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Mechanism of Cis–Trans Thermal Isomerization of Polyacetylene

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ABSTRACT: Isothermal cis–trans isomerization of polyacetylene (PA) films proceeds according to a stretched-exponential function of time with an exponent α ($0 < \alpha < 1$). A mechanism is proposed for the cis–trans isomerization. Cis–trans isomerization of PA occurs under the condition that the molecular axis is almost fixed. The interspace-diffusion model is effective in simply describing the intermolecular cooperative motions of neighboring chains to avoid the intermolecular constraints for cis–trans isomerization motion. If an interspace appears in the neighborhood of a cis bond (or moving unit of cis state), this cis unit is assumed to change to the trans state instantaneously. Using the continuous-time random walk model, the decay of survival probability of a cis unit can be expressed by the stretched-exponential function under the assumption of the distribution of activation energy for cis–trans isomerization. The relationship between the two-state model and the interspace-diffusion model is discussed.

1. Introduction

Structure and properties of a polyacetylene (PA) film are strongly affected by the aging temperature of the catalyst. High dc conductivity and stability[1,2] were found in a PA film synthesized with an aged catalyst at high temperature (for example, over 373 K). Mechanical properties such as Young's modulus, tensile strength, and stretchability were also improved[3] compared to the previous Shirakawa PA film (S-PA).[4] The difference in the conduction mechanism between highly stretchable PA (hs-PA) and S-PA was discussed based on the frequency (ω) and temperature (T) dependence of the complex conductivity $\sigma^*(\omega)$.[5] Reducing $\sigma^*(\omega)$ and ω by using the dc conductivity $\sigma(0)$, a master curve was obtained for hs-PA but not for S-PA. The difference in the conduction mechanism between hs-PA and S-PA arises from their morphological dissimilarities.

Isothermal cis–trans isomerization of PA has been studied by infrared spectroscopy (IR).[6,7] Differential scanning calorimetry (DSC) also gives various information on the isomerization. A two-state model, in which population probabilities for cis and trans states are assumed to change through the forward and backward reactions, was used to analyze DSC curves.[8] The enthalpy difference between the two states and the activation energy were determined from this analysis. Kyotani et al. also studied the isothermal cis–trans isomerization behavior by means of DSC.[9] By defining the isomerization ratio y by $y = (\Delta H_0 - \Delta H_t)/\Delta H_0$ where ΔH_0 and ΔH_t are the heats of isomerization for the as-polymerized film and for the film which was preheated for t hours, respectively, the experimental data were represented by the following stretched (fractional)-exponential function,

$$1 - y = \exp[-(k_0 t)^{\alpha}] \tag{1}$$

where k_0 and α are constant, and $0 < \alpha < 1$ experimentally. The temperature dependence of k_0 gives an activation energy of ca. 30 kcal/mol. Recently it was found that the previously reported IR data can also be described by eq 1.[10] This replotting gave an activation energy of ca. 28 kcal/mol independent of cis content.

Equation 1 with $0 < \alpha < 1$ is the same function as the Kohlrausch–Williams–Watts (KWW) function in the field of dielectric relaxation. If $\alpha > 1$, eq 1 is the same as the Avrami equation in the field of polymer crystallization from the molten state. In the case of isothermal cis–trans isomerization in PA, α is determined experimentally to be less than unity.

The above-mentioned two-state model suggests a single (simple)-exponential decay for the isothermal isomerization,[8] which is different from eq 1. On the other hand, nearly the same activation energy was derived by the two methods (heating rate dependence of peak temperature for cis–trans isomerization and the temperature dependence of k_0 in isothermal experiments).

This paper is concerned with the mechanism of cis–trans isomerization of PA and also with the derivation of eq 1 from this mechanism. The relationship with the two-state model is also discussed.

2. Interspace-Diffusion Model

X-ray diffraction studies have shown a continuous and monotonous shift of the initial diffraction of cis crystallites.[11,12] There is no direct evidence for the coexistence of cis and trans crystallites. The overall crystal structure is maintained during the partial isomerization within a chain. In other words, the partial isomerization of a chain does not change the crystallite lattice pattern. The phenomenon that chains with different chemical structures are drawn into another crystal structure is called isomorphism in crystals and is seen in copolymers and so on.

