Staistical Mechanics of Polymeric Systems:

Semiflexible Polymer Localization

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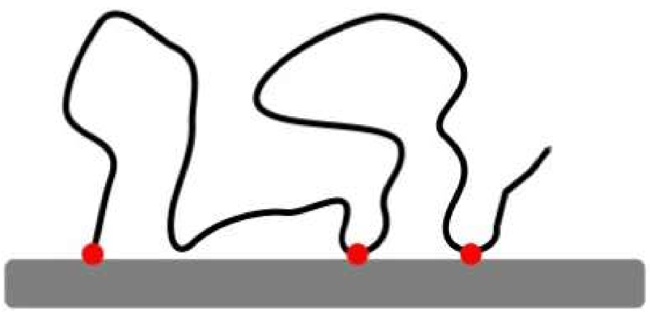
February 6, 2022

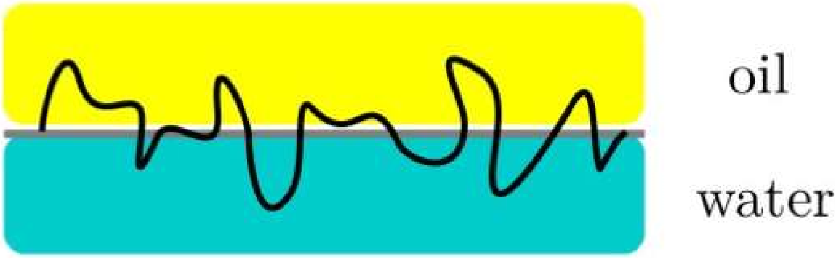
BrakFest
Melbourne, Australia

Polymer Zoo

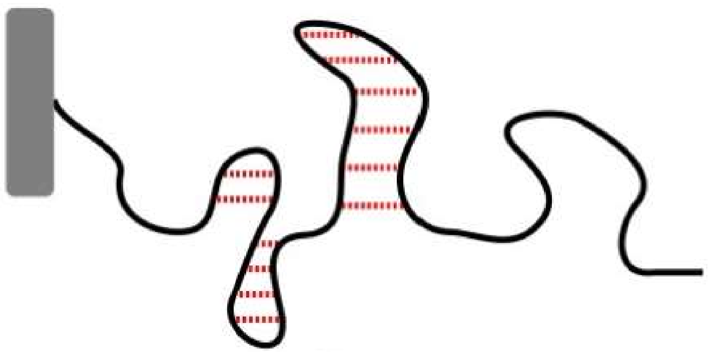
- Study the phase behaviour of various polymeric systems as the 'energy' varies



