BROWNIAN MOTION OF AN ELECTRIC DIPOLE

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According to the recent progress in experimental and simulation techniques, the ultrafast components of solvation dynamics become accessible to our observations. The typical situation we consider in the solvation dynamics is that after making up a solute change, each solvent molecule commences its reorientational motion in the fields of the solute and of the other solvent molecules. A given dipole interacts with other solvent molecules in a complicated fashion. Thus the influence of the polar solvent on this particular electric dipole can be modeled as a stochastic process. In the Debye theory, the randomness in the orientation of a dipole is treated as white noise since the fluctuations are assumed to be as a result of collisions.

In this paper, we study the rotational motion of a dipole under the influence of both a static electric field produced by a solute ion and the random electric fields coming from the other solvent molecules. The random electric field is introduced as an idealization of complex interaction between polar molecules and is idealized by the Gaussian Markov process. By applying the time-convolutionless projection operator method, a Fokker-Planck equation is derived from the stochastic model of dipoles when the random field is weak. In the case that the anisotropy of random fields presents due to the external electric field, the Fokker-Planck equation can be written in the polar coordinates as,

$$\begin{aligned}\frac{\partial}{\partial t}P(\theta,\phi,t) &= \left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\mu}{\zeta}\left[\frac{\mu}{\zeta}\left(\frac{\sin^2\theta}{2\tau_{\|}}+\frac{\cos^2\theta}{2\tau_{\perp}}-\delta\omega\cos\theta\right)\frac{\partial}{\partial\theta}+E_0\sin\theta\right]\right.\\ &\quad\left.+\frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi}\frac{\mu^2}{\zeta^2}\left(\frac{1}{2\tau_{\perp}}-\delta\omega\cos\theta\right)\frac{\partial}{\partial\phi}\right\}P(\theta,\phi,t), \qquad (1)\end{aligned}$$

where ζ is the rotational friction constant and μ is the magnitude of the permanent dipole moment. The coefficients $\tau_{\|}$, $\tau_{\perp}$ and $\delta\omega$ are written in terms of the time correlation functions of the radom electric fields $\delta\boldsymbol{E}(t)$,

$$\frac{1}{2\tau_{\perp}} = \int_0^{\infty}\mathrm{d}t_1\langle\delta E_x(t_1)\delta E_x(0)\rangle\cosh\left(\frac{E_0\mu}{\zeta}t_1\right), \qquad (2)$$

$$\frac{1}{2\tau_{\|}} = \int_0^{t}\mathrm{d}t_1\langle\delta E_z(t_1)\delta E_z(0)\rangle, \qquad (3)$$

$$\delta\omega = \int_0^{t}\mathrm{d}t_1\langle\delta E_x(t_1)\delta E_x(0)\rangle\sinh\left(\frac{E_0\mu}{\zeta}t_1\right). \qquad (4)$$

The Fokker-Planck equation reduces to the simple rotational diffusion equation of the Debye form as a special case, where the correlation of random electric fields is white and isotropic but not otherwise.

In order to solve Eq. (1), we expand $P(\theta,\phi,t)$ in terms of spherical harmonics $Y_l^m(\theta,\phi)$,

$$P(\theta,\phi,t)=\sum_{l=0}\sum_{m=-l}^{m=l}\sqrt{\frac{(l+|m|)!}{(2l+1)(l-|m|)!}}a_l^m(t)Y_l^m(\theta,\phi). \qquad (5)$$

