Theory of Charge Transport in Polypeptides

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We have derived phase space and diffusion theories for a new hopping model of charge transport in polypeptides and thence for distal chemical kinetics. The charge is transferred between two carbamide groups on each side of the C_α atom hinging two amino acid groups. When the torsional angles on the hinge approach a certain region of the Ramachandran plot, the charge transfer has zero barrier height and makes charge transfer the result of strong electronic correlation. The mean first passage time calculated from this analytic model of some 164 fs is in reasonable agreement with prior molecular dynamics calculation of some 140 fs and supports this new bifunctional model for charge transport and chemical reactions in polypeptides.

Introduction

One of the important problems of current chemistry is action at a distance. This can be charge transport over long distance (molecular wires), or even chemical reaction at a distance. The equation of local excitation at one end of a molecule and chemical reaction only at the other end of a molecule is not treated in the conventional theory of reaction kinetics. Typical reaction rate theory is local, where chemical reaction proceeds in the proximity of the site of excitation—we might refer to this as proximal kinetics. In contrast, chemical reaction only at a distance may be referred to as distal kinetics. Such processes are of considerable importance for many biological systems. Hence, to have a theory for such distal kinetics can be a subject of some interest.

Charge transfer in polypeptides is an important prototype for distal chemical reactions. The theory of such distal kinetics can bear on processes in molecular devices[1−4] and other areas.[5−8] In our examples excitation is at one place of the molecule, but chemical reaction will be at a site quite distant from the place of excitation. We understand charge transfer as a special charge hopping process as proposed by us for these systems in 1996,[9−14] we have recently carried out detailed molecular dynamics (MD) calculations on such a process.[15] The mean first passage time of 140 fs obtained here is in close agreement with our direct femtosecond timing experiments and supports our mechanism. The mechanism we proposed is essentially a bifunctional process in which the charge rests on an amino acid and then fires into the next amino acid when the internal Ramachandran rotations in the peptide chain are in a critical configuration. This "rest and fire" mechanism contains elements of both weak and strong coupling between sites, an essential aspect of our model. Here we propose a general analytical theory for such processes of internal rotations and firing as a phase space model spanned by the Ramachandran angles. The result of 164 fs for the mean first passage time found here is again in excellent agreement with our previous work.

Protein Charge Transport

In ref 4, we proposed a new mechanism of charge transfer of a chemical reaction at distance in a polypeptide chain, i.e., distal kinetics. MD simulation results support our model in providing a quite similar time scale for elementary processes. In this paper we explore an analytic phase space theory of our model. The basic idea of our model is that charge is excited first from a donor amino acid and injected into the polypeptide chain. In detail we consider the two nearly free rotations ψ, ϕ at the hinge carbon atom between two carbamide groups (Figure 1a). These angles can go over large excursions in the Ramachandran plot with nearly no barrier. The energetics of neighboring amino acids are not identical, even if two identical amino acids are involved, hence leading to considerable barriers. Baranov and Schlag have shown here interestingly that for one particular angular configuration where the carbonyl groups of neighboring amino acids approach to a critical distance, there is an orbital degeneracy leading to a hybrid state for the charge species.[16,17] This narrow range of angles then leads to facile charge transfer and thus presents a firing configuration. Hence the charge system can rotate over a phase space of large angular range as isolated species, but at a small subsection of this phase space firing sets in. We consider a rotational motion around the $C_\alpha - C$ and $C_\alpha - N$ bonds (see Figure 1b). This motion is mapped into the Ramachandran plot as a stochastic motion in phase space with torsional angles φ and ψ. There is a subregion, i.e., a gate, that corresponds to specific ratchet angles inside the Ramachandran plot. The waiting process is then becoming an escaping process inside a 2D disk with a gate.[5] The asymmetry of the hopping rate will make the electron transport to the acceptor more effective. The entropy driven escaping process is pictured as charge dumping its energy to the rotational degrees of freedom of the next site before vibrational motions become active.