For the molecular motion related to the thermal isomerization, Yamabe et al.[13] proposed a crankshaft motion of the –(CH=CH)– unit around two carbon–

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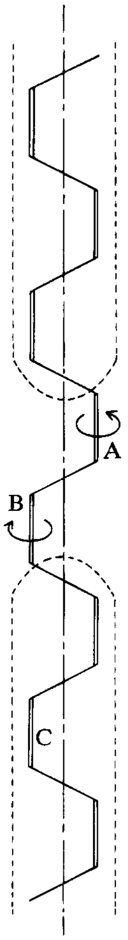

Figure 1. Model of intramolecular correlated vibrational/rotational motions for cis−trans thermal isomerization of PA.

carbon double bonds in cis−transoid form which is the most preferable conformation in as-polymerized PA films. They found that the energy barrier for the rotation to change the dihedral angle of one cis−transoid monomer unit by 180° is ca. 1 eV (23 kcal/mol). The calculation, however, did not include the effect of steric constraints imposed by the crystal lattice for this cis−trans isomerization in the solid state.

As suggested by X-ray results, the molecular axes do not move very much during thermal isomerization. This means that the effect of steric constraints during isomerization is very large and the intramolecular motions are limited within small spaces around the molecular axis. The intramolecular motions for cis−trans isomerization in the solid state would consist of vibrations/rotations of bonds or bond sequences around the molecular axis. An example is described in Figure 1. The part of the chain above the double bond A and the part of the chain below the double bond B are considered to be hard bodies (denoted by dashed lines). These parts vibrate/rotate cooperatively around bond A and bond B with the condition of inverse direction. Simultaneously the reorientation and/or torsions of the molecular axis occurs; otherwise, the molecular axis declines. This type of cooperative internal rotation is possible between bonds A and C and other pairs of bonds. Of course, other kinds of bond motions would be possible for intramolecular correlated vibrational/rotational motions around the molecular axis.

Even if the intramolecular cooperative motions such as shown in Figure 1 exist, the cis−trans isomerization does not occur because of the steric hindrances among chains in the solid state. Intermolecular correlated motions of neighboring chains are needed for thermal cis−trans isomerization. There are many possibilities for cooperative intermolecular motions responsible for cis−trans isomerization. Among them, the common essential point is to make space between chains, which make the cis−trans thermal isomerization possible. Figure 2 shows an example in which the incoherent intermolecular motions of chains make a space between neighboring chains. If these spaces are made by thermal fluctuations, a part of the neighboring chain is transformed from cis to trans states. Hereafter these spaces are called interspaces.

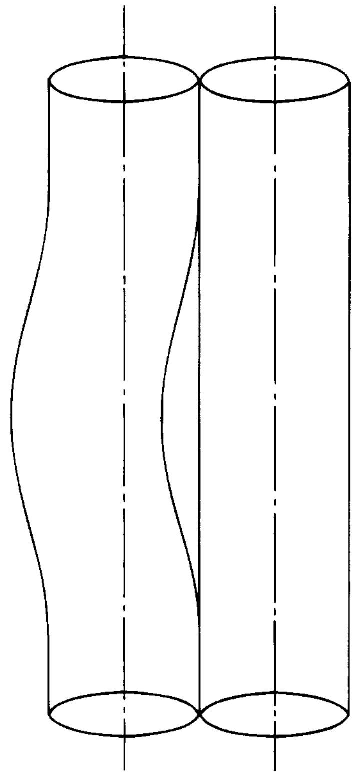

Figure 2. Model of intermolecular cooperative vibration/rotation of neighboring chains. The formation of interspaces is essential.

Suppose that the PA film contains mobile interspaces, which can move through thermal motions of PA chains. If an interspace reaches the site of a cis bond (or an elementary moving unit for cis−trans isomerization, if it exists), this cis bond changes to the trans state instantaneously. The diffusion of interspaces is essential in this model and is not necessarily limited to one dimension (along chain axis). Interspaces can diffuse in the directions parallel and perpendicular to the PA chain.

