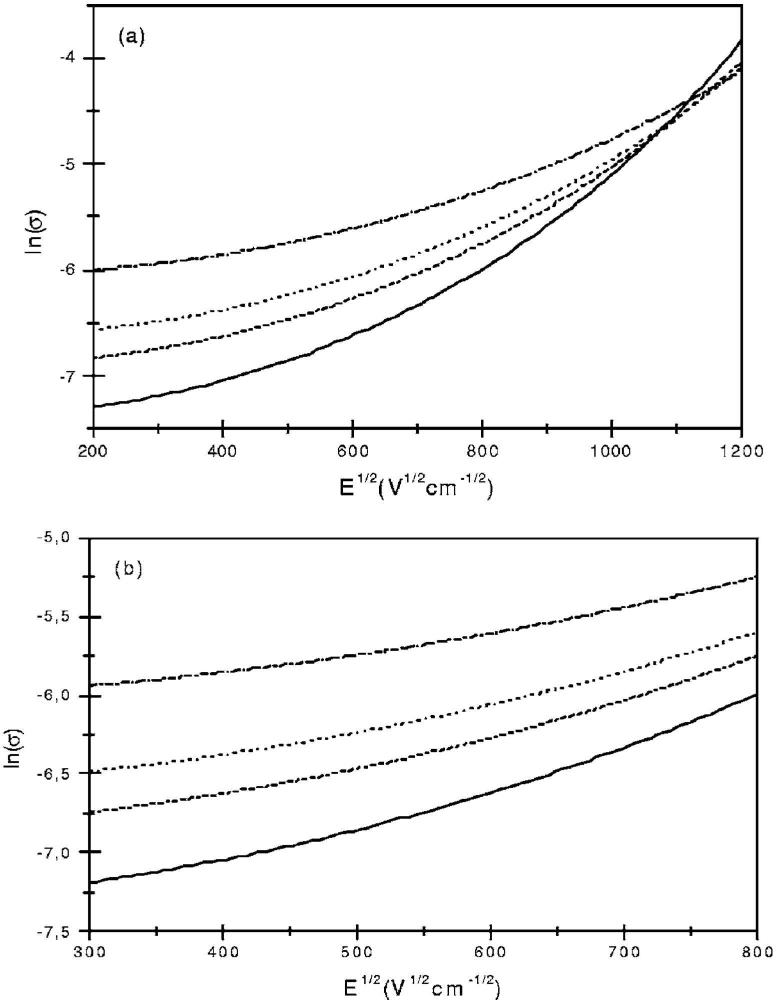

FIG. 1. Field dependences described by Eq. (14) for $\alpha^{-1}=2$ Å and $N_0=10^8$ eV^{-1} cm^{-1}. [(a) and (b)] Field dependences of the conductivity ($\ln\sigma$ vs $\sqrt{E}$) at different temperatures: 250 K (solid), 280 K (dash), 300 K (dot), and 350 K (dash-dot).

$$T_d(E)=\frac{d(d+1)}{N_0\gamma_d(E)k_B} \tag{12}$$

and

$$\sigma_d=\frac{e^2\langle F(\varepsilon)\rangle N\langle R^2(0)\rangle N_0}{6\Omega k_BT}\left[\frac{T_d(E)}{T}\right]^{1/(d+1)}. \tag{13}$$

The Mott law remains valid in the moderate- and high-field domains. The electrical field only modifies the value of the Mott temperature according to expression (12).

In the high-field region, the effective dimension of the electronic motion becomes one dimensional ($d=1$). In this case, Eq. (11) conducts to

$$\sigma(0)=\sigma_1^c\exp\left\{-\sqrt{\frac{4\alpha}{N_0k_BT}\left(1-\frac{eE}{2\alpha k_BT}\right)}\right\}. \tag{14}$$

In Fig. 1, we display the temperature and field dependencies of the conductivity according to Eq. (14), where we have set $\alpha^{-1}=2$ Å and $N_0=10^8$ eV^{-1} cm^{-1}.

For the Gaussian density of states $N(\varepsilon)=(n/\sqrt{2\pi a^2})\times\exp(-\varepsilon^2/2a^2)$, with a being the width of the distribution and n the total concentration of the localized states, the one-dimensional conductivity can be calculated numerically from Eqs. (6), (8), and (9) in the limit $\varepsilon^2/a^2\ll 1$. The results on the field dependence are reported in Fig. 2 and the temperature dependence in Fig. 3, where we have set $a=0.1$ eV, $\alpha^{-1}=2$ Å, and $n=10^{10}$ cm^{-1}. These values have been reported from the literature considering the transport in the molecularly doped polymers and conjugated polymers.[13,15,19,21,30,32]

In the one-dimensional systems, with an exponential density of states, $N(\varepsilon)=N_0\exp(\varepsilon/\varepsilon_0)$, the solution of Eq. (9) conducts to

$$\sigma=\sigma_1^e\exp\left[-\sqrt{\frac{4\alpha}{N_0k_BT}\left(1-\frac{eE}{2\alpha k_BT}\right)}\right], \tag{15}$$

which is identical to expression (14). Such a density of states could represent the localized part of the band tails.