For convenience we introduce matrices

$$\boldsymbol{b}_l^m = \begin{pmatrix} a_{2l-1}^m \\ a_{2l}^m \end{pmatrix}, \qquad \underline{Q}_{l,m}^{(-)} = \begin{pmatrix} q_{2l-1,m}^{(-2)} & q_{2l-1,m}^{(-1)} \\ 0 & q_{2l,m}^{(-2)} \end{pmatrix},$$
$$\underline{Q}_{l,m}^{(0)} = \begin{pmatrix} q_{2l-1,m}^{(0)} & q_{2l-1,m}^{(+1)} \\ q_{2l,m}^{(-1)} & q_{2l,m}^{(0)} \end{pmatrix}, \quad \underline{Q}_{l,m}^{(+)} = \begin{pmatrix} q_{2l-1,m}^{(+2)} & 0 \\ q_{2l,m}^{(+1)} & q_{2l,m}^{(+2)} \end{pmatrix}, \tag{6}$$

where

$$\begin{aligned}
q_{l,m}^{(-2)} &= \frac{\mu^2}{\zeta^2}\left(\frac{1}{2\tau_{\parallel}} - \frac{1}{2\tau_{\perp}}\right)\frac{(l-2)(l+1)(l-|m|)(l-|m|-1)}{(2l-1)(2l-3)}, \\
q_{l,m}^{(-1)} &= \left[\frac{\mu^2}{\zeta^2}\delta\omega(l-1) + \frac{\mu}{\zeta}E_0\right]\frac{(l+1)(l-|m|)}{2l-1}, \\
q_{l,m}^{(0)} &= -\frac{\mu^2}{\zeta^2}\left[\frac{(2l^2+2l-3)}{2\tau_{\perp}} + \frac{2l(l+1)}{2\tau_{\parallel}}\right]\frac{l(l+1)}{(2l-1)(2l+3)} - \frac{\mu^2}{\zeta^2}\left(\frac{1}{2\tau_{\perp}} - \frac{1}{2\tau_{\parallel}}\right)\frac{m^2(2l^2+2l+3)}{(2l-1)(2l+3)}, \\
q_{l,m}^{(+1)} &= \left[\frac{\mu^2}{\zeta^2}\delta\omega(l+2) - \frac{\mu}{\zeta}E_0\right]\frac{l(l+|m|+1)}{2l+3}, \\
q_{l,m}^{(+2)} &= \frac{\mu^2}{\zeta^2}\left(\frac{1}{2\tau_{\parallel}} - \frac{1}{2\tau_{\perp}}\right)\frac{l(l+3)(l+|m|+2)(l+|m|+1)}{(2l+3)(2l+5)}.
\end{aligned}$$

Then tridiagonal vector recurrence relation can be obtained

$$\frac{d}{dt}\boldsymbol{b}_l^m(t) = \underline{Q}_{l,m}^{(-)}\boldsymbol{b}_{l-1}^m + \underline{Q}_{l,m}^{(0)}\boldsymbol{b}_l^m + \underline{Q}_{l,m}^{(+)}\boldsymbol{b}_{l+1}^m. \tag{7}$$

After making the Laplace transform,

$$\tilde{\boldsymbol{b}}_l^m[s] = \int_0^\infty e^{-st}\boldsymbol{b}_l^m(t)\mathrm{d}t, \tag{8}$$

The solution is

$$\tilde{\boldsymbol{b}}_l^m[s] = \underline{\tilde{S}}_{l-1,m}[s]\tilde{\boldsymbol{b}}_{l-1}^m[s] + \tilde{\boldsymbol{d}}_l^m[s], \tag{9}$$

where

$$\underline{\tilde{S}}_{l-1,m}[s] = \left[s\underline{I} - \underline{Q}_{l,m}^{(0)} - \underline{Q}_{l,m}^{(+)}\underline{\tilde{S}}_{l,m}[s]\right]^{-1}\underline{Q}_{l,m}^{(-)}, \tag{10}$$
$$\tilde{\boldsymbol{d}}_l^m[s] = \left[s\underline{I} - \underline{Q}_{l,m}^{(0)} - \underline{Q}_{l,m}^{(+)}\underline{\tilde{S}}_{l,m}[s]\right]^{-1}\left(\boldsymbol{b}_l^m(0) + \underline{Q}_{l,m}^{(+)}\tilde{\boldsymbol{d}}_{l+1}^m[s]\right). \tag{11}$$

By truncating the above iteration procedure, the coefficients in Eq. (5) can be numerical determined. The numerical evaluation is now under investigation.