Adsorption

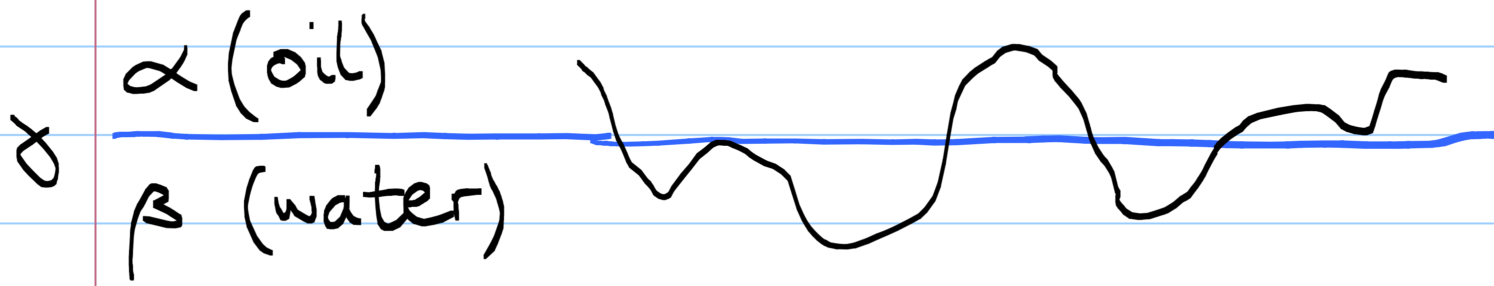


Localization

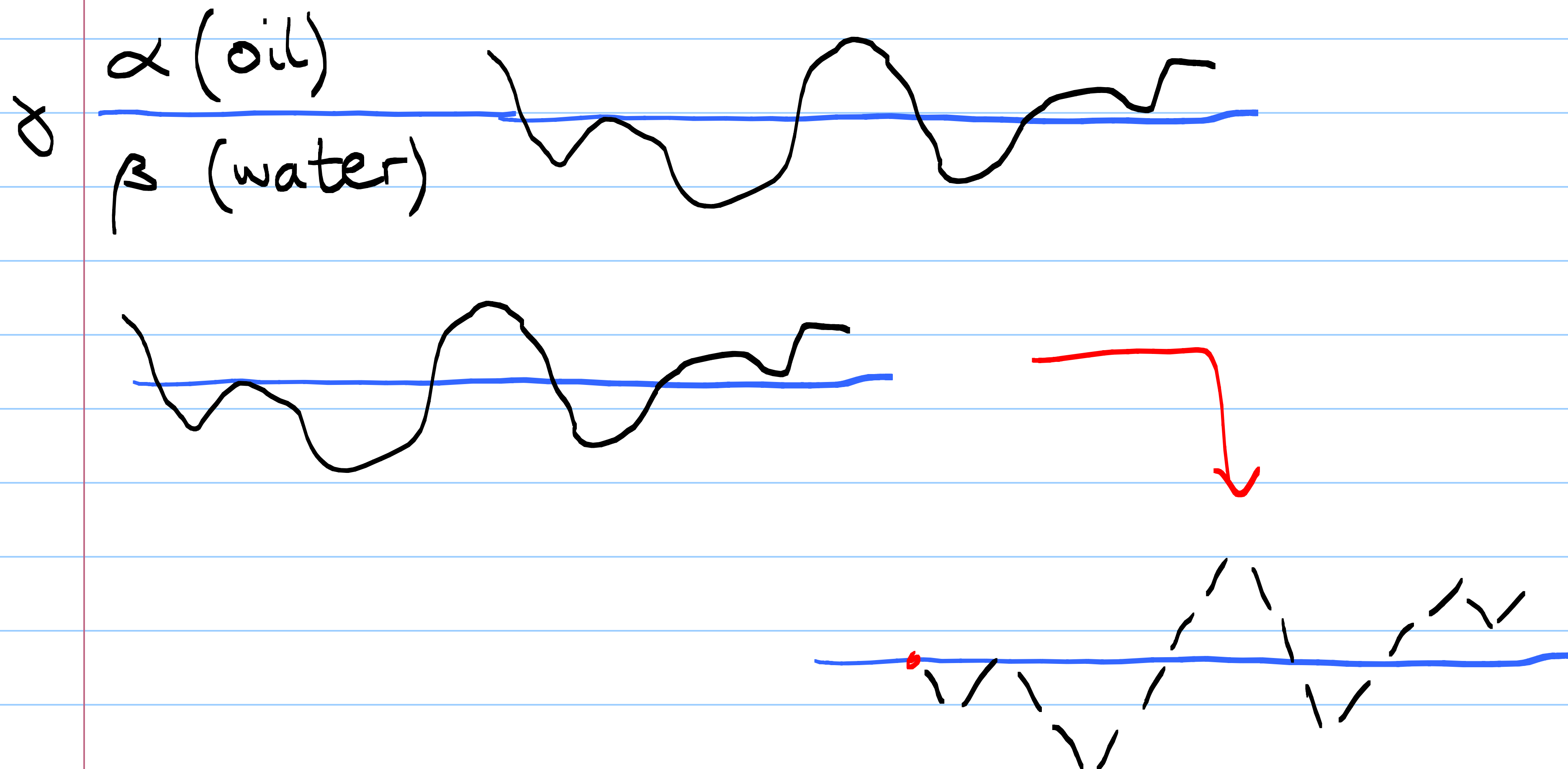


Collapse

Model: Homopolymer between two immiscible solvents



Model: Homopolymer between two immiscible solvents



Dyck Path Factorization

[Implicit Eq'ns
↓
Eliminate]

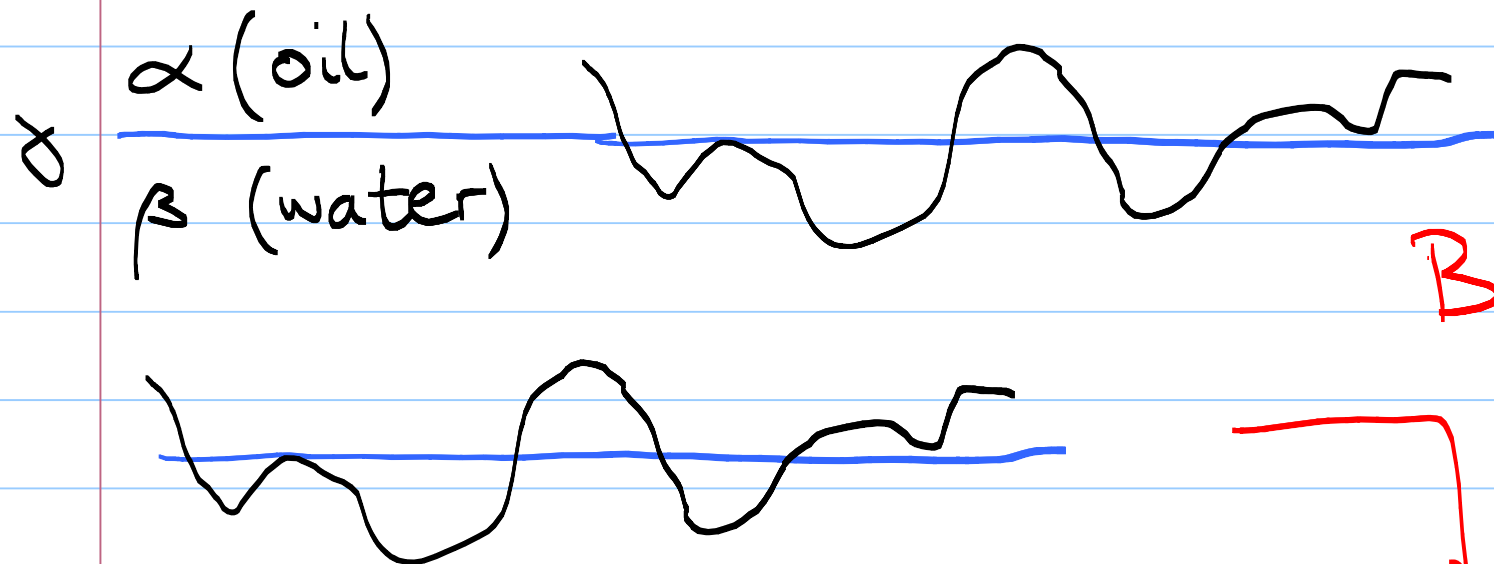
STEPS ① $$D(z) = 1 + z^2\left[D(z)\right]^2$$

CONTACTS ② $$D_H(c,z) = 1 + c\,z\,D(z)\,D_H(c,z)$$

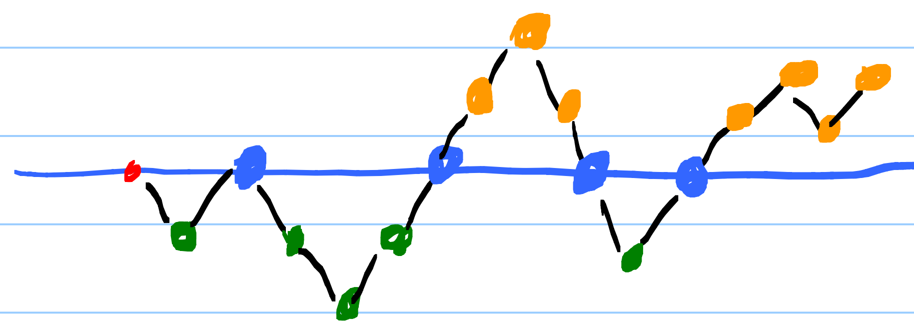
STIFF. ③ $$D_S(s,z) = 1 + z^2 \cdot D_S(s,z) + s^2 z^2\left[D_S(s,z) - 1\right] \cdot D_S(s,z)$$

CONTACTS + STIFF. ④ $$D_{HS}(c,s,z) = 1 + c z^2 D_S(s,z) + c s^2 z^2\left[D_S(s,z) - 1\right] D_{HS}(c,s,z)$$

