Force, density, and extension relations in adsorbing polymers subject to a force

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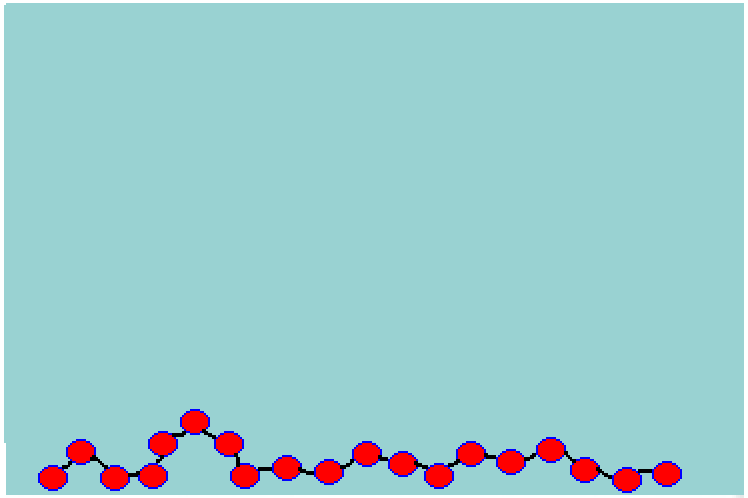
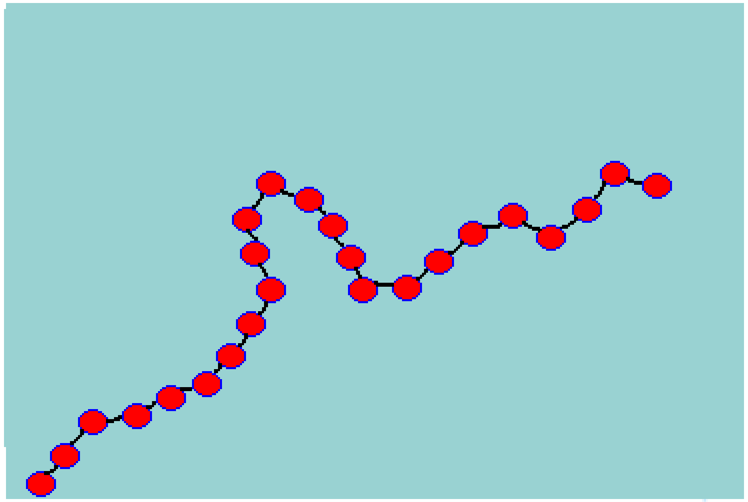
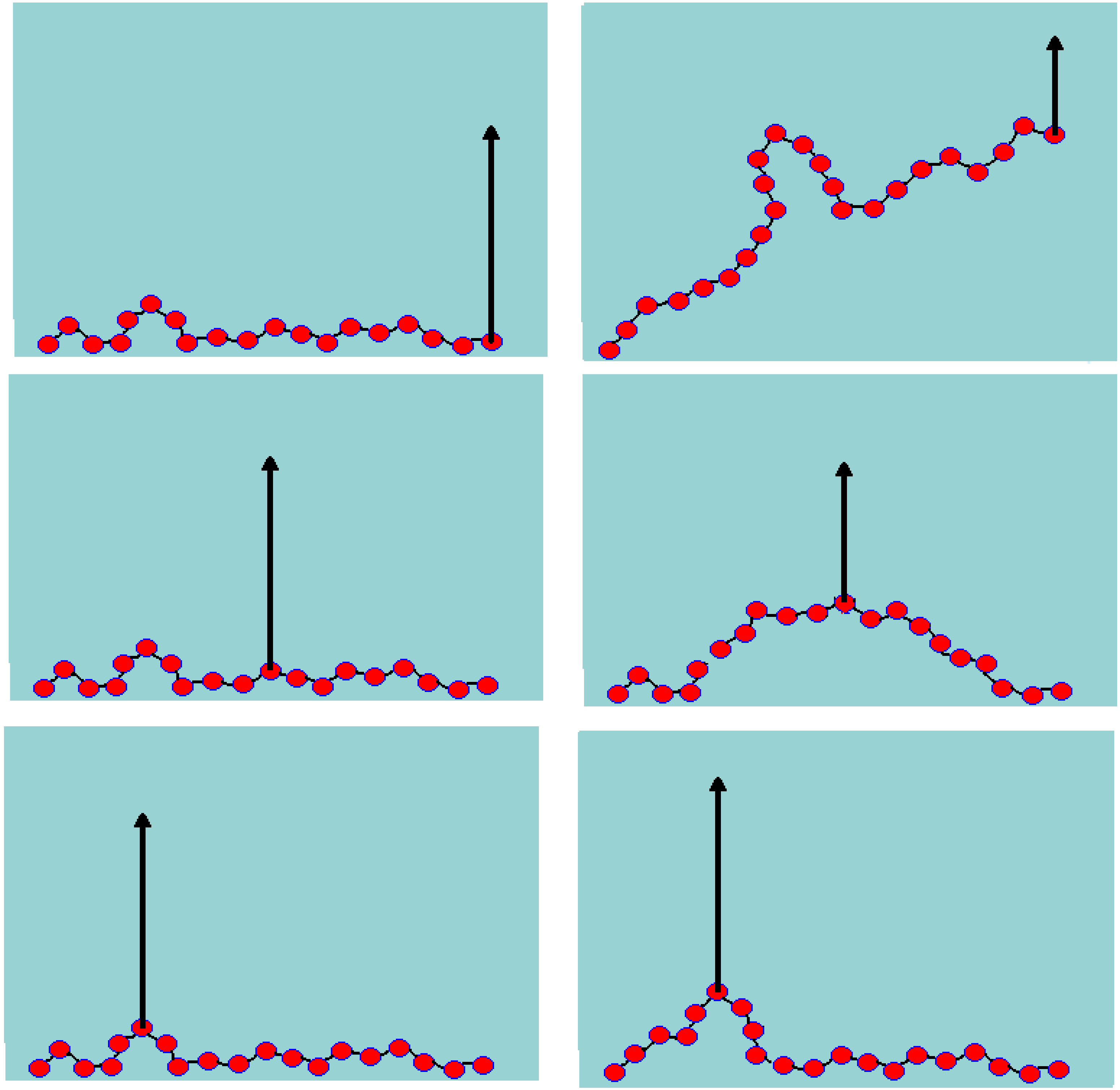
Polymer adsorption



