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Great Expectations: Can Artificial Molecular Machines Deliver on Their Promise?

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In the following, we derive the equations describing free energy changes of grafted polymers of molecular switches.

(1) Sparse grafting. The first case we consider deals with the case of the sparsely-grafted polymer brushes and, in general terms, derives from the Alexander's coarse-grained model. The polymer brush is characterized by following parameters:

h – brush height, polymer end-to-end distance

l – length of single segment, assumed equal to the Kuhn length

N – number of statistical segments (proportional to the degree of polymerization)

$N\,l$ – polymer contour length

n – number of grafted chains

V – total volume of the brush

S – area of the surface from on which the brushes are grafted (note that $V = S\,H$)

$\phi = N\,n\,/V$ (monomer concentration)

σ – grafting density; $n = \sigma S$

w – excluded volume parameter; $w = (1-2\chi)\,v$, where v is of the order of the segment's volume

χ – Flory interaction parameter, a small number for a good solvent

This system can be described by the free energy, G, per chain in kT units, $\frac{G}{nkT} = \frac{G_{el}}{nkT} + \frac{G_{\text{int}}}{nkT}$, where the elastic (entropic) contribution is $\frac{G_{el}}{nkT} = \frac{h^2}{Nl^2}$ and the interaction (enthalpic) contribution is $\frac{G_{\text{int}}}{nkT} = w\frac{N^2\sigma}{h} = \frac{w\sigma}{l}\frac{N^2 l}{h}$. By minimizing G with respect to h we obtain the equilibrium brush height,

$$h_{eq}^{i} = \frac{1}{\sqrt[3]{2}} lN\left(\frac{\sigma w}{l}\right)^{1/3} \cong lN\left(\frac{\sigma w}{l}\right)^{1/3} = l^{2/3}N(\sigma W)^{1/3} \qquad (S1)$$

and free energy

$$\frac{G_{eq}^{i}}{nkT} = \frac{3}{\sqrt[3]{2}} N\left(\frac{\sigma w}{l}\right)^{2/3} \cong N\left(\frac{\sigma w}{l}\right)^{2/3} \qquad (S2)$$

where superscript denotes that this is the "initial" configuration. This free energy (*S2*) can be expanded around its equilibrium value to give the following quadratic approximation:

$$\frac{G^i}{nkT}(h) = \frac{G^i_{eq}}{nkT} + \frac{3}{Nl^2}(h - h^i_{eq})^2 \qquad (S3)$$

Now, if l changes to $l+\Delta l$ upon external stimulus, then free energy of the new, "final" state can be written using quadratic approximation as:

$$\frac{G^f}{nkT}(h) = \frac{G^f_{eq}}{nkT} + \frac{3}{N(l+\Delta l)^2}(h - h^f_{eq})^2 \qquad (S4)$$

where $h^f_{eq} \cong (l+\Delta l)N\left(\frac{\sigma w}{l+\Delta l}\right)^{1/3} = (l+\Delta l)^{2/3} N(\sigma w)^{1/3}$. Next, we calculate, (S5)

$$\frac{\Delta G}{nkT} = \frac{G^f}{nkT}(H^i_{eq}) - \frac{G^f_{eq}}{nkT} = \frac{3}{N(l+\Delta l)^2}(h^i_{eq} - h^f_{eq})^2 \cong \frac{G_{eq}}{nkT}\left(\frac{\Delta l}{l+\Delta l}\right)^2 \cong N\left(\frac{\sigma w}{l}\right)^{2/3}\left(\frac{\Delta l}{l+\Delta l}\right)^2$$ which is the expression used in the main text. Note that this expression is only an order-of-magnitude approximation, since the excluded volume parameter w is not known and is here assumed to be constant. Importantly, however, our estimates indicate only a small fraction of kT can be retrieved as useful energy from a single "switchable" polymer unit.

(2) Dense grafting. The model discussed in the previous section is applicable for extended but coiled polymer brushes of reduced grafting densities, $\sigma w/l$, considerably smaller than unity (sparse grafting). When polymer chains are very densely grafted, however, they should be almost fully extended (unless trapped kinetically by, for example, entanglements) with the brush height, h, close to the contour length, Nl. The quadratic (in h) elastic term fails to describe properly the chains at strong extensions, and a different expression for entropic elasticity is used following Kuznetsov and Chen (*34*):

$$\frac{G_{el}}{nkT} = \frac{N}{1 - h/(Nl)} \qquad (S6)$$

This expression prevents the brush height, h, from exceeding the contour length, Nl. Upon minimization of G_{el} with respect to h, the following results are obtained (up to multiplicative constants of the order of unity):

$$h_{eq}^{i} \cong lN \text{ and } \frac{G_{el}^{i}}{nkT} \cong N \qquad (S7)$$

Note that the free energy per segment is of the order of *kT* and so the corresponding free energy change upon stimulus can be a fraction of *kT*. Also, the formulas used in the main text can now be derived by assuming that the chain is extended as a result of a constant net force acting on it In this case, the force needed to keep the polymer at extension *h* is $-\frac{\partial G_{el}(h)}{\partial h}$. Then, if *l* is changed upon stimulus from *l* to *l*+*Δl*, *h* has to change in linear proportion, $\frac{h}{l} = \frac{h+\Delta h}{l+\Delta l}$, to maintain the constant force. Taking h^i=*h*, and h^f=*h*+*Δh*, we can calculate the work as

$$\Delta W = \frac{\Delta G}{kT} = \frac{N}{1-h^i / N(l+\Delta l)} - \frac{N}{1-h^f / N(l+\Delta l)} \qquad (S8)$$

with $h^f = h^i(1+\Delta l / l)$.