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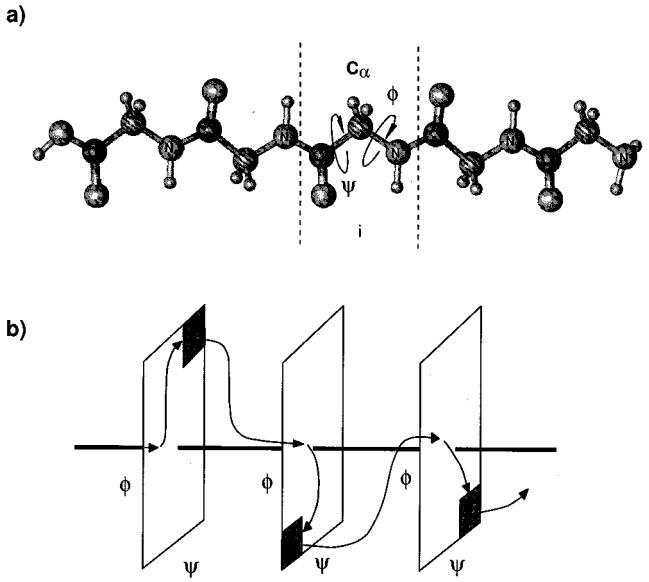

Figure 1. Electron hopping model. (a) Polypeptide chain for charge transport in the chain. (b) Sequential Ramachandran plots. Charge is excited from the donor and injected into the polypeptide chain. It will remain on the initial site of the C_α atom and wait until the rotation of $\phi_{i-1,i}$ and $\psi_{i,i+1}$ reaches the critical angle and the firing occurs. Then charge is transferred to the next amino acid. The rotational motion is similiar to a stochastic motion inside the Ramachandran plot. This transition will iterate until the charge reaches the final site in the polypeptide.

Now we turn to the study of the mean first passage time of the escaping process in a 2D disk. In the phase space version of the Ramachandran plot, we can imagine that a particle moves ballistically or randomly inside a square box. The ballistic motion only occurs if the two rotations contain an energy of some 0.2−0.5 eV. This is presumed to be obtained from the previous step. The particle motion follows a stochastic process as shown by the MD results. In the following we derive the survival time to escape out of a 2D disk with a gate on the perimeter.

Phase Space Theory

In this section, we study the quantum escaping rate of a virtual particle escaping out of a 2D disk. By applying the phase space theory in unimolecular reaction, the flux of the particle passing through the gate part[18−23] is described by cells and each cell size satisfies the uncertainty principle. The reaction rate in canonical ensemble, based on the transition state theory, is then defined by phase space cell change. This transition rate in our case is equivalent to the particle escaping rate of escaping process.

Let's consider a system consisting of two freely moving rotors. These two rotors correspond to the rotations around $C_\alpha - N$ and $C_\alpha - C$ bonds at the C_α hinge (see Figure 2), i.e., torsional angles ϕ and ψ, which are confined in a subregion of Ramachandran plot. This subregion is called Baranov−Schlag (BS) box.[15] The corresponding inertial moments of the rotors are denoted as I_ϕ and I_ψ. This two rotor system can be imagined as a virtual particle moving inside the BS box. Around the C_α hinge, the oxygen atoms that attach to nitrogen and carbon atoms of the C_α hinge will collide with each other when their positions come close to a certain distance, for example 2.84 Å, and the charge waiting in the N side is transferred to the C side with a hopping rate. The closest distance between these two oxygen atoms corresponds to a gate part on the perimeter of the BS box. It is feasible for us to write down the Hamiltonian of this system as