Model: Homopolymer between two immiscible solvents



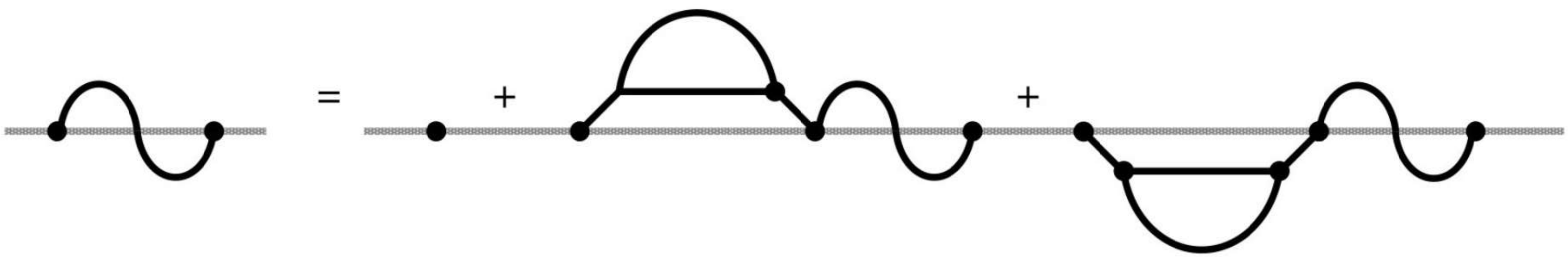
$B(a,b,c,z)$



$$a^7 b^5 c^4$$

e^α e^β e^γ

Bilateral Dyck Path Factorization

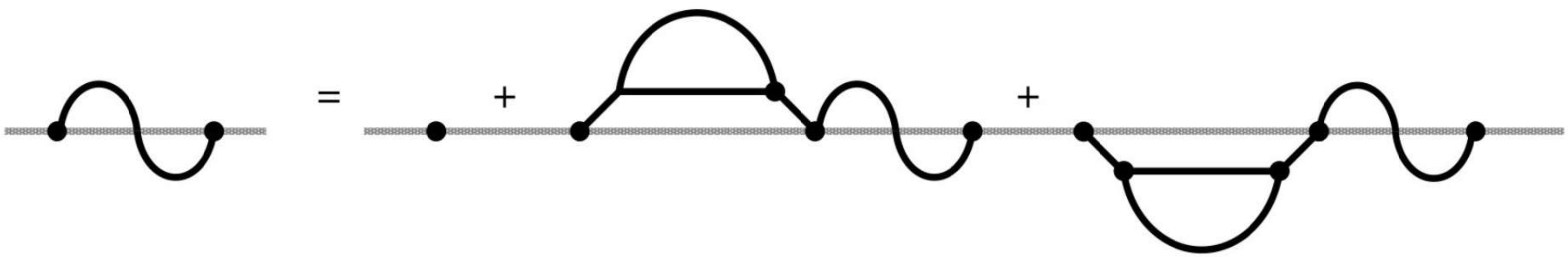


[No stiffness]

$$\textcircled{1}\quad B(a,b,c,z) = 1 + acz^2 \underbrace{D(az)} B(a,b,c,z) + bcz^2 \underbrace{D(bz)} B(a,b,c,z)$$

No interface contacts
[walk entirely in α/β]

BILATERAL DYCK PATH FACTORIZATION



LOCALIZATION FACTORIZATION [NO STIFFNESS]

$$① \; B(a,b,c,z) = 1 + acz^2 \underbrace{D(az)} B(a,b,c,z) + bcz^2 \underbrace{D(bz)} B(a,b,c,z)$$

$$\boxed{\kappa = -\log[z_c]}$$

NO INTERFACE CONTACTS
[WALK ENTIRELY IN α/β]

3 SINGULARITIES IN $B(a,b,c,z) \rightarrow z_1(a),\ z_2(b),\ z_3(a,b,c)$

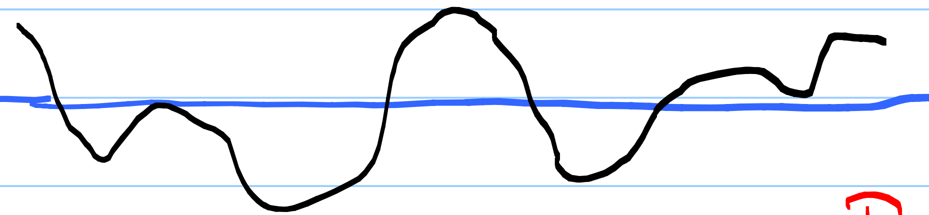
↳ SETTING $z_i = z_j$ DETERMINES $\beta_c(\alpha,\gamma)$ [PHASE BOUNDARY]

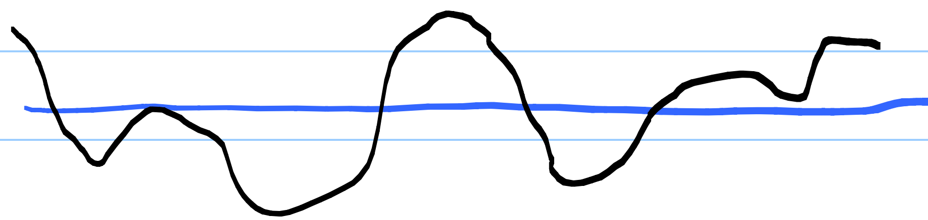
Model: Homopolymer between two immiscible solvents

α (oil)

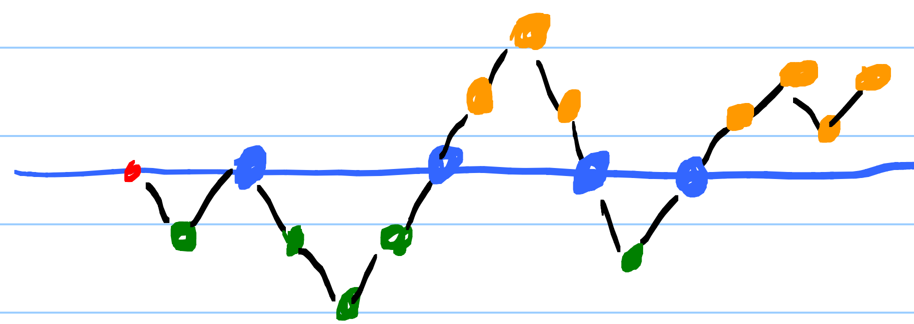
γ

β (water)

