

### Connection with experimental data

In order to express  $\beta f_{hyb}$  in terms of experimentally measurable quantities it is convenient to consider a dilute system of free DNA-chains (no colloids) with complementary sticky ends. In this system an A-type chain can hybridize with a B-type chain to form a longer DNA chain. In our coarse grained representation this system is modeled as a mixture of free A-type and B-type blobs that can react to form A-B dimers wherein the blobs are connected through a harmonic spring. Thus, the equilibrium concentrations of A, B, and AB species (i.e.,  $\rho_A$ ,  $\rho_B$ , and  $\rho_{AB}$ , respectively) are related through,

$$\mu_A + \mu_B = \mu_{AB}, \quad (1)$$

which for a dilute (ideal gas) system can be expressed as,

$$\ln \rho_A + \ln \rho_B = -\ln \Gamma - \ln q_{AB} + \ln \rho_{AB}, \quad (2)$$

where  $q_{AB}$ , the ratio of single molecule partition functions between products and reactants times the system volume, is given by

$$q_{AB(phantom)} = \int_0^\infty \exp[-\beta V_{har}(r)] 4\pi r^2 dr \quad (3)$$

$$q_{AB(saw)} = \int_0^\infty \exp[-\beta V_{bb}(r) - \beta V_{har}(r)] 4\pi r^2 dr \quad (4)$$

which for the coarse grained model used in this work gives the (constant and dimensionless) value of  $q_{AB(phantom)}=41.15$ ,  $q_{AB(saw)}=33.295$ .

In the above expressions the densities  $\rho$ 's, are expressed in units of  $R_g^{-3}$ . Thus, concentration in arbitrary units ( $\rho^*$ ) are related through

$$\Gamma q_{AB} R_g^3 = \frac{\rho_{AB}^*}{\rho_A^* \times \rho_B^*} = \frac{K_{\text{experimental}}}{\rho_0} \quad (5)$$

where the  $R_g$  have to be measured in units consistent with concentrations,  $K_{experimental}$  is the equilibrium constant measured for the real system, and  $\rho_0$  is the standard concentration assumed in the experiments (usually 1 mol/L or  $6.022 \times 10^{26} \text{ m}^{-3}$ ).

As experiments are usually performed between free strands of complementary DNA, as opposed to between long DNA chains with relatively short sticky ends, the conversion should be done **using the case of phantom chains** as they do not feel each other. If we have a solution with SAW chains and we perform a simulation, of course, the number of bonds formed in solution will be smaller by a fraction  $q_{ABsaw}/q_{ABphantom} \sim 0.8$ . However, this is already taken into account automatically in the simulations as blobs interact explicitly with each other through a Gaussian repulsion (not so if we were simulation the small sticky ends without large attached chains). Finally, matching the experimental results in free solution to the system with phantom chains, the value of  $\beta f_{hyb}$  can be estimated from

$$\beta f_{hyb} = -\ln \Gamma = \beta \Delta G_{experimental} + \ln(\rho_0 \times q_{AB(phantom)} \times R_g^3) \quad (6)$$

Note that it is more appropriate to match experiments to the phantom case, as in experiments free sticky ends do not have chains attached to them, and therefore they behave as if they were attached to a “phantom chain”.

For chains with  $R_g$  between 10 – 500 nm, we have that

$$\beta f_{hyb} = \beta \Delta G_{experimental} + (10 \sim 20) \quad (7)$$