The similar model was discussed by Shlesinger and Montroll[14] to derive the KWW polarization decay function similar to eq 1. Let a cis bond (or moving unit) be situated at the origin of a postulated lattice of V sites. Consider that N independent mobile interspaces are also on this lattice, but not initially at the origin. The cis content $P_c(t)$ at time t is the survival probability of cis units not yet transformed by meeting with an interspace. Let $F(x,t)$ be the probability density at time t that an interspace originally at x reaches the origin for the first time. The probability that the interspace does not reach the origin in the time interval $(0,t)$ is then given by $[1 - \int_0^t F(x,t)\,dt]$. The survival probability

$P_c(t)$ of cis units is expressed as

$$P_c(t) = \sum_{x_1=1}^{V} \cdots \sum_{x_N=1}^{V} \prod_{i=1}^{N} [1 - \int_0^t F(x_i,t)\,dt]\, u(x_1,x_2,\ldots,x_N) \tag{2}$$

where $u(x_1,x_2,\ldots,x_N)$ is the initial distribution function of interspace positions. If the interspaces are initially randomly distributed, $u(x_1,x_2,\ldots,x_N) = 1/V^N$, then

$$P_c(t) = \exp[-c\int_0^t K(t)\,dt] \tag{3}$$

where

$$K(t) \equiv \sum_{x\neq 0} F(x,t) \tag{4}$$

in the thermodynamic limit that N and V becomes infinite with fixed c, where $c = N/V$ is the concentration of interspaces.

It is convenient to use the continuous-time random walk (CTRW) model by Montroll and Weiss[15] in order to calculate the first-passage-time probability density $F(x,t)$. The CTRW is composed of an alternation of steps and pauses. The detailed derivation is briefly shown in the Appendix. In CTRW, the pausing-time (or hopping time) distribution function $\psi(t)$ plays an essential role. In the case of interspace diffusion, $\psi(t)$ is assumed to be based on a distribution of activation energy barriers. For a distribution of barrier heights,

$$\psi(t) = \int_0^\infty d\lambda\, w(\lambda)\, \lambda \exp(-\lambda t) \tag{5}$$

where

$$w(\lambda) = \int_0^\infty dE\, g(E)\, \delta(\lambda - \lambda(E)) \tag{6}$$

is a weighted distribution function and

$$\lambda(E) = \nu_0 \exp(-E/k_B T) \tag{7}$$

E is the activation energy, ν_0 the prefactor, k_B the Boltzmann constant, and T the absolute temperature. When $g(E) \propto \delta(E-E_1)$, $\psi(t)$ is described by a Poisson distribution function (see eq A19). The exponential form of the barrier density is assumed for $g(E)$ as follows:[17]

$$g(E) = \begin{cases} 0 & E < E_0 \\ (k_B T_0)^{-1} \exp[-(E-E_0)/k_B T_0)] & E > E_0 \end{cases} \tag{8}$$

where E_0 and $k_B T_0$ are the peak position and the width of the distribution of $g(E)$, respectively. Equations 6−8 yield

$$w(\lambda) = \begin{cases} 0 & \lambda > \nu \\ \left(\frac{\alpha}{\nu}\right)\left(\frac{\lambda}{\nu}\right)^{\alpha-1} & \lambda < \nu \end{cases} \tag{9}$$

with

$$\nu \equiv \nu_0 \exp(-E_0/k_B T) \tag{10}$$

and

$$\alpha \equiv T/T_0 \tag{11}$$

Substituting eq 9 into eq 5,

$$\psi(t) = (\alpha/\nu^\alpha) t^{-1-\alpha} \gamma(\alpha+1, \nu t) \tag{12}$$

where $\gamma(z,p)$ is the first kind of incomplete Γ function.[18] The barrier density (eq 8) approaches a delta-function if the halfwidth $T_0 \rightarrow 0$, i.e., $\alpha \rightarrow \infty$. In this case $\psi(t)$ approaches a Markoffian process (eq A19). When νt is large, eq 12 gives

$$\psi(t) \cong \frac{\alpha\Gamma(\alpha+1)}{\nu^\alpha} t^{-1-\alpha} - \alpha\frac{e^{-\nu t}}{t} \quad (t \rightarrow \infty) \tag{13}$$

The Laplace transform of eq 13 is approximated by

$$\psi^*(u) \cong 1 - \frac{\alpha\pi}{\sin \alpha\pi}\left(\frac{u}{\nu}\right)^\alpha + \frac{\alpha}{1-\alpha}\left(\frac{u}{\nu}\right) \quad (\alpha \neq 1) \tag{14}$$

under the condition that u is small, where the Laplace transform of $\psi(t)$ is given by

$$\psi^*(u) \equiv \int_0^\infty \psi(t)\, e^{-ut}\, dt \tag{15}$$

When $0 < \alpha < 1$, eq 14 is approximated as $\psi^*(u) \cong 1 - A(u/\nu)^\alpha$ and eqs A16 and A18 give

$$K^*(u) \approx (0.659/A)(\nu/u)^\alpha \quad (u \rightarrow 0) \tag{16}$$

and also

$$K(t) \approx [0.659/A\Gamma(\alpha)]\nu^\alpha t^{\alpha-1} \quad (t \rightarrow \infty) \tag{17}$$

where $A \equiv \alpha\pi/\sin \alpha\pi$.