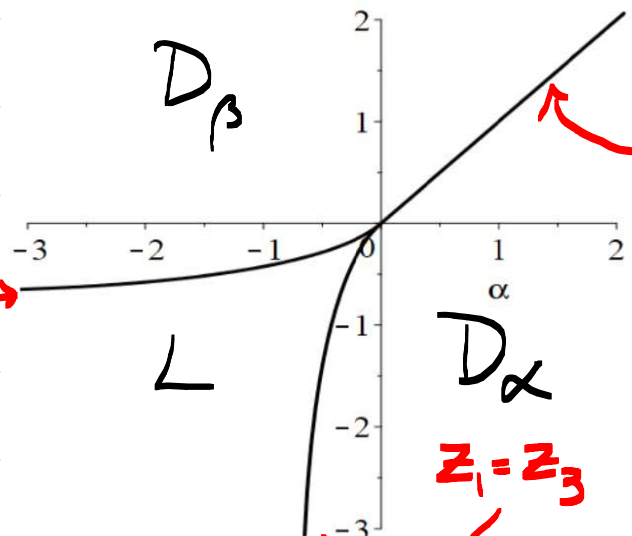




$B(a,b,c,z)$

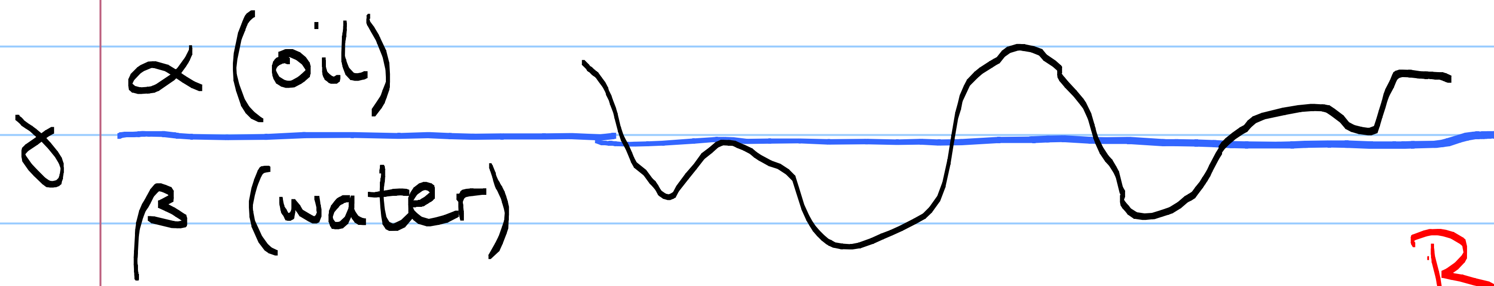


$a^7 b^5 c^4$

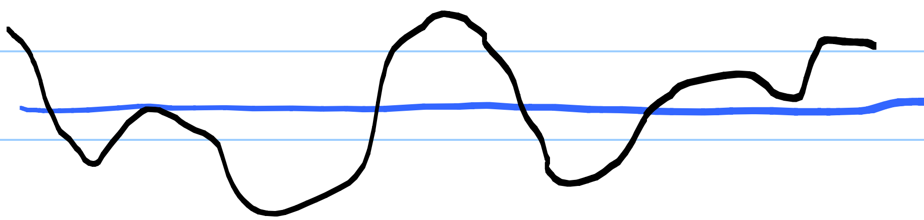


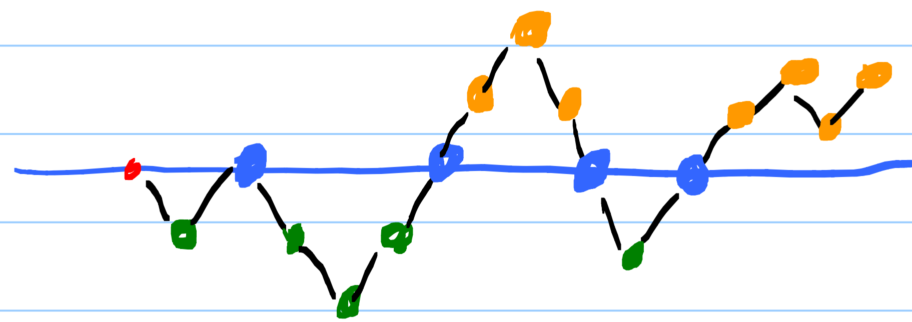
$[\gamma = 0, c = 1]$

Model: Homopolymer between two immiscible solvents

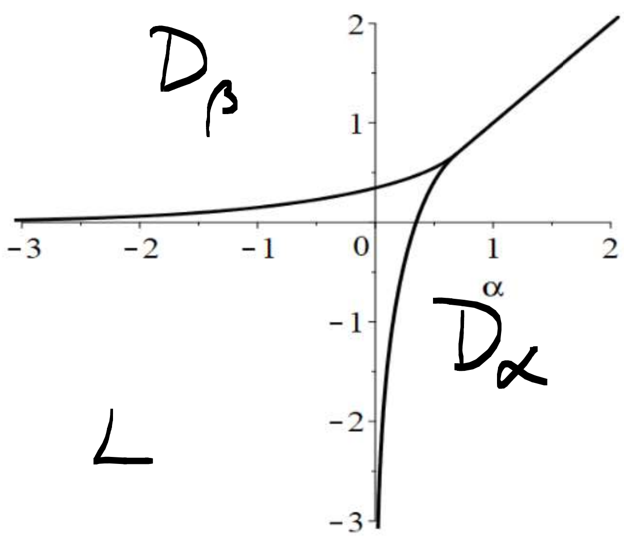


$B(a,b,c,z)$



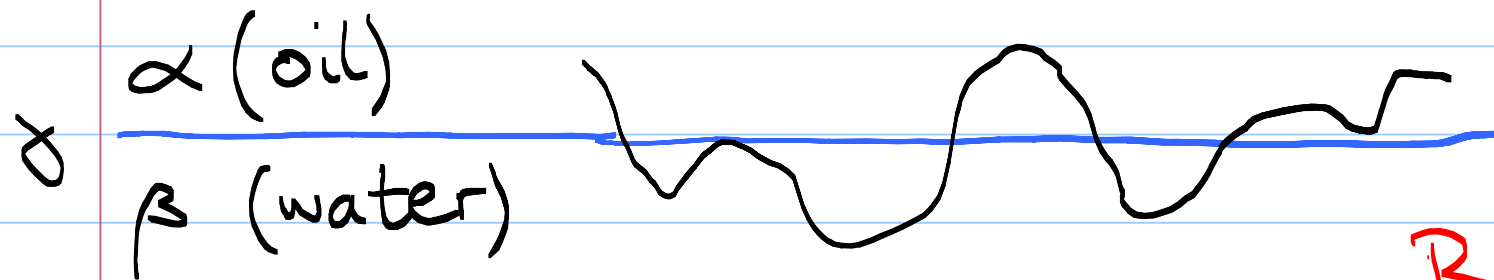


$a^7 b^5 c^4$

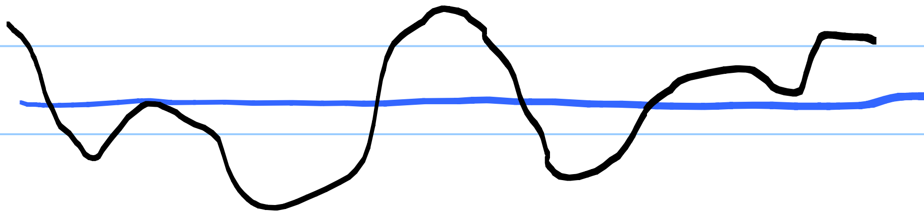


