Fractional Einstein relation for strongly disordered semiconductors

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A novel Einstein relation (fractional Einstein relation, FER) for the electric conduction in non-crystalline semiconductors is presented. FER and the generalized Einstein relation (GER) [Phys. Rev. E 8, 1296 (1998)] are compared to the result of the Monte Carlo (MC) simulation, and is confirmed that FER exhibits better agreement than GER. The crucial feature of FER is that it reflects the violation of the detailed balance in the coarse-grained hopping process, while it is preserved in the original Einstein relation or GER.

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Introduction.– Fluctuation-dissipation theorem (FDT) is one of the most fundamental principles in statistical mechanics. A significant example of FDT in kinetics is the Einstein relation (ER) [1], discovered in the Brownian motion. The generic form of ER is given by \( D = \frac{k_B T}{q} \), where \( T \) is the temperature and \( k_B \) is the Boltzmann constant. Here, \( D \) is the diffusion coefficient (fluctuation), and \( q = v/F \) is the mobility (dissipation), where \( v \) is the steady drift velocity and \( F \) is the external force. Explicit examples of ER can be found in various situations. For instance, the Stokes-Einstein relation, \( D = k_B T/(6\pi \eta d) \), where \( d \) the diameter of a sphere immersed in a fluid and \( \eta \) the viscosity, is well known.

For charged particles (carriers) in semiconductors, ER reads

\[
\frac{D}{\mu} = \frac{k_B T}{q}, \tag{1}
\]

where \( q \) is the electric charge of the particle. Such a relation is crucial for understanding the collective behavior of carriers, because it is hard in general to measure the diffusion coefficient, while it is relatively easy to measure the mobility. However, it is known that ER does not hold in non-crystalline materials, neither under equilibrium [2, 3] nor nonequilibrium [4, 5] conditions. Roichman et al. [2, 3] have proposed a modification of ER for the equilibrium case in terms of the density of states (DOS). Instead of Eq. (1), they have postulated the following relation,

\[
\frac{D}{\mu} = \frac{p}{q \eta}, \tag{2}
\]

where \( p \) is the particle concentration and \( \eta \) is the chemical potential. The particle concentration \( p \) is expressed in terms of DOS, which we denote \( g(\varepsilon) \) with \( \varepsilon \) the energy, and the Fermi-Dirac distribution, \( f(\varepsilon, \eta) \), as \( p = \int_{-\infty}^{\varepsilon_0} dg(\varepsilon) f(\varepsilon, \eta) \).

Establishing a valid ER for nonequilibrium cases has been partially accomplished by Barkai et al. [3, 12, 13]. They have focused on the facts that the hopping conductance [8, 14, 15] is the dominant mechanism of the electric conduction in disordered materials, and collective behaviors of carriers show anomalous diffusion-advection [16, 17], which is believed to be described by the continuous time random walk (CTRW) [18]. They have shown that CTRW is further described by the fractional Fokker-Planck equation [19] under weak external fields, and the generalized Einstein relation (GER),

\[
\langle x^2(t) \rangle = 2 \frac{k_B T}{F} \langle x(t) \rangle, \tag{3}
\]

holds under the assumption that the anomalous exponent of the waiting time of the system with and without a driving force, \( \alpha_F \) and \( \alpha_0 \), are the same. Here, \( \langle x^2(t) \rangle \) is the mean-square displacement of the carriers in the absence of an external field, \( \langle x(t) \rangle \) is the mean displacement in the presence of an external field, and \( F \) is the external force exerted on the carriers. A representative case where GER is valid can be found in actin networks [20, 21]. However, although Barkai [13] has conjectured that GER would hold for the hopping conduction, quantitative comparisons of GER with the experimental results or simulations have not been performed.

In this letter, we propose a novel ER valid for the electric conduction of non-crystalline semiconductors, which we refer to as the “fractional Einstein relation (FER)”. For illustration, we consider the “disorder model” [8] of the hopping conduction, where it is assumed that the electric conduction is dominated by the static energy disorder of the hopping sites. We compare FER and GER with the results of the Monte Carlo (MC) simulation, and confirm that FER exhibits good agreement with MC, while GER does not.