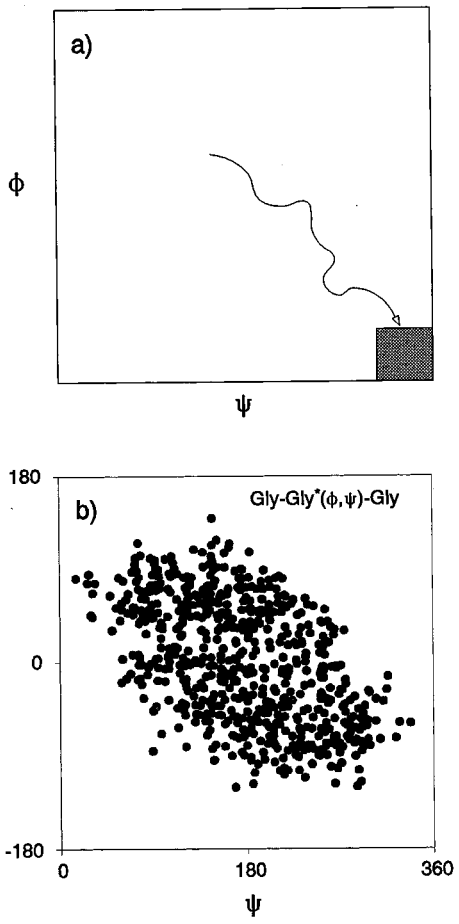

Figure 2. (a) Ramachandran plot for the rotation around the C_α−N and C_α−C bonds. The shadow part is the exit or gate. (b) Molecular dynamic simulation of torsional angles nearby the second C_α atom in 3 Gly peptide. The charge dumps 0.4 eV (ca. 2000 K) energy to the rotors. The dot represent the ϕ and ψ angles near the second C_α atom when the O−O distance of the carbonyl groups approaches 3 Å. The dotted part shows an elliptic area and the existence of the gate in the Ramachandran plot.

$$H = E = \frac{p_\phi^2}{2I_\phi} + \frac{p_\psi^2}{2I_\psi} \tag{1}$$

where p_ϕ and p_ψ are the rotational momentums of the rotors and E is the total energy.

Having built up the model system, we are now interested in solving the collision frequency between O−O atoms or the escaping rate of the particle escaping process. To achieve this purpose, we first define the phase space volume (PSV) as

$$\begin{aligned} \mathrm{PSV} &= \int \mathrm{d}p_\phi\, \mathrm{d}\phi\, \mathrm{d}p_\psi\, \mathrm{d}\psi \\ &= V_{\phi\psi} \int \mathrm{d}p_x\, \mathrm{d}p_y\, J \end{aligned} \tag{2}$$

where $V_{\phi\psi}$ represents the volume in coordinates. Note that no degeneracy is assumed in eq 2 and J is the jacobian defined by $J = 2E\sqrt{I_\phi I_\psi}$. Therefore, eq 2 can be simplified into PSV $= 2\pi E\sqrt{I_\phi I_\psi} V_{\phi\psi}$. The related quantity such as the sum of states is just equivalent to the PSV divided by the square of the Planck constant h^2, i.e., $N(E) = (2\pi/h^2)E\sqrt{I_\phi I_\psi} V_{\phi\psi}$. Eventually, the energy derivative of the sum of states provides us the density

of states $\rho(E) = dN(E)/dE = (2\pi/h^2)\sqrt{I_\phi I_\psi}V_{\phi\psi}$ which is independent of the rotational energy E. With this density of states, we are able to calculate the transition rate or the escaping rate.

Next we turn to study the escaping rate constant. The basic assumption of calculating the rate constant is "the population density ρ over the whole volume of the phase space is uniform".[24] We follow this idea and define the ratio of particles near the gate region to the total particles dN/N as equal to the ratio of the phase space at the gate region to the total phase space and

$$= \frac{dN(q^\ddagger,p^\ddagger)}{N}$$

$$= \frac{dq^\ddagger\, dp^\ddagger \int_{H=E-E_t-E_0} \cdots \int dq_1^\ddagger \cdots dq_{n-1}^\ddagger\, dp_1^\ddagger \cdots dp_{n-1}^\ddagger}{\int_{H=E} \cdots \int dq_1 \cdots dq_n\, dp_1 \cdots dp_n} \quad (3)$$

where E_0 is activation energy and E_t is translational energy. Note that $dq_n\, dp_n = h =$ the cell size in phase space and is taken out of the integration. ‡ lables the position of the critical region or gate part. According to unimolecular reaction theory, the flux in phase space is $dN(q^\ddagger,p^\ddagger)/dt$. Note in particular that, in the unimolecular reaction case, there is only one degree of freedom involved. However, in our case there are two rotors; i.e., there are two degrees of freedom involved. Hence, the ratio of particles near the gate part to the total particles is extended to

$$\frac{dN}{N} = \left[\int_{H=E} \cdots \int d\phi\, dp_\phi\, d\psi\, dp_\psi\right]^{-1} \left[\int_{H=E-E_t-E_0} \cdots \int [\delta(\phi-\phi^\ddagger)\,\bar{H}(\psi-\psi^\ddagger) + \bar{H}(\phi-\phi^\ddagger)\,\delta(\psi-\psi^\ddagger)]\, d\phi\, dp_\phi\, d\psi\, dp_\psi\right] \quad (4)$$

where $\bar{H}$ is the Heaviside step function and δ is the Dirac delta function. Now the first-order escaping rate is defined as the change of the ratio of particles near the gate part via

$$\frac{-dN}{N\,dt} = k(E) = \left[\int_{H=E} \cdots \int d\phi\, dp_\phi\, d\psi\, dp_\psi\right]^{-1} \left[\int_0^E dE_\phi \int_{H=E-E_\phi} \cdots \int H(\psi-\psi^\ddagger)\, d\psi\, dp_\psi + \int_0^E dE_\psi \int_{H=E-E_\psi} \cdots \int H(\phi-\phi^\ddagger)\, d\phi\, dp_\phi\right] \quad (5)$$