Adsorbed



Desorbed



- Partition function

$$Z_n(T) = \sum_{\omega} e^{-E(\omega)/kT}$$

- Intensive free energy

$$\kappa_n(T) = \frac{1}{n} \log Z_n(T)$$

- Limiting intensive free energy

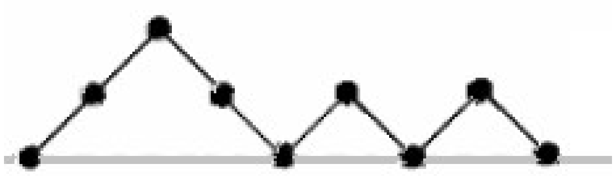
$$\kappa(T) = \lim_{n \to \infty} \kappa_n(T)$$

Look at asymptotic behaviour

$$\sum_{n=0}^{\infty} Z_n(T) z^n$$

Dyck paths

- Walk on Z^2 such that:
  - Starts at the origin
  - Steps only NE or SE
  - Has non-negative *y*-coordinates
  - Ends at $y=0$



Dyck paths

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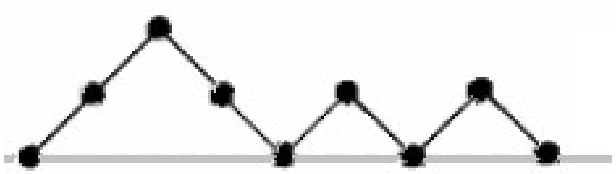

$$d_{2n} = C_n = \frac{1}{n+1}\binom{2n}{n} \qquad D(z) = \sum_{n=0}^{\infty} d_{2n} z^{2n}$$

Dyck paths

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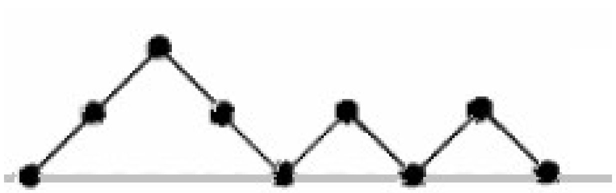

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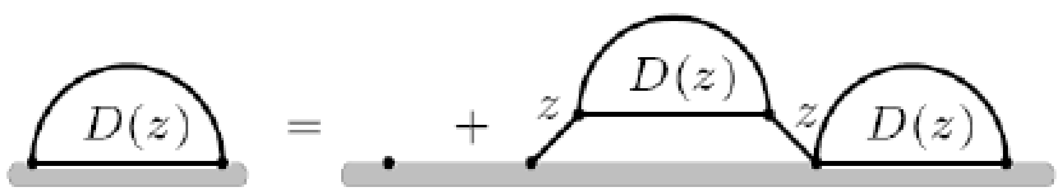
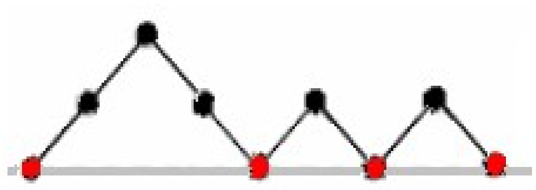