Figures 1(a) and 2(a) describe the temperature and field dependences of the conductivity for constant and Gaussian density of states (DOS). As shown in these figures, these different DOS lead to very similar field dependence of the conductivity, $\ln\sigma\propto E$. A similar behavior has been found by the CDM with a Gaussian density of states[13] and by a numerical solution of the rate equation.[21] In the range of fields considered in the experimental studies as illustrated in Figs. 1(b) and 2(b),[10,11,20,21,32,33] the field dependence of the conductivity can be approximated by a Poole-Frenkel law, $\ln\sigma\propto\sqrt{E}$. Figures 4 and 3 illustrate the temperature dependence

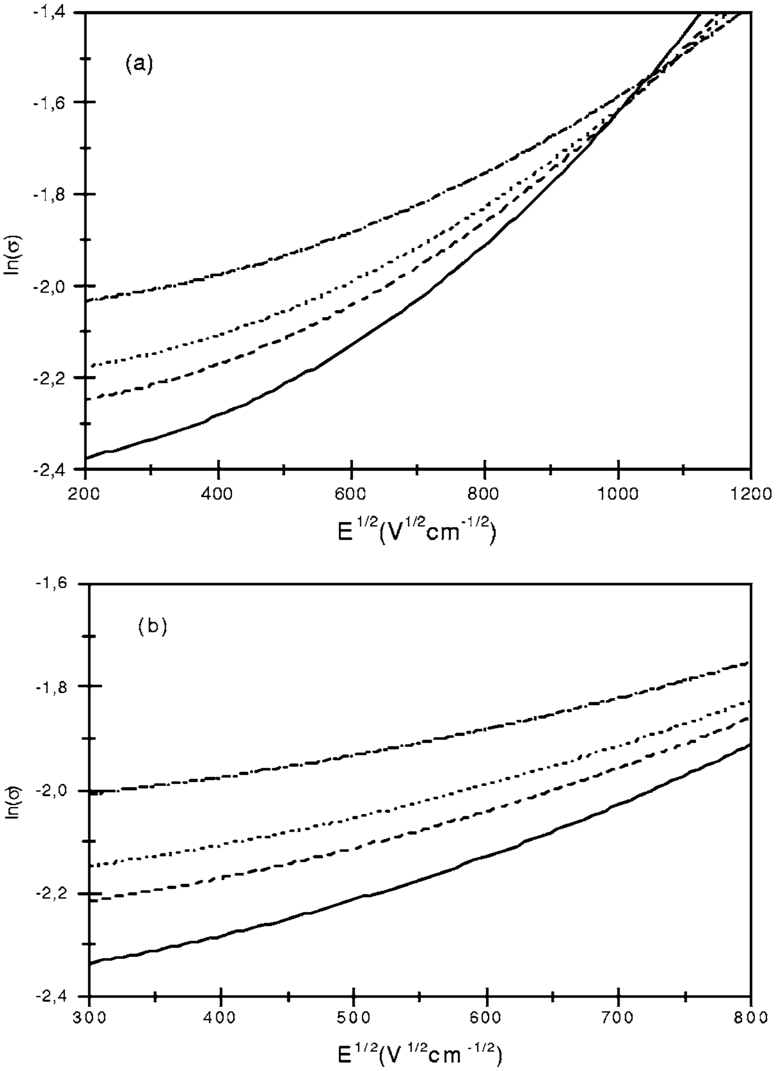

FIG. 2. Field dependences of the conductivity $\ln\sigma$ vs $\sqrt{E}$ for a Gaussian density of states with $a=0.1$ eV, $\alpha^{-1}=2$ Å, and $n=10^{10}$ eV^{-1} cm^{-1} at different temperatures: 250 K (solid), 280 K (dash), 300 K (dot), and 350 K (dash-dot).

of the conductivity in the high-field region, for a constant and a Gaussian density of states, respectively. In both cases, the conductivity follows the law $\ln\sigma \propto 1/T$. This result is supported by the numerical solution of the master equation applied to π-conjugated polymers.[21] We also find that in the intermediate-field regime, with increasing temperature, the conductivity is enhanced, whereas in the high-field regime, the conductivity decreases with increasing temperature (see Figs. 4 and 3). The same behavior has been obtained by the molecular GFM and it has been attributed to the competition