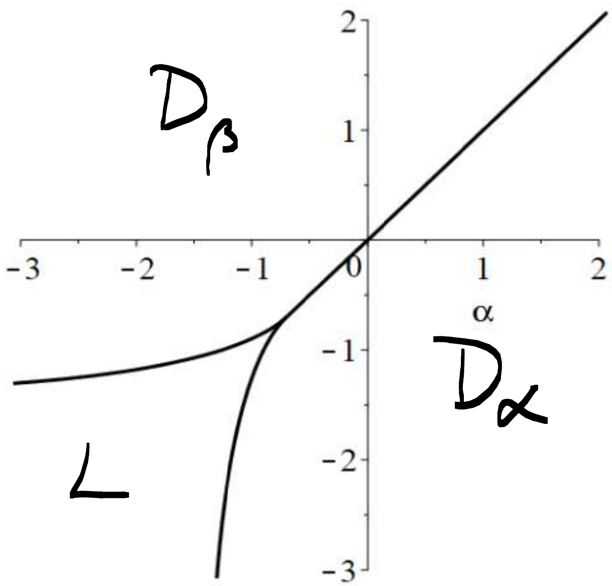
$\gamma > 0,\ c > 1$

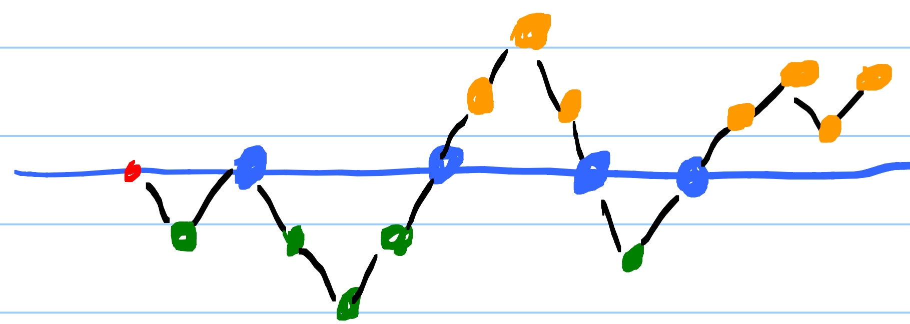
Model: Homopolymer between two immiscible solvents



$B(a,b,c,z)$



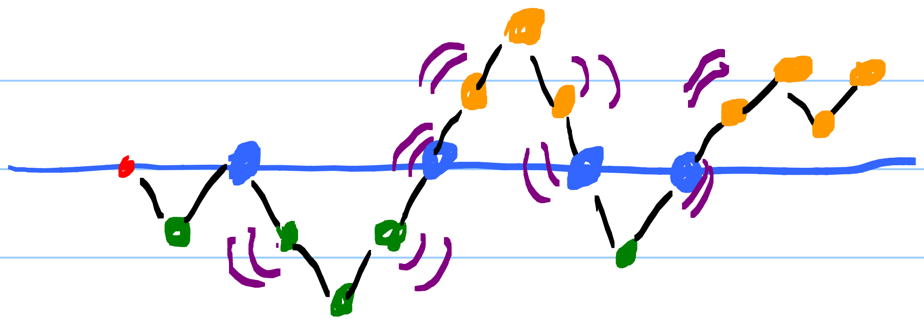




$a^7 b^5 c^4$

$\gamma<0,\ c<1$

Add “stiffness” by decorating pairs of collinear steps



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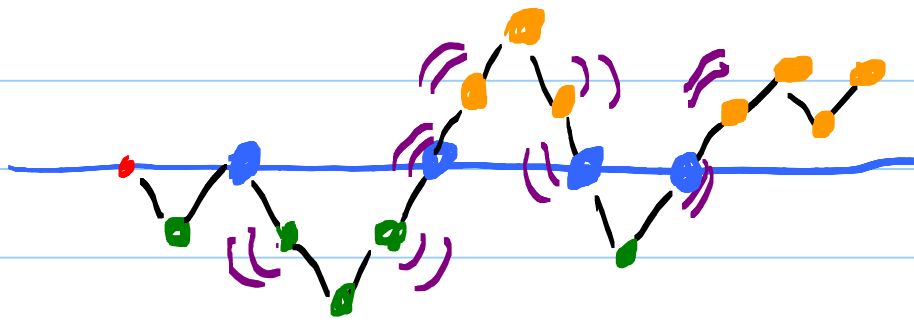
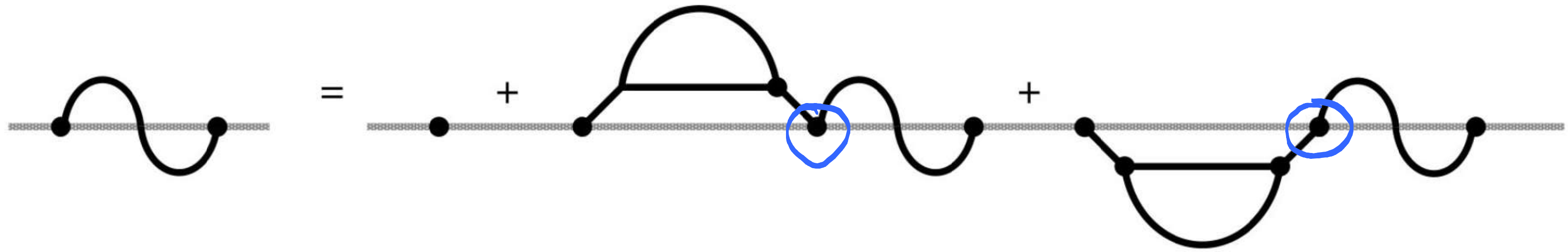