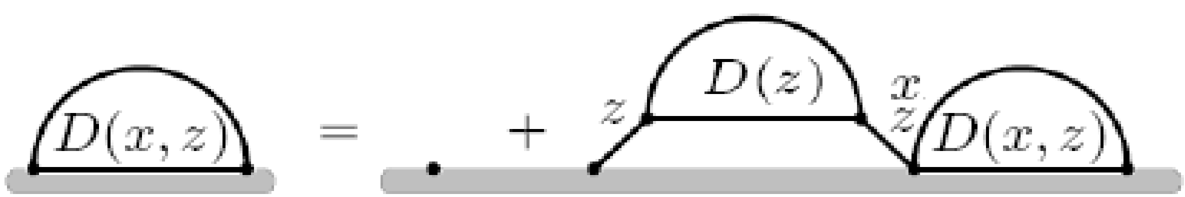
$$D(z) = 1 + z^2 \left(D(z)\right)^2$$

$$D(z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2}$$

- Dyck paths with visits



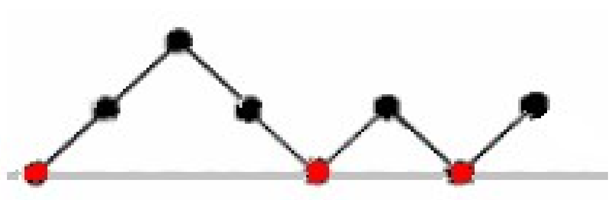
$$D(x,z) = \sum_{n,v} d_{2n}(v) x^v z^{2n}$$



$$D(x,z) \quad = \quad 1 \quad + \quad z^2 x D(z) D(x,z)$$

$$D(x,z) = \frac{2}{2 - x\left(1 - \sqrt{1 - 4\,z^2}\right)}$$

- Dyck paths with visits and a free end

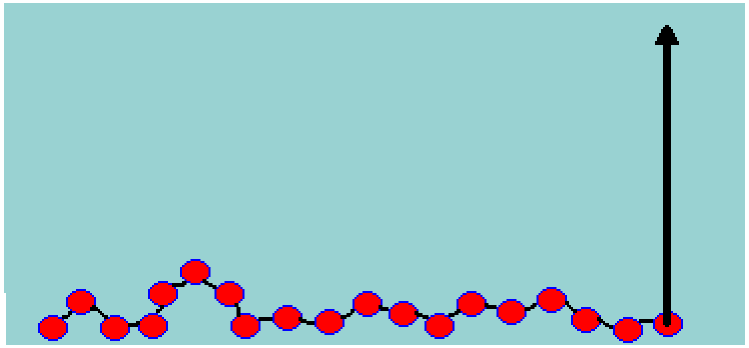


$$D(x,y,z)=\sum_{n,v,h} d_{2n}(v,h)x^v y^h z^{2n}$$

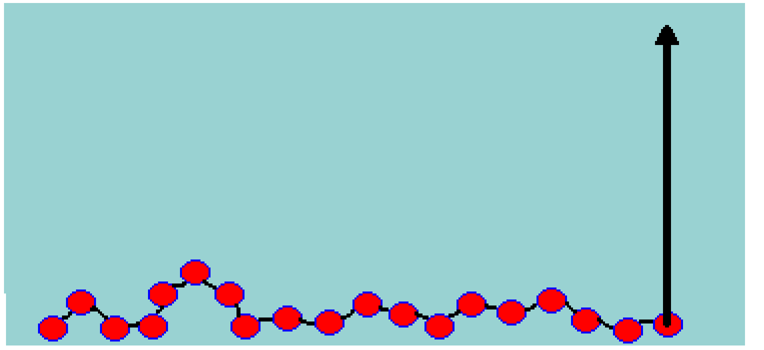
$$D(x,y,z) = D(x,z) + zyD(x,z)D(1,y,z)$$

$$D(x,y,z) = \frac{4z}{\left(2-x+x\sqrt{1-4\,z^2}\right)\left(2\,z-y+\sqrt{1-4\,z^2}y\right)}$$

Apply force at free end



Apply force at free end



- Adsorption/desorption transition?