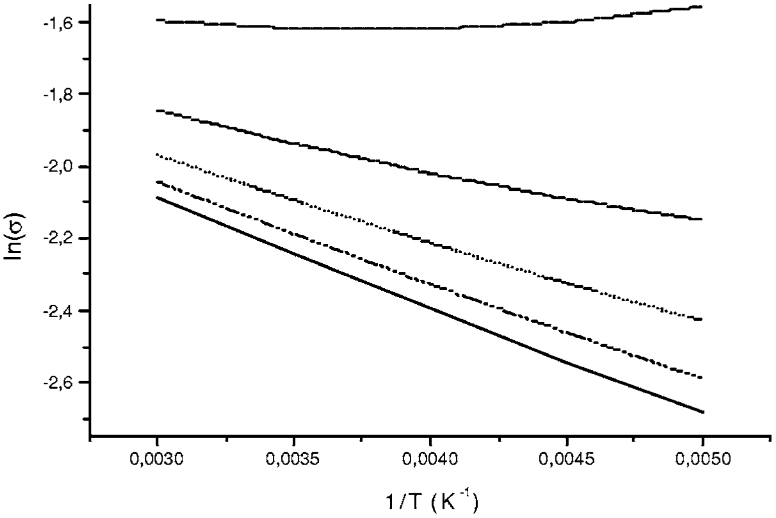

FIG. 3. Temperature dependences of the conductivity ($\ln\sigma$ vs $1/T$) for a Gaussian density of states with $a=0.1$ eV, $\alpha^{-1}=2$ Å, and $n=10^{10}$ eV^{-1} cm^{-1}, at different fields: 10^4 V/cm (solid), 10^5 V/cm (dash), 2.5×10^5 V/cm (dot), 5×10^5 V/cm (dash-dot), and 10^6 V/cm (dash-dot-dot).

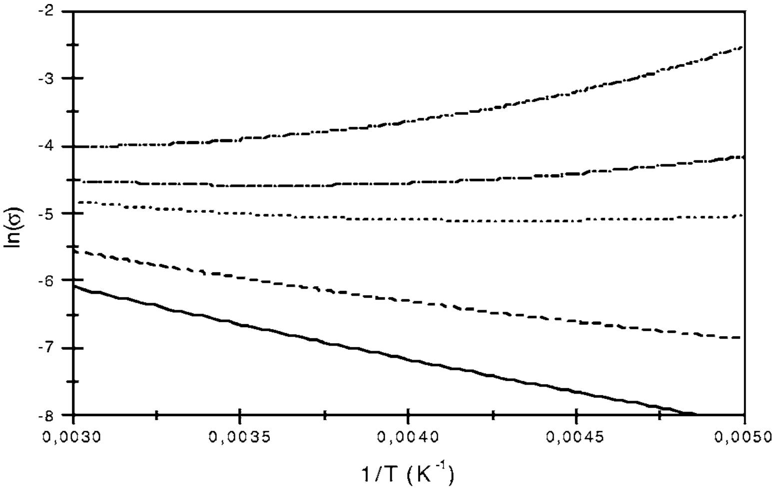

FIG. 4. Temperature dependences of the conductivity ($\ln \sigma$ vs $1/T$) according to Eq. (14) for $\alpha^{-1}=2$ Å and $N_0=10^8\ \mathrm{eV}^{-1}\,\mathrm{cm}^{-1}$ at different fields: 10^5 V/cm (solid), 5×10^5 V/cm (dash), 10^6 V/cm (dot), 1.2×10^6 V/cm (dash-dot), and 1.5×10^6 V/cm (dash-dot-dot).

between the thermal-assisted hopping and the field-assisted hopping.[14,15,17]

At high fields, the carrier path becomes essentially one dimensional along the applied field axis. Thus, one-dimensional transport models can be valid at high fields but not at low fields.[13–15,31]

We see that relation (9) represents a basic equation to determine the conductivity behavior for different types of density of states.

IV. CONCLUSION

We have shown that the field dependence conductivity observed in disordered organic materials and conjugated polymers seems to be universal; this is a common feature of all disordered systems. We have found a different law that takes a Poole-Frenkel form in the region of fields considered in the experimental investigations. This result has been linked to that observed for conductivity in conjugated polymers. We have found two regimes, due to the field-induced crossover on the temperature-dependent conductivity. In the first regime, the conductivity increases according to the temperature, while in the second regime, it decreases when the temperature increases. The same behavior has been found by the molecular GFM and has been attributed to the competition between the thermal-assisted hopping and field-assisted hopping.[14,15] This study is valid in the high-field regime where the transport path becomes one dimensional.

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