$$a^7 b^5 c^4 s^8$$

$$B(a,b,c,s,z)$$



$$① \; B(a,b,c,z) = 1 + acz^2 D(az)B(a,b,c,z) + bcz^2 D(bz) B(a,b,c,z)$$

↳ SPLIT INTO B_{up} & B_{DOWN} TO TRACK

* STIFFNESS DECORATION @ "GLUE PTS" *

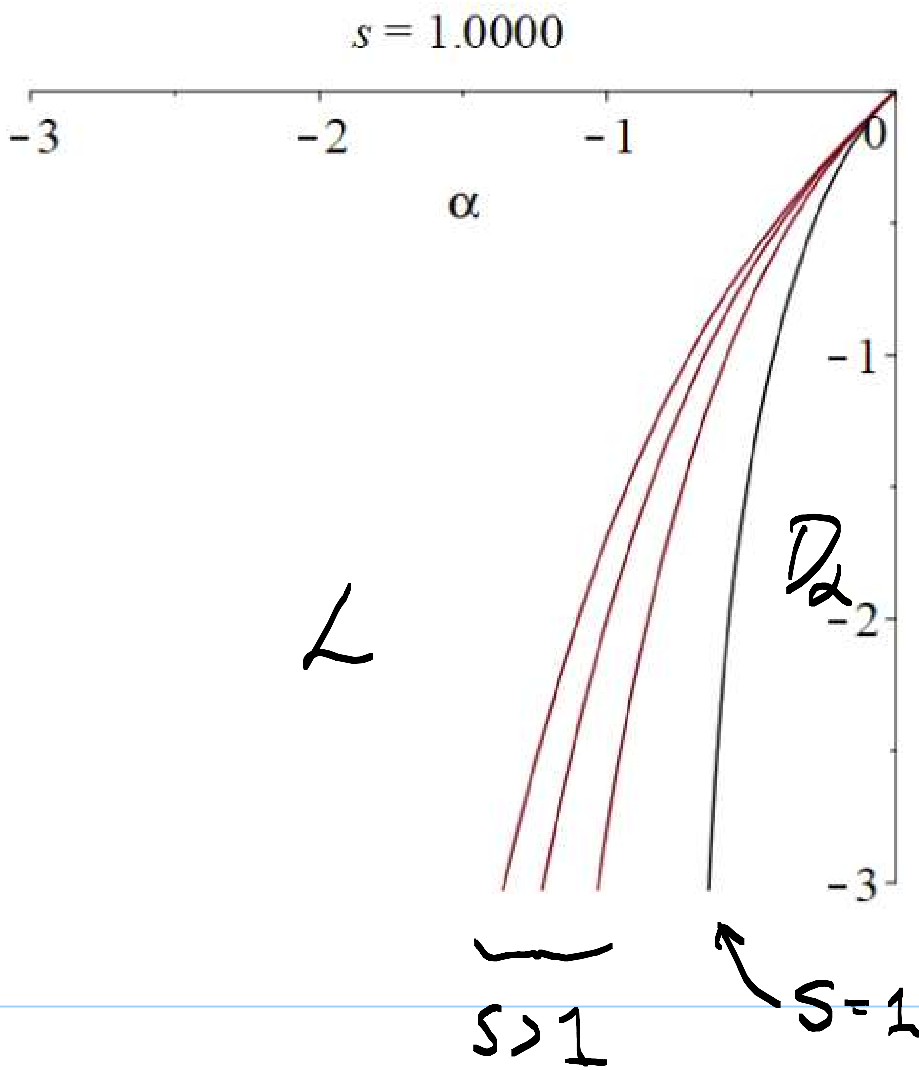
$$B_{up}(a,b,c,s,z) = 1 + acz^2 + (\qquad\qquad)z^4 + \ldots$$

$$B_{DOWN}(a,b,c,s,z) = bcz^2 + (\qquad\qquad)z^4 + \ldots$$

↳ SINGULARITIES → $z_1 = \frac{1}{a(s+1)}$ $\quad z_2 = \frac{1}{b(s+1)}$

$Z_3(a,b,c,s)$ [QUARTIC IN z^2]

At fixed $c = 1$, setting $z_1(\alpha, s) = z_3(\alpha, \beta, s)$ (animated over $1 < s < 5$)

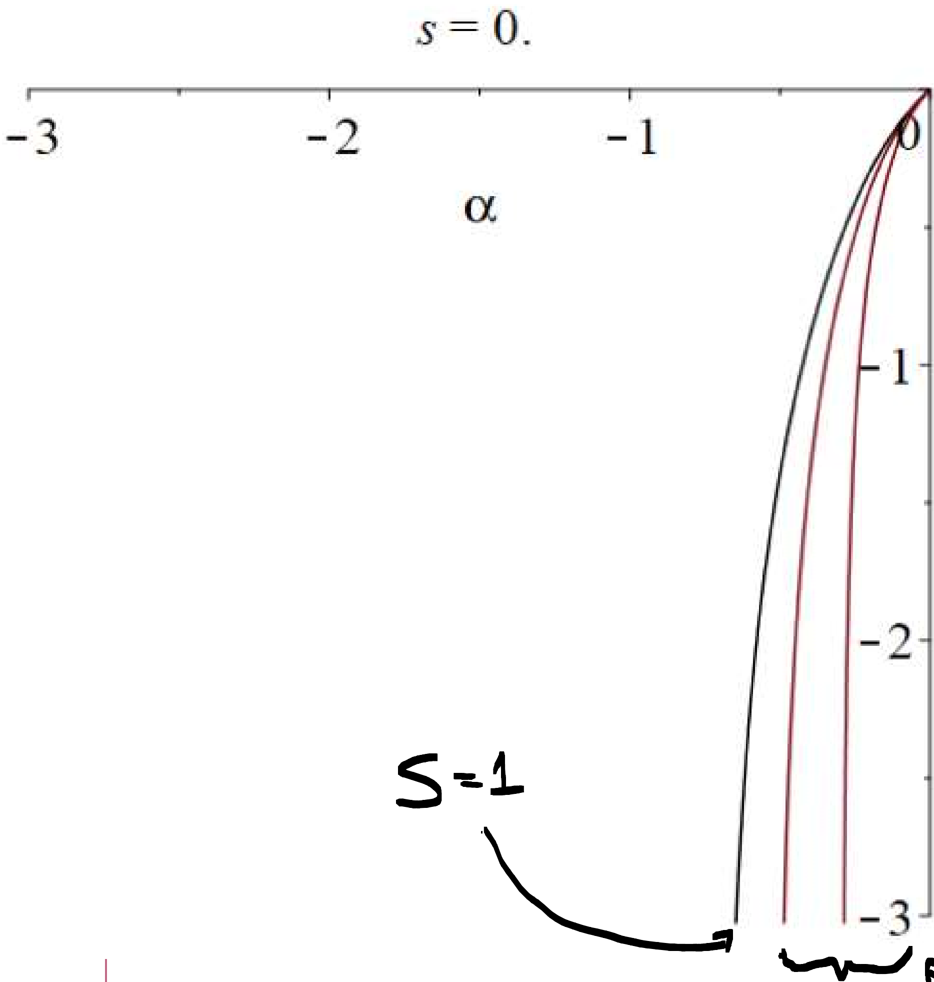


COLLINEAR STEPS "REWARDED"
$S > 1$

AS $S \to \infty$,

D_α GROWS
+ $\mathcal{L}$ SHRINKS

[POLYMER TENDS TO GO OFF INTO BULK MORE EASILY]