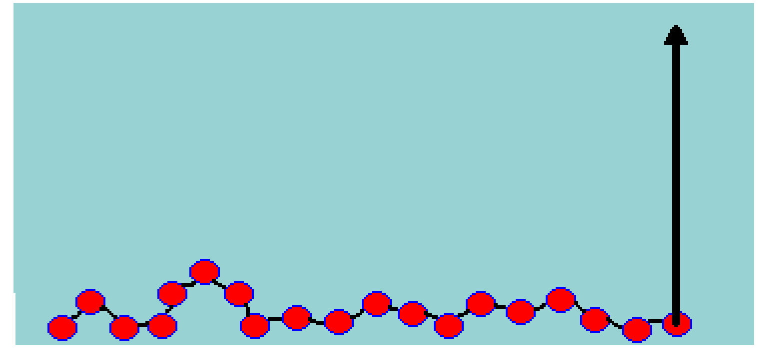
$$x = e^{-\epsilon/kT} = e^{1/T} \qquad y = e^{f/kT} = e^{f/T}$$

- If *f* = *0*:

$$x_c = 2 \text{ (equivalently } T_c = 1/\log 2)$$

- Min. force to desorb?

Apply force at free end



- Adsorption/desorption transition?

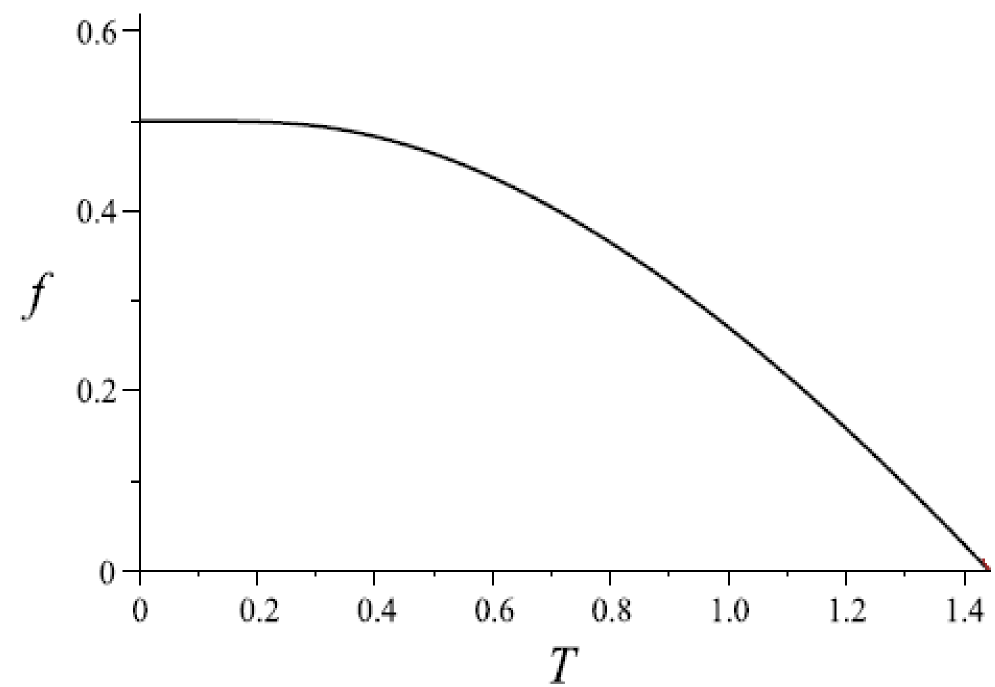
$$x = e^{-\epsilon/kT} = e^{1/T} \qquad y = e^{f/kT} = e^{f/T}$$

- If $f = 0$:

$$x_c = 2 \text{ (equivalently } T_c = 1/\log 2)$$

- Min. force to desorb?