The above rate expression can actually be split into a more simple expression containing two independent degrees of freedom such as

$$\frac{-dN}{N\,dt} = \frac{1}{h}\frac{\int_0^E dE_\phi\, \rho_1^{\bar{H}}(E_\psi) + \int_0^E dE_\psi\, \rho_1^{\bar{H}}(E_\phi)}{\rho_2(E)} \quad (6)$$

where $\rho_2(E) = dN_2(E)/dE$, $N_2(E) = h^{-2}\int_{H=E}\cdots\int d\phi\, dp_\phi\, d\psi\, dp_\psi$ and $\rho_1^{\bar{H}}(E_i) = dN_1^{\bar{H}}(E_i)/dE$, where $i = \phi$ or ψ. Here, in evaluating the densities of states, the sums of states are defined by $N_1^{\bar{H}}(E_\psi) = h^{-1}\int_{H=E-E_\psi}\cdots\int d\phi\, dp_\phi\, \bar{H}(\phi-\phi^\ddagger)$ and $N_1^{\bar{H}}(E_\phi) = h^{-1}\int_{H=E-E_\phi}\cdots\int d\psi\, dp_\psi\, \bar{H}(\psi-\psi^\ddagger)$. $\phi^\ddagger$ and $\psi^\ddagger$ are the gate positions in each dimension. We solve the phase space volume as $PSV_1^{\bar{H}}(E_\psi) = h^{-1}(\phi^{max}-\phi^\ddagger)\sqrt{2I_\phi(E-E_\psi)}$ and the corresponding density of states as $\rho_1^{\bar{H}}(E_\psi) = (\partial/\partial E)\,PSV_1^{\bar{H}} = [\sqrt{2I_\phi}(\phi^{max}-\phi^\ddagger]/[2h\sqrt{(E-E_\psi)}]$, where ϕ^{max} is the maximum length of the BS box in ϕ direction. The same method can be applied to solve $\rho_1^{\bar{H}}(E_\phi)$. Finally, the rate constant becomes

$$k = \frac{1}{2\pi V_{\phi\psi}}\left[\Delta\psi\omega_\phi\sqrt{1+\frac{I_\psi}{I_\phi}\left(\frac{\omega_\psi}{\omega_\phi}\right)^2} + \Delta\phi\omega_\psi\sqrt{1+\frac{I_\phi}{I_\psi}\left(\frac{\omega_\phi}{\omega_\psi}\right)^2}\right] \quad (7)$$

In eq 7, the volume in coordinates is $V_{\phi\psi} = \phi\psi - \Delta\phi\Delta\psi$, where $\Delta\phi = \phi^{max} - \phi^\ddagger =$ the gate length in the ϕ dimension and $\Delta\psi = \psi^{max} - \psi^\ddagger =$ the gate length in the ψ dimension. Here ψ^{max} is the maximum length of the BS box in ψ dimension. We can simplify the general rectangular box into a special square box. Assuming that these two rotors have the same rotation frequency $\omega_\phi = \omega_\psi$, the gate size is equivalent in each dimension $\Delta\phi = \Delta\psi$, and the ratio of the length of the gate part relative to the perimeter length of the BS box is $\theta/2\pi = [\Delta\phi + \Delta\psi]/[2(\phi+\psi)] = \Delta\phi/2\phi$ (we set $\phi = \psi$), we simplify the transition rate expression to

$$k = \frac{2}{\pi}\frac{\omega_\phi}{\phi}\frac{\sqrt{2}\dfrac{\theta}{2\pi}}{1-4\left(\dfrac{\theta}{2\pi}\right)^2} \quad (8)$$

In eq 8, the frequency part ω_ϕ of the escaping rate is just the rotational frequency of the rotor or the velocity of the free motion of the vitual particle inside the BS box. Hence, the frequency part of the escaping rate, in this case, is in the range of 100 fs. It is interesting to know that the activation part of the escaping rate only depends on the relative gate opening angle $\theta/2\pi$, and hence, the escaping process is entropy controlled. When the gate size is small, i.e., $\theta/2\pi \to 0$, the transition rate approaches

$$k \sim \frac{2\sqrt{2}}{\pi}\frac{\theta}{2\pi}\frac{\omega_\phi}{\phi} \quad (9)$$

and is proportional to the first order of the gate size, i.e., $\theta/2\pi$.