COLLINEAR STEPS "PENALIZED"
S < 1

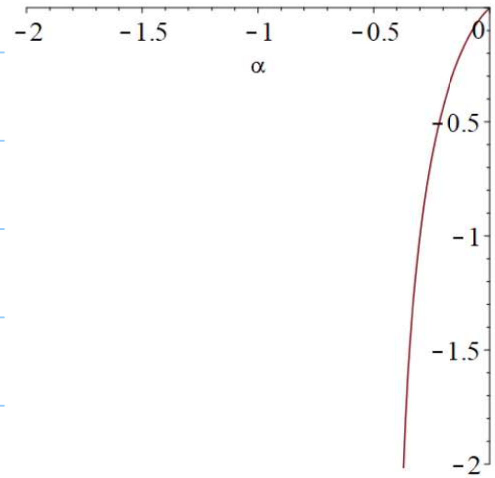
AS S → 0,

D_α SHRINKS
→ L GROWS

[POLYMER TENDS TO RETURN TO THE INTERFACE MORE EASILY]

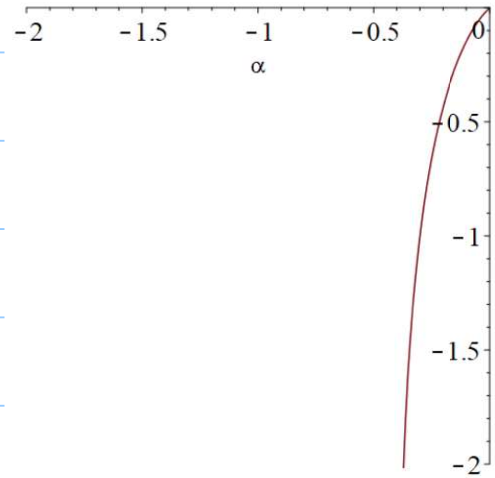
At fixed $c = 1$, setting $z_1(\alpha, s) = z_3(\alpha, \beta, s)$ (animated over $0 < s < 1$)

But that only happens if we "simplify/symbolic" in Maple!



$C = 1, \ S = 1/2$

But that only happens if we "simplify/symbolic" in Maple!



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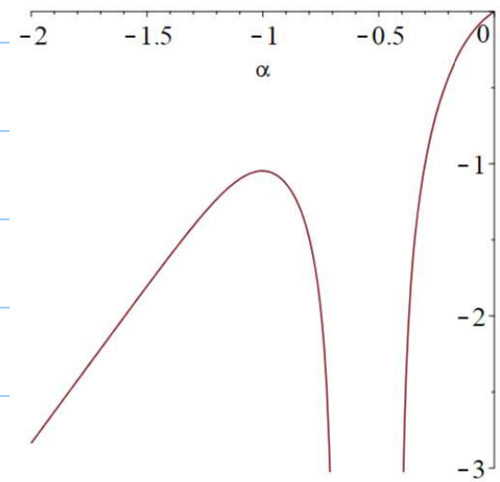
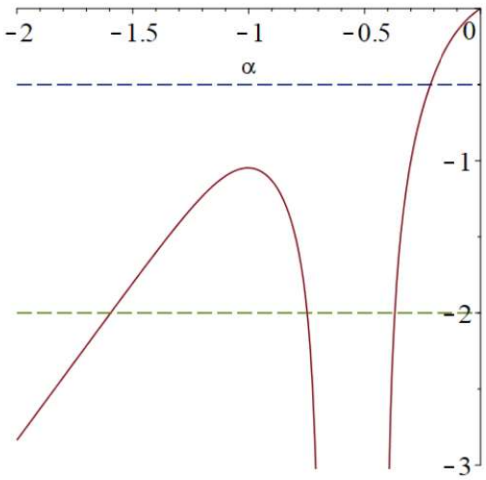
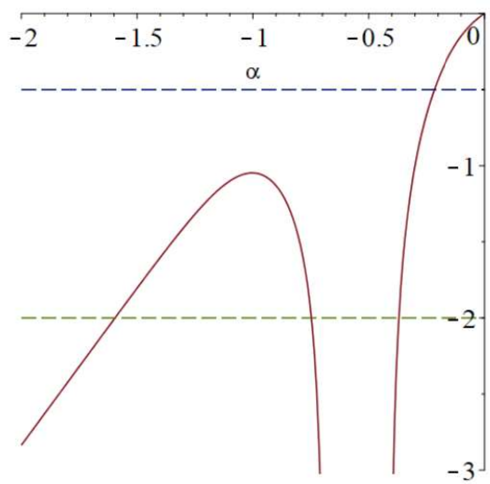


Otherwise...

Is it real? What to track?



Fix $c = 1$ and $s < 1$ and consider two β regimes.



