1 Theory: Stochastic bond breakage

We calculate the time-dependent breakage probability of a chain, $P_{\text{chain}}(t)$, as a function of the breakage probabilities of its constituent bonds, $\{P_i(t)\}$. An expression for $P_{\text{chain}}(t)$ is obtained by observing that the *survival* probability of the chain is the product of the survival probabilities of the individual chemical bonds. Mathematically,

$$\begin{aligned} 1 - P_{\text{chain}}(t) &= \prod_i [1 - P_i(t)] \\ P_{\text{chain}}(t) &= 1 - \prod_i [1 - P_i(t)] \end{aligned} \tag{1}$$

where the product is over all the load-bearing chemical bonds in the chain. The bond breakage probabilities $\{P_i(t)\}$ depend on the load on a chemical bond, which changes (and is tracked) during the course of a simulation as the network evolves. Consequently, $\{P_i(t)\}$ are not available in analytical form, but are numerically computed as discussed next.

A polymer chain is viewed as a sequence of chemical bonds. Breakage rate of the i^{th} bond is given by the Arrhenius-like expression from harmonic Transition State Theory (hTST):

$$k_i = k_{0,i} \exp\left[-\frac{E_{a,i}}{k_B T}\right] \tag{2}$$

where k_B = Boltzmann's constant, T = temperature, $E_{a,i}$ = activation energy for breakage, and $k_{0,i}$ = prefactor. Load on a bond modifies the potential energy landscape, and changes both the energy barrier $E_{a,i}$, and the prefactor $k_{0,i}$, leading to a change in the bond-breakage rate. Since the activation energy appears in the exponential, the change in the prefactor is assumed to be negligible. E_a^* is calculated over a range of forces and saved in a lookup table.

The hTST rates for bond-breakage computed above were used to numerically compute the bond-breakage *probabilities* $\{P_i(t)\}$ as follows. Assuming bond breakage times are distributed exponentially, the instantaneous PDF of bond breakage times is given by

$$f_i(t) = k_i \exp\left[-k_i t\right] \tag{3}$$

and the bond-breakage probability after a time t is given by the cumulative distribution function as

$$\begin{aligned} P_i(t) &= \int_0^t f_i(s) \mathrm{d}s \\ &= \int_0^t k_i \exp\left[-k_i s\right] \mathrm{d}s \end{aligned} \tag{4}$$

The integration is done numerically in the simulation, because bond breakage rates k_i depend on the load experienced by a bond, which is in turn a complex function of network geometry and difficult to obtain in analytical form. $P_i(t)$ is the probability of breakage of the i^{th} chemical bond in the system, and also accounts for its loading history. Individual $\{P_i(t)\}$ will be used to compute chain breakage probability, P_{chain}.

Combining equations 1 and 4, we get:

$$P_{\text{chain}}(t) = 1 - \prod_i \left\{ 1 - \int_0^t k_i \exp[-k_i s] \, \mathrm{d}s \right\} \tag{5}$$

where the product is over all bonds in the chain, and the different k_i are given by equation 2.

2 Implementation in stoB object

3 Test cases

The stoB object is tested for the following cases that have analytical solutions. All test cases are driven using the `testStoB.cpp` program. All test cases are run until the probability P_{chain} exceeds 0.99.

3.1 Single bond with no load

This test is run using the `run_single_bond` function. The following parameters are used:

$$\begin{aligned} k_0 &= 1 \times 10^{12}\,\mathrm{s}^{-1} \\ E_a &= 1.2\,\mathrm{eV} \\ T &= 300\,\mathrm{K} \\ \Delta t &= 10\,\mathrm{s} \end{aligned}$$

The numerical results are saved in the file `single-bond-F-0nN`, and the analytical solution is obtained from equation 5 as

$$P_{\mathrm{chain}} = 1 - \exp\left[-k_0 \exp\left(-\frac{E_a}{k_B T}\right) t\right] \tag{6}$$

3.2 Single bond with constant load

The parameters used are the same as before. The dependence of E_a on the applied load is given as

$$E_a^* = E_a + E_a^{(\mathrm{slope})} F$$

with

$$\begin{aligned} E_a^{(\mathrm{slope})} &= -0.1 \times 10^9 \\ F &= 1\,\mathrm{nN} \end{aligned}$$

The applied load leads to a reduction in energy barrier of 0.1 eV, and the numerical results are saved in the file `single-bond-F-0nN`. The analytical solution is obtained from equation 5 as

$$P_{\mathrm{chain}} = 1 - \exp\left[-k_0 \exp\left(-\frac{E_a^*}{k_B T}\right) t\right]$$

3.3 Single bond with varying load

The applied load on the bond is varied as

$$F(t) = F_0 \cos(\omega t)$$

The parameters used are the same as before, which leads to an analytical solution of
(Is analytical solution even possible here?)

3.4 Two bonds with no load

3.5 Two bonds with constant load

3.6 Two bonds with varying load