Note that the “disorder model” we consider is a well established model, which is one of the two major microscopic models of the hopping conductance. The other is the “polaron model” [22, 24], where it is assumed that the electric conduction is dominated by the strong electron-phonon coupling. To show the validity of FER in the “polaron model” is a future task, but we believe that FER also holds in this model. Note also that the representative phenomenological models of the hopping conductance, namely the “multiple trapping model (MTM)” [25, 27],
The theory is organized as follows. First we explain the disorder model and derive FER analytically. Next, we compare FER and GER with MC simulation, and demonstrate that FER is in good agreement with MC simulation, while GER is not. Then we discuss the relation of our results to the previous studies. Finally, we summarize our results.

Theory. We start with the introduction of the “disorder model” \[^8\] for the hopping conductance, which is essentially equivalent to the one considered in Refs. \[^31,33\]. The two crucial ingredients of the model are (i) the probability distribution of the energy difference of the hopping sites and (ii) the hopping rate of the carriers.

The distribution of the energy difference, which we denote \(h(\xi ij)\) with \(\xi ij \equiv \epsilon ij - \epsilon i\), is determined by the DOS, \(g(\epsilon)\). Note that \(h(\xi ij)\) is normalized, i.e., \(\int_{-\infty}^{\infty} dh(\epsilon) = 1\), and it satisfies \(h(-\xi ij) = h(\xi ij)\). For inorganic amorphous semiconductors, \(g(\epsilon)\) is approximated by the exponential function \[^{25,27,32}\], and its tail is referred to as the Urbach tail \[^{33}\]. In this case, \(h\) is the Laplace function. For organic ones, \(g(\epsilon)\) is approximated by the Gaussian function \[^{8,34,36}\], and \(h\) is also Gaussian.

As for the hopping rate of the carriers, a realistic three-dimensional model is somewhat complicated for theoretical considerations, and might shadow the essence. To elucidate the discussion, we adopt a simplified one-dimensional model, where carriers can move only to either of the first-nearest neighboring sites in a single hop (Fig. 1). This implies that we are focusing on a time scale where hopping to the second-nearest neighboring sites is negligible. We also assume that the number density of the carriers is small enough so that the occupation of the states can be neglected. With these assumptions, the hopping rate of the carrier from site \(i\) to site \(i \pm 1\), which we denote \(\nu_{\pm}\), is approximately given by

\[ \nu_{\pm} = \nu_0 e^{-2a/\xi - (\epsilon_{\pm} + \epsilon_0)/\Theta(\epsilon_{\pm} + \epsilon_0)/k_B T}, \]

where \(a\) is the lattice spacing, \(\xi\) is the localization length of the localized state, \(\nu_0\) is the typical magnitude of the hopping rate, \(\epsilon_{\pm} \equiv \epsilon_{i+1} - \epsilon_i\), \(\Theta(x)\) is the Heaviside’s step function, where \(\Theta(x) = 1\) for \(x > 0\) and 0 otherwise, and \(-F\) (\(F > 0\)) is a constant external force exerted on the carrier \[^{14,15}\]. For instance, \(F\) can be a force due to an electric field \[^{57}\]. Note that the detailed balance is assumed in deriving Eq. \(4\).

To describe the coarse-grained collective motion of the carriers, we consider a continuum model of the hopping conductance. We assume that the hopping process is described by CTRW with the waiting time density \(\langle w(t) \rangle \sim (\alpha A_\alpha / \Gamma(1 - \alpha)) t^{-(1 + \alpha)}\) (\(0 < \alpha < 1\)) for \(t \to \infty\). Here, \(\Gamma\) is the Gamma function and \(A_\alpha\) is a constant. This assumption is at least suitable for the exponential DOS \[^{30,31,38}\] and the Gaussian DOS \[^{38}\]. In fact, simple approximate analytic expressions for \(\alpha\) can be derived in terms of the microscopic parameters such as the width of the DOS, both for the diffusive system \[^{30}\] and the system under a constant external field \[^{31}\]. Then, by utilizing the mathematical technique presented in Ref. \[^{10}\], we can show that the probability density of the carrier, \(P(x,t)\), satisfies the following fractional diffusion-advection equation (FDAE) in the continuum limit, i.e. \(a \to 0\) and \(A_\alpha \to 0\) with the generalized diffusion coefficient \(D_\alpha \equiv a^\alpha / (2A_\alpha)\) kept finite:

\[ \frac{\partial P(x,t)}{\partial t} = \partial_x \mu_\alpha + \frac{\partial^2}{\partial x^2} P(x,t). \]

Here, the operator \(\partial_x^\alpha\) is the fractional derivative, which is defined by the Riemann-Liouville operator,

\[ \partial_x^\alpha P(x,t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t (t-t')^\alpha P(x,t') dt'. \]

\[ \mu_\alpha = \langle (W_+) - (W_-) \rangle \frac{D_\alpha}{a} \]

is the generalized mobility, where \(\langle W_- \rangle\) is the coarse-grained hopping probability. Note that \(\langle W_+ \rangle + \langle W_- \rangle = 1\) holds by definition. It is natural to give \(\langle W_\pm \rangle\) in terms of the bare (microscopic) hopping probability \(\nu_\pm\) by

\[ \langle W_\pm \rangle \equiv \langle \nu_\pm / (\nu_+ + \nu_-) \rangle, \]

where \(\cdots = \int_0^\infty d\epsilon_+ h(\epsilon_+) \int_0^\infty d\epsilon_- h(\epsilon_-) \cdots\) is the average with respect to the distribution of the energy difference. It is straightforward to derive the following expression for \(\langle W_+ \rangle\) from Eqs. \(4\) and \(7\),

\[ \langle W_+ \rangle = \frac{1}{2} - \frac{1}{2} \hat{F} \left[ \frac{1}{2} \int_0^\infty d\hat{\epsilon}_+ \hat{h}(\hat{\epsilon}_+) \frac{1}{\cosh^2 \left( \frac{\hat{\epsilon}_+}{2T} \right)} \right. \]

\[ \left. + \int_0^\infty d\hat{\epsilon}_- \int_0^\infty d\hat{\epsilon}_- \hat{h}(\hat{\epsilon}_+) \hat{h}(\hat{\epsilon}_-) \frac{1}{\cosh^2 \left( \frac{\hat{\epsilon}_+ - \hat{\epsilon}_-}{2T} \right)} \right] + O \left( \left( \hat{F} / \hat{T} \right)^2 \right), \]

where the dimensionless variables are defined by \(\hat{\epsilon}_\pm = \epsilon_\pm / \epsilon_c\), \(\hat{F} = F a / \epsilon_c\), \(\hat{T} = k_B T / \epsilon_c\), and \(\hat{h} = \epsilon_c h\), with \(\epsilon_c\)
the typical energy scale of the DOS. Then, the following ER, which we refer to as the “fractional Einstein relation (FER)”, is obtained from Eqs. (6) and (8).

$$
\frac{\mu_{\alpha}}{D_{\alpha}} = \frac{\tilde{F}}{T} \left[ \frac{1}{2} \int_{-\infty}^{\infty} d\tilde{\varepsilon} \tilde{h}(\tilde{\varepsilon}) \frac{1}{\cosh^{2}(\frac{\tilde{\varepsilon}}{2T})} \right] + \int_{-\infty}^{\infty} d\tilde{\varepsilon} \int_{-\infty}^{\infty} d\tilde{\varepsilon} \tilde{h}(\tilde{\varepsilon}) \tilde{h}(\tilde{\varepsilon} \pm 1) \frac{1}{\cosh^{2}(\frac{\tilde{\varepsilon} \pm 1}{2T})} + O \left( (\tilde{F} / \tilde{T})^2 \right). \tag{9}
$$