By substituting eq 17 into eq 3, the fraction of cis units decreases as

$$P_c(t) = \exp[-(t/\tau)^\alpha] \quad (t \rightarrow \infty) \tag{18}$$

where

$$\tau \equiv (A\Gamma(\alpha)\, \alpha/0.659c)^{1/\alpha} \nu_0^{-1} \exp(E_0/k_B T) \tag{19}$$

Equation 18 is the same form as eq 1 and the relaxation time is shown in eq 19, the prefactor of which depends on c, α, ν_0, and E_0. The activation energy is given by E_0.

When $\alpha > 1$, eq 14 is approximated as $\psi^*(u) \cong 1 - [\alpha/(\alpha - 1)](u/\nu)$ and $P_c(t)$ is expressed by a single-exponential function. When $\alpha = 1$, $\psi^*(u) \cong 1 - (u/\nu) \ln(1 + \nu/u)$ and it is impossible to get $K(t)$ and $P_c(t)$ analytically.

3. Discussion

DSC curves were analyzed by us based on the two-state model.[8] A relationship exists between the two-state model and the interspace-diffusion model, which is discussed below. The information derived by the interspace-diffusion model is also discussed.

Time-Dependent Rate Constant. From eq 3,

$$dP_c(t)/dt = -cK(t)\, P_c(t) \tag{20}$$

The rate constant $K(t)$ depends on time t, which means this system has a memory effect. Therefore, eq 20 can be replaced by

$$dP_c(t)/dt = -c\int_0^t \phi(t-\tau)\, P_c(\tau)\, d\tau \tag{21}$$

where $\phi(t)$ is the memory function. This function is related to $K(t)$ as in eqs 22 and 23.

$$cK(t) = -\mathrm{d}[\ln P_c(t)]/\mathrm{d}t \qquad (22)$$

$$c\phi^*(u) = [P_c(0) - uP_c^*(u)]/P_c^*(u) \qquad (23)$$

If this $\phi(t)$ is described by a delta-function, no memory effect exists. Sequential transitions described by CTRW will make the transition rate of the primary relaxation process time-dependent (different from a delta-function). In the interspace-diffusion model, the distribution of the activation energy causes a non-Markovian nature of the pausing-time distribution function as shown in eq 5.

Relationship between the Two-State Model and the Interspace-Diffusion Model. The two-state model previously analyzed[8] is represented by

$$\mathrm{d}P_c/\mathrm{d}t = -k_f P_c + k_f \exp(-\epsilon/k_B T)P_t \qquad (24)$$

where $k_f = W \exp(-E_0/k_B T)$, $P_c + P_t = 1$, and W is the preexponential factor (attempt frequency). E_0 and ϵ are the barrier height and energy difference between cis and trans states, respectively. From a comparison of eqs 20 and 24, it is clear that the interspace-diffusion model is characterized as (1) ϵ being very large and $\exp(-\epsilon/k_B T)$ infinitely small and then the second term in the right-hand side of eq 24 is neglected and (2) the forward rate constant k_f being time-dependent. In the two-state model, the distribution of the activation energy is not taken into account, while in the interspace-diffusion model, the backward reaction from trans to cis states is neglected.

