Sluggish solvents and fast reactions: Dynamical arrest of electron transfer

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What if Boltzmann does not work?

Dynamical solvent control:
\[
\frac{\hbar}{V_{ET}} \approx \tau_s, \quad k \ll \tau_s^{-1}
\]

Dynamical arrest:
\[
k \propto \tau_s^{-1}
\]
\[
k^{-1} \approx \tau_s
\]

Strong ergodicity breaking: “Equilibrium is when all fast things have happened, and slow things not yet” (Feynman)

Weak ergodicity breaking: things keep happening....
...not quite, vibrations are done
Spectroscopic Evidence

- MTHF
- 

\[ \Delta V_{\text{st}} / \Delta V_{\text{st, eq}} = \text{function of } T/T_{g} \]

- quinoxaline
- \( \tau_{\text{obs}} = 1 \text{ ms} \)
- (R. Richert)

- complex 1
- \( \tau_{\text{obs}} = 10 \text{ ns} \)
- (Verhoeven et al.)

- Hoffman and Ratner, 1996

\[ \lambda(\text{obs}) / \lambda(\text{eq}) = \exp[- D/(T-T_{g})] \]

- Complex 1
- quinoxaline
Natural Photosynthesis

[Diagram showing the process of natural photosynthesis with labels for BM, BL, HM, HL, QM, QL, FE, and H+.]
Ergodicity breaking
Trick: Step-wise Frequency Filter

Equilibrium reorganization energy:

$$\lambda_s = \frac{\langle (\delta \Delta E)^2 \rangle}{2k_B T} = \int_0^\infty \chi''(\omega) \frac{d\omega}{\pi \omega}$$

Donor-acceptor energy gap

Nonergodic reorganization energy:

$$\lambda(\omega_{obs}) = \int_{\omega_{obs}}^\infty \chi''(\omega) \frac{d\omega}{\pi \omega}$$

Cutting off low frequencies below

$$\omega_{obs} = 1/\tau_{obs}$$

Fluctuation-dissipation theorem

Dielectric continuum

$$\chi''(\omega) \propto \frac{\epsilon''(\omega)}{|\epsilon(\omega)|^2}$$
\[ \lambda_s = \left\langle (\delta \Delta E)^2 \right\rangle / 2k_B T \]

\[ c_v / k_B = 3/2 + \frac{\left\langle (\delta E)^2 \right\rangle}{N(k_B T)^2} \]

\[ \chi_P = (k_B T V)^{-1} \left\langle (\delta M)^2 \right\rangle \]
Stokes Shift in Supercooled Solvents

\[ \lambda(\omega_{\text{obs}}) = \int_{\omega_{\text{obs}}}^{\infty} d\omega \int F[\Delta E, \chi(k, \omega)] dk \]

Field of atomic charges, calculated from quantum mechanics

Microscopic correlations between the dipoles

\[ \chi(k, s) = \chi(0,0) \left[ \frac{S(0)}{S(k)} + \frac{1}{1 + p'(k \sigma)^2} \frac{\chi(0,0) - \chi(0, s)}{\chi(0, s)} \right]^{-1} \]

Given in terms of the Cole-Davidson dielectric constant \( \varepsilon(s) \) (experiment)
Stokes Shift Correlation Function

Experiment

Theory

quinoxaline/butyronitrile

$\nu/10^3 \text{ cm}^{-1}$

$\ln(t/\tau_{CD})$

$\nu_p/10^3 \text{ cm}^{-1}$

$\tau_{KWW}$

$\nu_x(0) = 21350 \text{ cm}^{-1}$

$\nu_x(\infty) = 21066 \text{ cm}^{-1}$

$\beta_{KWW} = 0.44$
Electron Transfer Rates

\[ \omega_{obs} = k_{ET} \]
\[ \lambda = \int_{k_{ET}}^{\infty} d\omega \ldots \]

Nonergodic thermodynamics:
\[ \Delta G(k_{ET}, T) = f(k_{ET}, T) \Delta G_s(T) \]
\[ \lambda(k_{ET}, T) = f(k_{ET}, T) \lambda_s(T) \]

Self-consistent Franck-Condon factor:
\[ k_{ET} = \left( \frac{2\pi V_{ET}^2}{\hbar} \right) e^{-S} \sum_n \frac{(S^n/n!)}{G_n(k_{ET})} \]
\[ G_n(k_{ET}) \propto \exp \left[ -\frac{E_a(k_{ET})}{k_B T} \right] \]

Wasielewski et al, JACS’01
Dynamical Arrest in Liquid Crystals

Nematics are sluggish solvents capable of producing dynamical arrest of sub-nanosecond rates at room temperature.
ET Rates in the Isotropic Phase

\[ k_{ET}^{-1} = \int_0^\infty dt \int_{-\infty}^\infty dX \, P(k_{ET}, X, t) \]

Time of diffusion to the barrier top (Sumi-Marcus, Bixon-Jortner, Barbara et al.)
Energy Gap Law

![Graph showing the Energy Gap Law](image)

- **CR**
- **Barbara et al.**
- **Jortner-Bixon**
- **Inflection region**
- **Sharp change of nonergodicity**

The graph illustrates the relationship between the natural logarithm of the ER rate constant ($\ln(k_{ER} \times \text{ns})$) and the energy difference ($\Delta G_{CR}(eV)$).
Apparent $\beta$

For ergodic reactions: 
\[
\log(k_{CR}) = 2 \log(V_{ET}) + \text{Const}
\]

The barrier depends on $V_{ET}$ through the nonergodicity function in the inflection region of the energy gap law!

$$\beta = \beta_{el} / (2 - 3)$$
In the regime of **ergodicity breaking**, dynamics dramatically affect the rates through altering the activation barrier (**dynamical arrest of equilibrium solvation**)

\[
k_{ET} \propto \frac{1}{\tau_s} \exp \left[ -\frac{E_a(\ldots)}{k_B T} \right]
\]

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