Simulation.—The validity of Eq. (9) is examined by MC simulation of the hopping conduction, where the hopping probability is given by Eq. (4). We consider the exponential DOS, $g_{\exp}(\varepsilon) = e^{-\varepsilon/k_BT_c}/k_BT_c \ (-\infty \leq \varepsilon \leq 0)$, and the Gaussian DOS, $g_{\text{Gauss}}(\varepsilon) = e^{-\varepsilon^2/2\sigma^2}/\sqrt{2\pi}$ $(-\infty \leq \varepsilon \leq \infty)$, which are well established for irroganic and organic amorphous semiconductors, respectively. Here, $k_BT_c$ and $\sigma$ are the typical widths of the DOS, which correspond to $\varepsilon_c$ in the previous section. The dimensionless DOS are given by $\tilde{g}_{\exp} = e\tilde{\varepsilon}$ and $\tilde{g}_{\text{Gauss}} = e^{-\tilde{\varepsilon}^2/2\sqrt{2\pi}}$, and the corresponding distribution functions of the energy differences $\tilde{\varepsilon}_ \pm (-\infty \leq \tilde{\varepsilon}_ \pm \leq \infty)$ are given by $\tilde{h}_{\exp} = e^{-|\tilde{\varepsilon}_ \pm|/2}$ and $\tilde{h}_{\text{Gauss}} = e^{-\tilde{\varepsilon}_ \pm^2/4\sqrt{2\pi}}$, respectively.

The simulation method is the same as that in Refs. [30, 31]. The conditions are as follows: the number of carriers (which is essentially the number of the trials of the simulation performed) is $N_P = 10^6$, and the parameters are chosen as $a/\xi = 10$, $2T/T_c = (0.1 - 1.0)$, $2k_BT/\sigma = (0.1 - 1.0)$, and $Pa/k_BT = 0.1$. Note that the external force $F$ is constatly scaled with respect to the temperature $T$. Both of the ranges, $2T/T_c = (0.1 - 1.0)$ and $2k_BT/\sigma = (0.1 - 1.0)$, correspond to $0.1 \leq \alpha \leq 1$. Initially, all the carriers are rested at the origin. The generalized mobility can be estimated from the relation $\langle x(t) \rangle_F = \mu_{\alpha} t^\alpha / \Gamma(\alpha + 1)$. The generalized diffusion coefficient can be estimated from the mean-squared displacement of the carriers, $\langle x^2(t) \rangle_F = 2\mu_{\alpha}^2 t^{2\alpha}/\Gamma(2\alpha + 1) + 2D_{\alpha} t^\alpha / \Gamma(\alpha + 1)$. However, because the effective waiting time in the weak field is almost the same as that in the diffusive case [12, 31], we can estimate $D_{\alpha}$ from $\langle x^2(t) \rangle_0 = 2D_{\alpha} t^\alpha / \Gamma(\alpha + 1)$. This also makes it possible to compare FER with GER directly.

In Fig. 2, we show the comparison of FER and GER with MC simulation. The result of MC simulation is sampled at the dimensionless time $t \equiv \nu_0 t = 10^{14}$. The result of FER is obtained by performing the integrals in Eq. (9) numerically. Fig. 2 (a) is the result for the exponential DOS, while Fig. 2 (b) is that for the Gaussian DOS. The horizontal axes are the dimensionless temperature, while the vertical axes are the dimensionless ratio of the generalized mobility to the generalized diffusion coefficient, $\mu_{\alpha} a / D_{\alpha}$. The solid line, the dashed line, and the circles correspond to FER, GER, and MC simulation. From Fig. 2 (a) and (b), one can see that FER exhibits the monotonically increasing tendency of $\mu_{\alpha} a / D_{\alpha}$ against the dimensionless temperature, observed in MC simulation, which is clearly beyond the reach of GER. In addition, the quantitative agreement of FER and MC simulation is surprisingly good for the case of exponential DOS, whereas the agreement is less accurate for the case of Gaussian DOS.