DSC Curve Based on the Interspace-Diffusion Model. DSC is measured under the condition of constant heating rate $q = \mathrm{d}T/\mathrm{d}t$. By changing time variable t to temperature variable T, eq 20 gives

$$\mathrm{d}P_c/\mathrm{d}T = -\nu_1^{\alpha} \exp(-\alpha E_0/k_B T)[(T - T_0)/q]^{\alpha-1}(1/q)P_c \qquad (25)$$

and

$$\ln[P_c(T)/P_c(T_0)] = -\int_{T_0}^{T} \nu_1^{\alpha} \exp(-\alpha E_0/k_B T)[(T - T_0)/q]^{\alpha-1}(1/q)\,\mathrm{d}T \qquad (26)$$

where $T = T_0 + qt$ and

$$\nu_1 \equiv [0.659c/A\Gamma(\alpha)]^{1/\alpha}\nu_0 \qquad (27)$$

The observed DSC curve is proportional to $\mathrm{d}P_c/\mathrm{d}T$. In numerical calculation, care must be taken of T_0. Figure 3 shows the T_0 dependence of the DSC curve. The effect from T_0 appears largely at T_0 above 100 K.

The parameter α has a large effect on the peak position and the width of the DSC curve for cis–trans isomerization, as shown in Figure 4. As α decreases from 1 to 0.5, the peak position shifts to a higher temperature (from 410 to 440 K) and the width becomes broader. The case of $\alpha = 1$ apparently corresponds to the two-state model with $\epsilon \to \infty$.

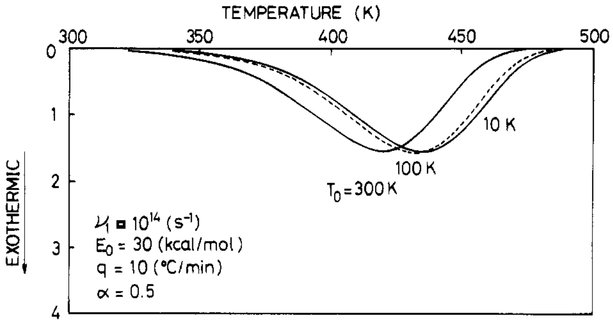

Figure 3. Effect of T_0 on DSC curve. T_0 must be selected below 100 K. Calculated using eqs 25 and 26 with $\nu_1 = 10^{14}$ (s^{-1}), $E_0 = 30$ (kcal/mol), $q = 10$ (°C/min), and $\alpha = 0.5$.

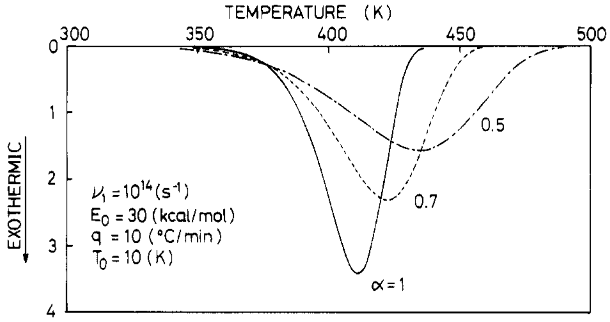

Figure 4. Effect of the exponent α on the DSC curve. Calculated using eqs 25 and 26 with $\nu_1 = 10^{14}$ (s^{-1}), $E_0 = 30$ (kcal/mol), $q = 10$ (°C/min), and $T_0 = 10$ (K).

At the peak position $T = T_p$ in the DSC curve, the following relation is derived from eq 20 after changing t to T.

$$(\nu/q)^{\alpha} = \left[\frac{\alpha E_0}{k_B T_p^{\,2}} + \frac{\alpha - 1}{T_p - T_0} + \frac{1}{c}\frac{\mathrm{d}c}{\mathrm{d}T}\right](T_p - T_0)^{1-\alpha}\left(\frac{1}{ck_1}\right) \qquad (28)$$

where

$$k_1 \equiv 0.659/A\Gamma(\alpha) \qquad (29)$$

The right-hand side of eq 28 is nearly constant with changing q. From $(\nu/q)^{\alpha} \approx$ const.,

$$\ln q + E_0/k_B T_p \approx \text{const.} \qquad (30)$$

Equation 30 indicates that the q dependence of peak position T_p gives the activation energy E_0. This method does not depend on the values of α. This is the reason why the two-state model and the interspace-diffusion model give nearly the same activation energy (ca. 30 kcal/mol for cis–trans isomerization of PA). The activation energy does not depend on the polymerization conditions.[9]

The activation energy reflects the energy barrier for the rotation to change the dihedral angle of one cis–transoid monomer unit by 180°, because interspace diffusion is activated by the main-chain motions. Its energy barrier calculated by Yamabe et al.[13] is ca. 23 kcal/mol which is not contradictory to our result.