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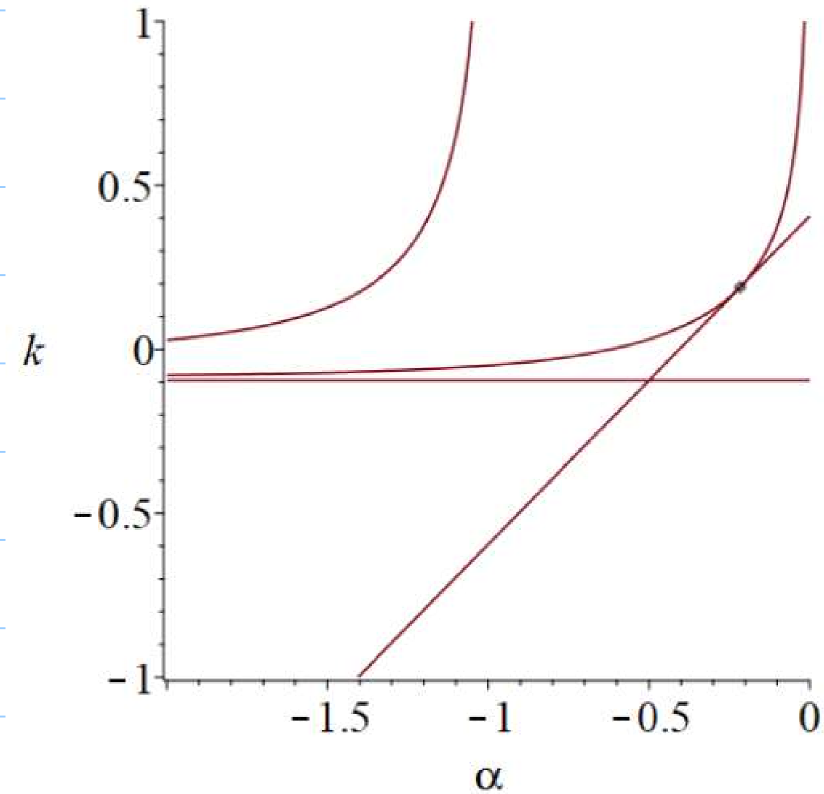
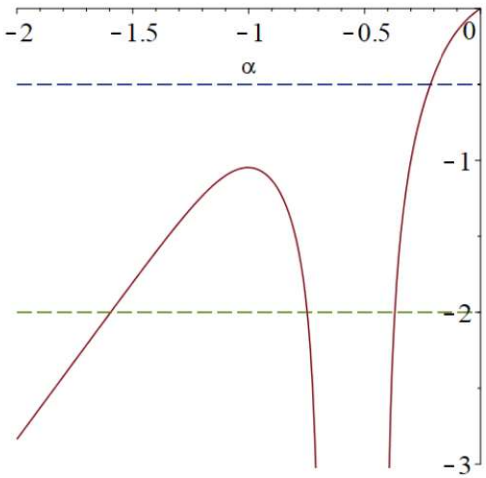


Implicit plots of the free energy ($\kappa = -\log z_c$)

$\kappa(\alpha)$ vs α for $\beta^* < \beta < 0$



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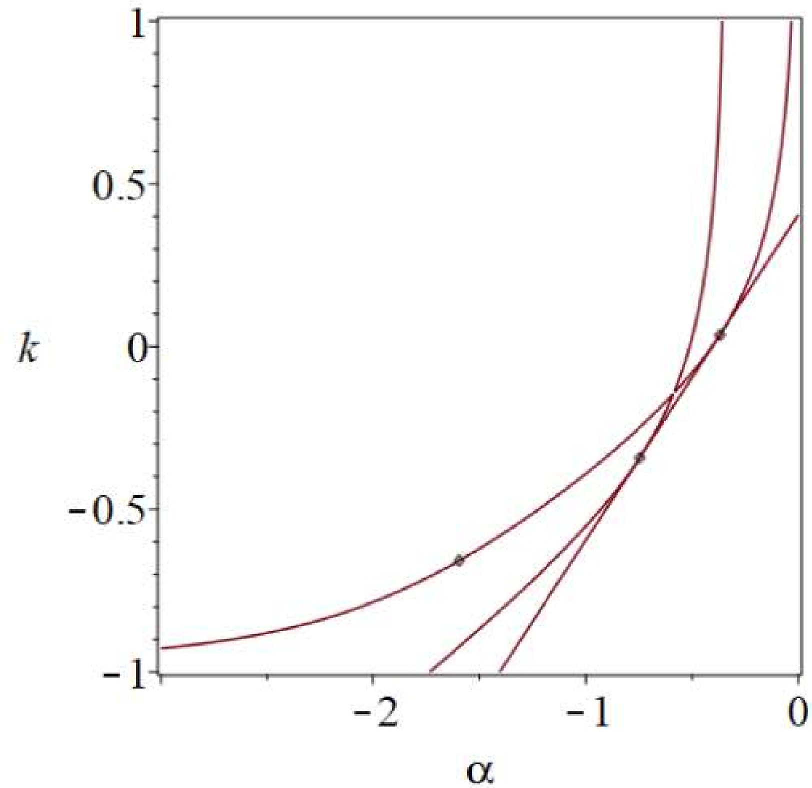
Implicit plots of the free energy ($\kappa = -\log z_c$)

$\kappa(\alpha)$ vs α for $\beta < \beta^*$



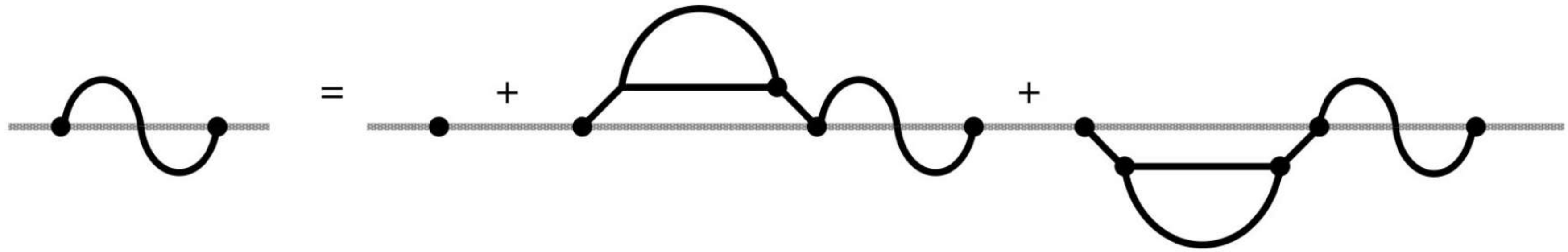
ANIMATIONS IN MAPLE

↳ FIX $S = 1/2$, VARY β

↳ PLOT $K(\alpha)$ VS α

↳ FIX β IN 2 REGIMES $[\beta_H$ & $\beta_L]$
AND VARY $0 < S < 1$

↳ PLOT $K(\alpha)$ VS α



① $B(a,b,c,z) = 1 + acz^2 D(az) B(a,b,c,z) + bcz^2 D(bz) B(a,b,c,z)$

↳ SPLIT INTO B_u + B_D TO BE ABLE TO TRACK "STIFFNESS" DECORATION @ "GLUE PTS"

$$B_u(a,b,c,s,z) = 1 + acz^2 + (\qquad\qquad)z^4 + \dots$$

$$B_d(a,b,c,s,z) = \qquad bcz^2 + (\qquad\qquad)z^4 + \dots$$

↳ SINGULARITIES → $z_1 = \frac{1}{a(s+1)}$ $\quad z_2 = \frac{1}{b(s+1)}$

$z_3(a,b,c,s)$