Discussion.—In this section, we discuss the relation of our results to the previous studies. First of all, let us consider the limit $\epsilon_c \to 0$, which corresponds to the high-temperature limit, $T = k_BT/\epsilon_c \to \infty$. In this case, the carriers are thermally excited up to the conduction band, and hence the Ohmic conduction dominates the hopping conduction. Theoretically, $\epsilon_c \to 0$ results in $\alpha \to 1$ and
The hopping probability where the detailed balance is imposed. The detailed balance is imposed to the coarse-grained model such as CTRW in GER \[9, 12, 13\]. On the other hand, we have imposed the detailed balance to the microscopic hopping process, where the bare hopping rate is given by Eq. (4). In this case, it is notable that the detailed balance is violated by the coarse-graining, which is manifested in the coarse-grained hopping rate \(<W_+>\) given by Eq. (5). It is clear from Eqs. (9) and (11) that FER includes corrections which depend on the microscopic details of the system, such as DOS, while such a correction is absent in GER. These corrections are crucial in describing the non-trivial dependence of $\mu a/D_\alpha$ on the dimensionless temperature, for the case of constant $Fa/k_BT$. Hence, we can see that the significant features of FER originate in the violation of the detailed balance in the coarse-grained hopping process. Imposing the detailed balance to the coarse-grained hopping process, which has been conventionally performed, neglects the essential features of this process.

Finally, we compare FER with the result of MC simulation presented in Ref. \[6\]. In Ref. \[6\], the hopping sites are distributed on a three-dimensional cubic lattice with periodic boundary conditions, and the external force $F$ is given by $F = eE$, where $e$ is the elementary charge and $E$ is a constant electric field. DOS is given by a Gaussian function with width $\sigma$. The result of MC simulation of Ref. \[6\] is shown by (red) circles with error bars in Fig. 3, where the horizontal axis is $(\sigma/k_BT)^2$ and the vertical axis is $eD/\mu k_BT$. The upward arrows in Fig. 3 show that the data become larger as time goes on, which implies that the calculation performed is not long enough for these conditions (probably due to limited calculational resource at that time). For $\sigma/k_BT = 2.5$, we show the range of this time evolution with a dashed line, which is obtained from the inset of Fig. 2 in Ref. \[6\]. The result of FER with the corresponding conditions is also shown by a (blue) solid line in Fig. 3. We have estimated $eD/\mu k_BT$ by $D_\alpha \tilde{F}/\mu a \tilde{T}$, since the diffusion is dominant for the system under weak external fields. From Fig. 3 we can see that both the result of Ref. \[6\] and FER exhibit a monotonically increasing tendency of $eD/\mu k_BT$ with respect to the inverse dimensionless temperature. Moreover, the quantitative agreement of the two results seem to be relatively well, considering that FER is derived for a simplified one-dimensional model. Deriving FER for two- or three-dimensional models is a future work, although we expect that the essential features of the hopping conductance of non-crystalline semiconductors are already captured in this letter by the simplified one-dimensional model.

**Summary.** In this study, we have presented a novel Einstein relation, which we refer to as the “fractional Einstein relation (FER)\(^a\), for the electric conduction in non-crystalline semiconductors. FER is derived from the fractional diffusion-advection equation (FDAE), together with coarse-graining the bare (microscopic) hopping probability where the detailed balance is imposed. The striking feature of FER is that it includes microscopic properties such as the probability distribution of the energy difference of the hopping sites, which can be obtained from DOS. This is not the case for the original ER, nor for the generalized Einstein relation (GER). It has been shown by comparing with MC simulation that the dependence of FER on DOS is essential to reproduce the non-trivial dependence of the ratio of the mobility to the diffusion coefficient on the dimensionless temperature. The crucial difference between FER and the original ER, or GER, is that the detailed balance of the coarse-grained hopping process is violated in FER, while it is preserved in others. This indicates that the violation of the detailed balance of the coarse-grained hopping process is a key feature for the electric conduction in non-crystalline semiconductors.

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