Now we turn to examine the temperature-dependent rate constant which is defined by $k(T) = \int_0^\infty dE\, k(E)\, P(E,T)$ where the Boltzmann distribution factor is denoted as $P(E,T) = \rho(E)e^{-E/k_BT}/Q(T)$ and the partition function is equivalent to $Q(T) = \int_0^\infty \rho(E)e^{-E/k_BT}\, dE = (2\pi/h^2)\sqrt{I_\phi I_\psi}V_{\phi\psi}k_BT$. Here T is the temperature and k_B denotes the Boltzmann constant. Hence the Boltzmann factor is $P(E,T) = e^{-E/k_BT}/k_BT$. Finally, we have the temperature-dependent rate constant

$$k(T) = \frac{\sqrt{2\pi}}{4\pi}\frac{1}{V_{\phi\psi}}\left(\frac{\Delta\psi}{\sqrt{I_\phi}} + \frac{\Delta\phi}{\sqrt{I_\psi}}\right)\sqrt{k_BT} \quad (10)$$

In the above equation, the temperature-dependent rate constant is proportional to the square root of temperature and there is no activation part in the rate expression. Hence, the entire process is entropy driven.

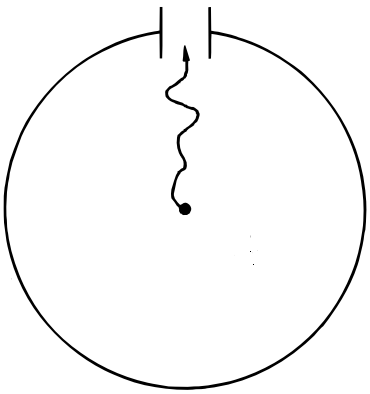

Figure 3. Escaping process in a 2D disk. The particle is initially thermally distributed inside the disk. The gate size is θ.

According to our previous MD simulation results,[15] the torsional angle ranges are $\phi = 95°$ and $\psi = 116°$ and gate sizes are ca. $\Delta\psi = 43.925°$ and $\Delta\phi = 25.1°$. The corresponding escaping time which is the inverse of the escaping rate are $\langle t\rangle_{4000K} = \ln 2/k(E) = 115.7$ fs, $\langle t\rangle_{2000K} = 163.5$ fs, and $\langle t\rangle_{300K} = 423$ fs. It should be noted that the 300K result here only refers to slower rotations and incorrectly ignores many-body effects as seen in the MD calculations.

In the following sections, we will discuss the classical limiting cases for the escaping process.

Diffusion Motion

One of the limiting case of the escaping process is the diffusion motion of the rotors when the protein is dissolved in polar solvent. The solvent dynamic effects slow the virtual particle motion inside the BS box. As an alternative approach we consider diffusional motion of the particle inside a 2D disk (see Figure 3). The particle is initially thermal distributed. The equation of motion of the particle satisfies the 2D Smoluchowsky equation

$$\frac{\partial}{\partial t}\rho = D_0\nabla^2\rho + \int \mathrm{d}\Omega\ \sigma(\Omega,t)\ \rho(r,t) \tag{11}$$

where ρ is the particle density and σ term is the surface reaction kernel which can be solved by a self-consistent method.[18] On the other hand, the modified radiation boundary condition is

$$\bar{H}(\theta(t) - \theta)k_0\rho(r,t) = 2\pi D_0 R\,\hat{r}\cdot\vec{\nabla}\rho(r,t) \tag{12}$$

where $\theta(t)$ can be any time-dependent gating function. Here, in the present paper, $\theta(t)$ is time-independent function. k_0 is the particle reaction rate on the gate part, and D_0 is the particle diffusion constant. The other quantity $\hat{r}$ is the unit vector from the center of the disk to its boundary. The general solution can be obtained by following our previous method[18] and the escaping time is obtained as

$$\tau = \sqrt{2}\frac{2\pi}{\theta} \tag{13}$$

where θ is the maximum opening angle of the gate and is small. The relative gate opening angle is the same as the one obtained in eq 9. Note that τ is characterized by the time scale R^2/D_0. Here the escaping time is twice of the phase space result. For a 2D disk there exists a 1D entropy potential surface (see Appendix 1 and Figure 4) along the radial axis. The angular part does not contribute more to the entropy potential surface. Thus, the surface diffusion part is replaced by a random walk along the θ axis. Moreover, the escaping rate is proportional to the relative gate opening angle.