Exponent α. The temperature dependence of the exponent α is shown in Figure 5, which has been measured by DSC[9] and IR[6] methods. The value of α slightly increases with temperature, as suggested by eq 11. As α is nearly 0.5, T_0 is about 800 K. The width of the activation energy distribution is characterized by

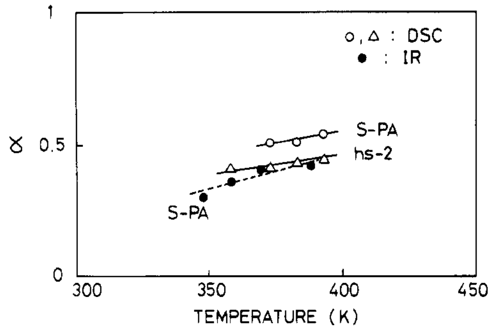

Figure 5. Temperature dependence of α for various PA films, measured by DSC[9] and IR[6] methods.

$k_BT_0 \approx 1.6$ kcal/mol which is a rather small fluctuation compared to $E_0 \approx 30$ kcal/mol.

Effect of *c*. The effect of c on τ^{-1} is very interesting (see eq 19). If α is 0.5, $c^{1/\alpha}$ changes an order of magnitude when c changes by more than 3 times. The exothermic peak position of cis−trans thermal isomerization shifts to 20−30 K lower temperature, as suggested in Figure 6 of ref 8, because the preexponential factor W in ref 8 is related to the inverse of τ and to $c^{1/\alpha}$. Although the calculation in ref 8 corresponds to the case of $\alpha = 1$ (see Figure 4), the qualitative nature is nearly the same.

Experimentally, S-PA shows a higher temperature peak position around 443 K in cis−trans thermal isomerization. On the other hand, hs-PA has a lower temperature peak position around 413 K. As suggested in ref 22, hs-PA has a more disordered structure of crystallites than that of S-PA. A more disordered structure of crystallites gives a larger value of c and a lower temperature of the exothermic peak. This seems to be one of the reasons why hs-PA shows a lower temperature peak position than that of S-PA since there is no large difference between α's of S-PA and hs-PA.

S-PA has the two DSC exotherms near 440 K (main peak) and 420 K (shoulder). These have nearly the same activation energy. Accordingly, the difference of these two peak positions can be attributed to the difference in c. That is, S-PA has two kinds of solid structure (the more and less ordered structures). The same result has been derived in ref 22.

4. Conclusion

In order to explain the stretched-exponential function with exponent α ($0 < \alpha < 1$) which has been found in the isothermal cis−trans isomerization behavior of PA films, the interspace-diffusion model was discussed. As X-ray diffraction experiments suggested, the cis−trans thermal isomerization of PA occurs under the condition of the molecular axis being nearly fixed. Not only intramolecular cooperative motions of cis bonds (or units) but also intermolecular cooperative motions among neighboring chains are unavoidable.

The interspace-diffusion model is proposed to simply describe the intermolecular cooperative motions of neighboring chains. If an interspace reaches a cis bond (or moving unit of cis state), this cis bond changes to trans bond instantaneously. Using a continuous-time random walk model, the decay of survival probability of cis units can be expressed by the stretched-exponential function under the assumption of the distribution of the activation energy for cis−trans isomerization. The relationship between the previously analyzed two-state model and the interspace-diffusion model was discussed. The interspace-diffusion model takes into account the correlation of cis unit motions (the distribution of the activation energy). The experimental temperature dependence of the exponent α is not inconsistent with the interspace-diffusion model.

Appendix. Continuous-Time Random Walk

CTRW was introduced by Montroll and Weiss[15] to consider the situation that the jumps of random walker do not occur at regular time intervals but are made with the pausing-time distribution (or hopping time distribution).