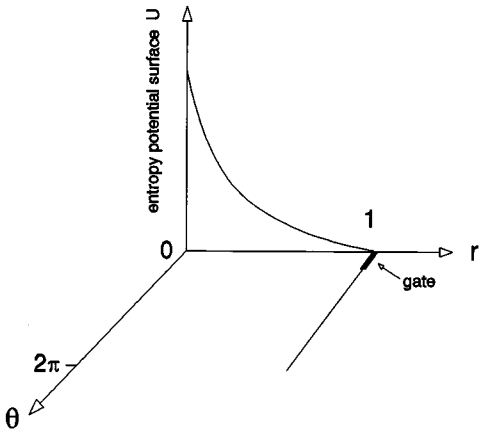

Figure 4. Entropy potential surface for a diffusion motion inside a 2D disk. Here r is the radial part and θ is the angular part.

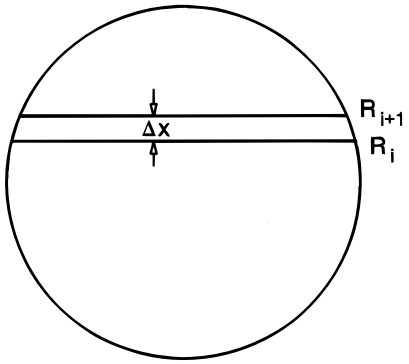

Figure 5. Averaged length of the trajectory. Here $R_{i+1}(R_i)$ means the trajectory at time equals to $t + \mathrm{d}t(t)$.

Ballistic Motion

In this section, we study the ballistic motion of a particle (or billiard ball) inside a 2D disk with a gate. This is a classical limit of the motion of the rotors in gas phase when the inertial moments are relative large or the polypeptide chain is long.

Now let us first consider the basic characteristic quantities for the billiard ball moving inside the 2D disk. The characteristic time (or the mean free time), between two successive collisions within the disk wall, for the ballistic motion inside the 2D disk with a particle velocity v can be defined as $t_r = \langle R\rangle/v$. Here $\langle R\rangle$ is the averaged distance (or the mean free path) for the billiard ball freely traveling inside the disk before colliding the disk wall and can be estimated in the following way as $\langle R\rangle = (\Sigma_{i=1}^{N} R_i)/N$, where N is the number of trajectories R_i in the disk $= 2R/\Delta x$, $R =$ radius of the disk, and $\Delta x =$ the thickness of the slice of R_i (see Figure 5). Note that R_i is the free path of the billiard ball and is independent of the hinge position. When the thickness Δx approaches zero, we obtain a relationship $\Sigma_{i=1}^{N} R_i\ \Delta x\ \underrightarrow{\Delta x \to 0}\ 2R\langle R\rangle$. Hence, the mean free path for the billiard game is $\langle R\rangle = \pi/2\ R$ and the mean free time becomes $t_r = (\pi/2)R/v \equiv \pi/2\ R/\omega_\phi$.

With the above two fundamental characteristic scales, we are able to study the escaping time. Since, on the perimeter of the 2D disk, there exists a gate with opening angle θ, which occupies a fraction $\theta/2\pi$ of the disk boundary, we are able to define the escaping probability for the billiard game, which is equivalent to $P = \theta/2\pi =$ relative gate part. With the probability

for not escaping out of the disk ($1 - P$), we define the mean first passage time as the averaged time for the billiard particle to first arrive at the gate by counting the multicollision time. More precisely, the mean first passage time is the weighted sum of the escaping probability times the averaged time to stay inside the disk. For example, in the one-collision case, the escaping probability is P and the averaged time to escape out of the disk is equal to the mean free time. Moreover, for the two-collision case, the particle does not escape out from the disk at the first try. Hence, the escaping probability is $P(1 - P)$ and the time for the billiard ball to escape after one collision is about twice the mean free time. We then sum the averaged time to obtain the mean first passage time, which is also denoted as the escaping time, as

$$\begin{aligned}\langle t\rangle &= \text{one collision} + \text{two collisions} + \text{three collisions} + ... \\ &= t_r \cdot P + 2\, t_r \cdot P \cdot (1 - \mathrm{P}) + ... \\ &= \frac{t_r}{P} \end{aligned} \tag{14}$$

Note that, in the phase space theory, the velocity v of the billiard ball inside the 2D disk is equivalent to the oscillation frequency of the rotor ω. The total energy of the rotors, i.e., $^1/_2 I_\phi \omega_\phi^2 + {}^1/_2 I\psi \omega_\psi^2$, is the input energy and is equivalent to $k_B T$. So that each degree of freedom has energy $^1/_2 k_B T = {}^1/_2 I_\phi \omega_\phi^2$. Here we assume that these two rotors are equivalent. Therefore, the mean free time can be expressed in terms of temeprature (or input energy) as $t_r = (\pi/2)(\sqrt{I_\phi/k_B T})R$. It turns out that the final result of the escaping time then becomes

$$\begin{aligned}\langle t\rangle &= \frac{\pi}{2}\sqrt{\frac{I_\phi}{k_B T}} R \frac{1}{\frac{\theta}{2\pi}} \\ &\equiv \frac{\pi}{2}\frac{\phi}{\omega_\phi}\frac{2\pi}{\theta} \end{aligned} \tag{15}$$

It is interesting to note that the escaping time of the billiard motion is $\sqrt{2}$ times the escaping time of the quantum particle escaping out of the BS box. Remember that the phase space result includes the quantum effect. Hence the classical ballistic escaping time is longer than the quantum escaping time.

Conclusion

We present the results of a new analytic theory for "distal" kinetics as a result of a long charge transport model in polypeptides. This is a bifunctional model that in essence contains two basic processes at each amino acid site, a low-frequency rotation between adjacent amino acids and an electronic hopping process, proceeding inside a phase space defined by the Ramachandran plot. This bifunctional process constitutes the hopping juncture between two amino acids. When the particle reaches the gate part, i.e., the oxygen atoms on either side of the same C_α hinge rotate to their contact distance, the charge transfers. The charge transport process is a hopping process that depends on the hopping rate. Hence this hopping process is enthalpy driven and the asymmetry of the hopping rate decides the efficiency of charge transport. On the other hand, the escaping process is entropy driven. The mean first passage time for the escaping process is seen to be proportional to the inverse of the opening gate angle. The results suggest mean first passage times of 115−163 fs for an activated process. As mentioned previously, this kinetics can be described in the language logic ON and OFF states. This agrees very well with previous molecular dynamics calculations where the spread between the ON and OFF states was even larger. The result obtained is the proper time scale required for our model of high efficiency hopping in polypeptides, as observed experimentally. It provides a new ansatz for an analytic theory treating kinetic phenomena at long distance.

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Appendix 1: Entropy Potential Surface in 2D Disk

In this appendix, we choose the 2D spherical coordinate (r,θ) which is related to the Cartesian coordinate (x, y) through the relationships $x = r\cos\theta$, $y = r\sin\theta$, and $r = \sqrt{x^2+y^2}$. The equation of motion for the Brownian particle satisfies the 2D Smoluchowsky equation $\partial/\partial t = \rho D_0\{(1/r)(\partial/\partial r)[(r\partial/\partial r)\rho] + (1/r^2)(\partial^2/\partial\theta^2)\rho\}$. Now we set the new ansatz $n = r\rho$ and rewrite the Smoluchowsky equation in terms of the new variable n as $(\partial/\partial t)n = D_0\{(\partial/\partial r)(e^{\beta U}(\partial/\partial r)e^{-\beta U}n) + (1/r^2)(\partial/\partial\theta)(e^{\beta U}(\partial/\partial\theta)e^{-\beta U}n)\}$. Due to the last equation we find that the entropy potential surface U is

$$U = -k_B T \ln r \tag{16}$$

Here the 2D entropy potential surface is different from the 3D one. As we can see there is no angular part involved. This means that the surface diffusion motion on the 2D disk is just a random motion along a line segment without curvature.

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