Random walk at regular time intervals on a periodic lattice is described by the probability $P_n(s)$ of being at site s after n steps.

$$P_{n+1}(s) = \sum_{s'} p(s-s')\, P_n(s') \qquad \text{(A1)}$$

where $p(s)$ is the probability of a single jump having a displacement s and $\sum_s p(s) = 1$. Let $F_n(s)$ be the probability that a random walker reaches site s for the first time at the nth step.

$$P_n(s) = \delta_{n,0}\delta_{s,0} + \sum_{j=1}^{n} F_j(s)\, P_{n-j}(0) \qquad \text{(A2)}$$

By introducing the generating functions,

$$G(s,z) = \sum_{n=0}^{\infty} P_n(s)\, z^n, \quad P_0(s) = \delta_{s,0} \qquad \text{(A3)}$$

$$H(s,z) = \sum_{n=0}^{\infty} F_n(s)\, z^n \qquad \text{(A4)}$$

eq A1 gives

$$G(s,z) - z\sum_{s'} p(s-s')\, G(s',z) = \delta_{s,0} \qquad \text{(A5)}$$

For a finite lattice with periodic boundary conditions,

$$G(s,z) = N^{-3}\sum_{k} \frac{\exp(iks)}{1 - z\lambda(k)} \qquad \text{(A6)}$$

$$\lambda(k) = \sum_{s} p(s)\exp(-iks) \qquad \text{(A7)}$$

$$H(s,z) = \frac{G(s,z) - \delta_{s,0}}{G(s=0,z)} \qquad \text{(A8)}$$

and $k = 2\pi r/N$ (r = integer).

The probability density $\psi_n(t)$ for the occurrence of the nth step (jump) at time t is

$$\psi_n(t) = \int_0^t \psi(\tau)\, \psi_{n-1}(t-\tau)\, d\tau \qquad \text{(A9)}$$

where $\psi(t)$ is the pausing-time distribution function (the hopping time distribution function). The probability density $F(s,t)$ for reaching site s for the first time at time t is

$$F(s,t) = \sum_{n=0}^{\infty} F_n(s)\, \psi_n(t) \qquad \text{(A10)}$$

The probability density $R(s,t)$ for reaching site s (or to just arrive at s) at time t (not necessarily for the first time) is

$$R(s,t) = \sum_{n=0}^{\infty} P_n(s)\, \psi_n(t) \tag{A11}$$

The probability $P(s,t)$ of being at s at time t is

$$P(s,t) = \int_0^t R(s,\tau)\, \Psi(t-\tau)\, \mathrm{d}\tau \tag{A12}$$

where

$$\begin{aligned} \Psi(t) &= 1 - \int_0^t \psi(t)\, \mathrm{d}t \\ &= \int_t^{\infty} \psi(\tau)\, \mathrm{d}\tau \end{aligned} \tag{A13}$$

where Ψ represents the probability that a walker remains fixed in time interval $(0,t)$. The probability $P(s,t)$ includes the effect of staying at s during $t - \tau$ after just reaching at s. The Laplace transform of $P(s,t)$ is given by

$$P^*(s,u) = G[s,\psi^*(u)]\frac{1 - \psi^*(u)}{u} \tag{A14}$$

and also

$$F^*(s,u) = H[s,\psi^*(u)] \tag{A15}$$

Using eqs A8 and A15, the Laplace transform of $K(t)$ becomes

$$\begin{aligned} K^*(u) &= \sum_{x \neq 0} F[x,z{=}\psi^*(u)] \\ &= \frac{1}{[1 - \psi^*(u)]G(0,\psi^*(u))} - 1 \end{aligned} \tag{A16}$$

Here,

$$\sum_s G(s,z) = \frac{1}{1 - z} \tag{A17}$$

was used since $\sum_s p(s-s') = 1$ in eq A5.

For a three-dimensional simple cubic lattice,[15]

$$G(0,z) = 1.516 - (3/\pi)(3/2)^{1/2}(1 - z)^{1/2} + \ldots \tag{A18}$$

when z approaches unity.

The pausing-time distribution function $\psi(t)$ introduces a memory function into the master equation (ME) of $P(s,t)$,[16] which is called the generalized master equation (GME).

When $\psi(t)$ is described by a Poisson distribution function,[16]

$$\psi(t) = \lambda_1 \exp(-\lambda_1 t) \tag{A19}$$

with

$$\lambda_1 = \nu_{\mathrm{p}} \exp(-E_1/k_{\mathrm{B}}T) \tag{A20}$$

where E_1 is an activation barrier height, ν_{p} the prefactor attempt frequency, k_{B} the Boltzmann constant, and T the absolute temperature. No memory effect appears in this case.

Generalization of Montroll–Weiss CTRW was made by Scher and Lax[19] using $\psi(s,t)$ depending on hopping distance. This GCTRW is proved to be the same with GME by Klafter and Silbey.[20,21]

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