$$f_c(T) = \max\left\{0, \frac{T}{2}\log\left(e^{1/T} - 1\right)\right\}$$



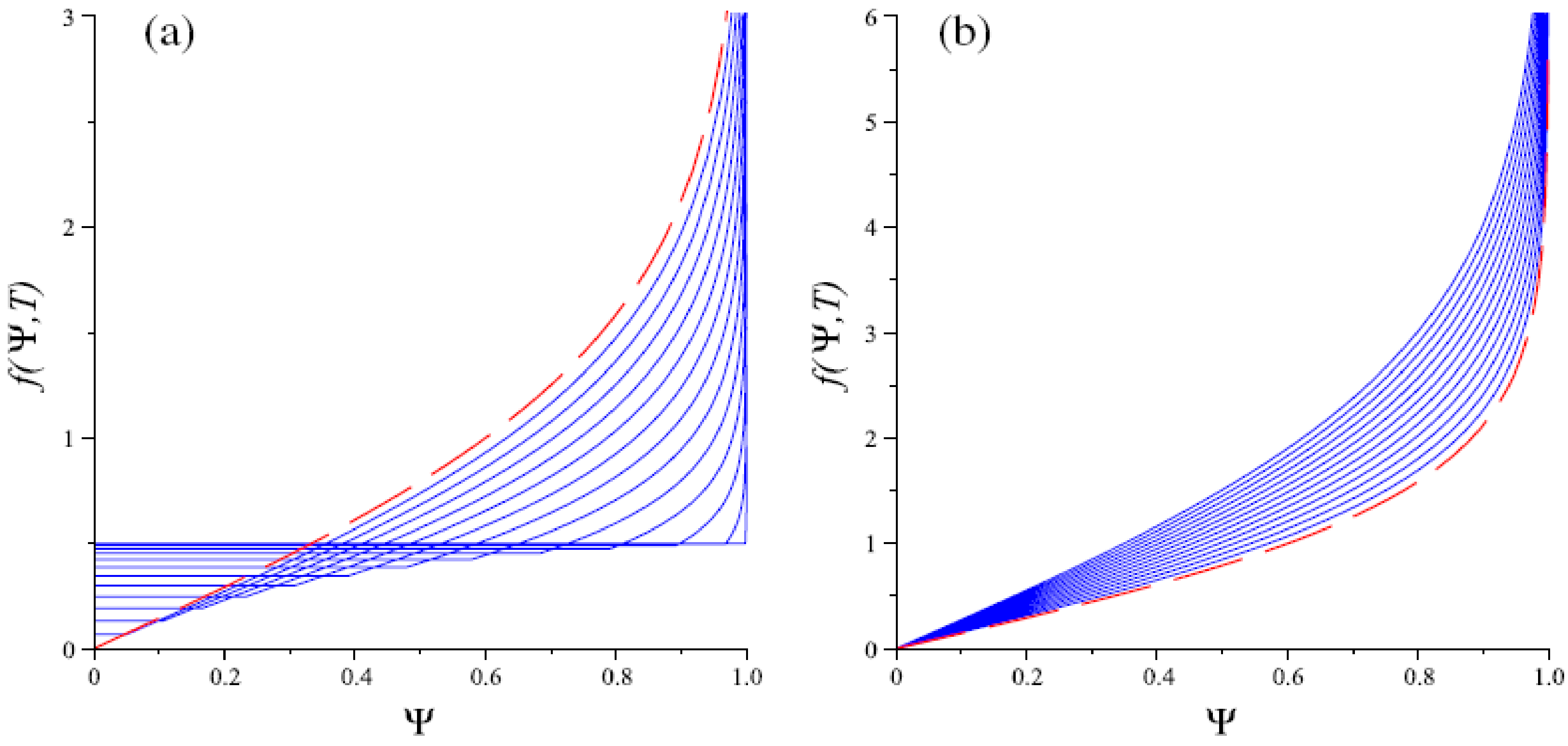
Force and normalized extension

$$\Psi(f,T) = \lim_{z \to z_c^-} \frac{\langle h \rangle}{\langle n \rangle} = \frac{y(\partial/\partial y)\log(B(x,y,z))|_{z=z_c,x=\mathrm{e}^{1/T},y=\mathrm{e}^{f/T}}}{z(\partial/\partial z)\log(B(x,y,z))|_{z=z_c,x=\mathrm{e}^{1/T},y=\mathrm{e}^{f/T}}}$$

Force and normalized extension

$$f(\Psi,T)=\begin{cases}\dfrac{T}{2}\ln\left(e^{1/T}-1\right) & 0<\Psi<1-2e^{-1/T}\\[2ex] \dfrac{T}{2}\ln\left(\dfrac{1+\Psi}{1-\Psi}\right) & 1-2e^{-1/T}\le\Psi<1\end{cases}\qquad 0\le T<T_c$$

$$f(\Psi,T)=\frac{T}{2}\ln\left(\frac{1+\Psi}{1-\Psi}\right)\qquad 0\le\Psi<1\qquad T_c\le T$$



Density and normalized extension

$$\sigma(\Psi,T)=\lim_{z\to z_c^-}\frac{\langle v\rangle}{\langle n\rangle}=\frac{x(\partial/\partial x)\log(B(x,y,z))\big|_{z=z_c,x=e^{1/T},y=e^{f(\Psi,T)/T}}}{z(\partial/\partial z)\log(B(x,y,z))\big|_{z=z_c,x=e^{1/T},y=e^{f(\Psi,T)/T}}}$$

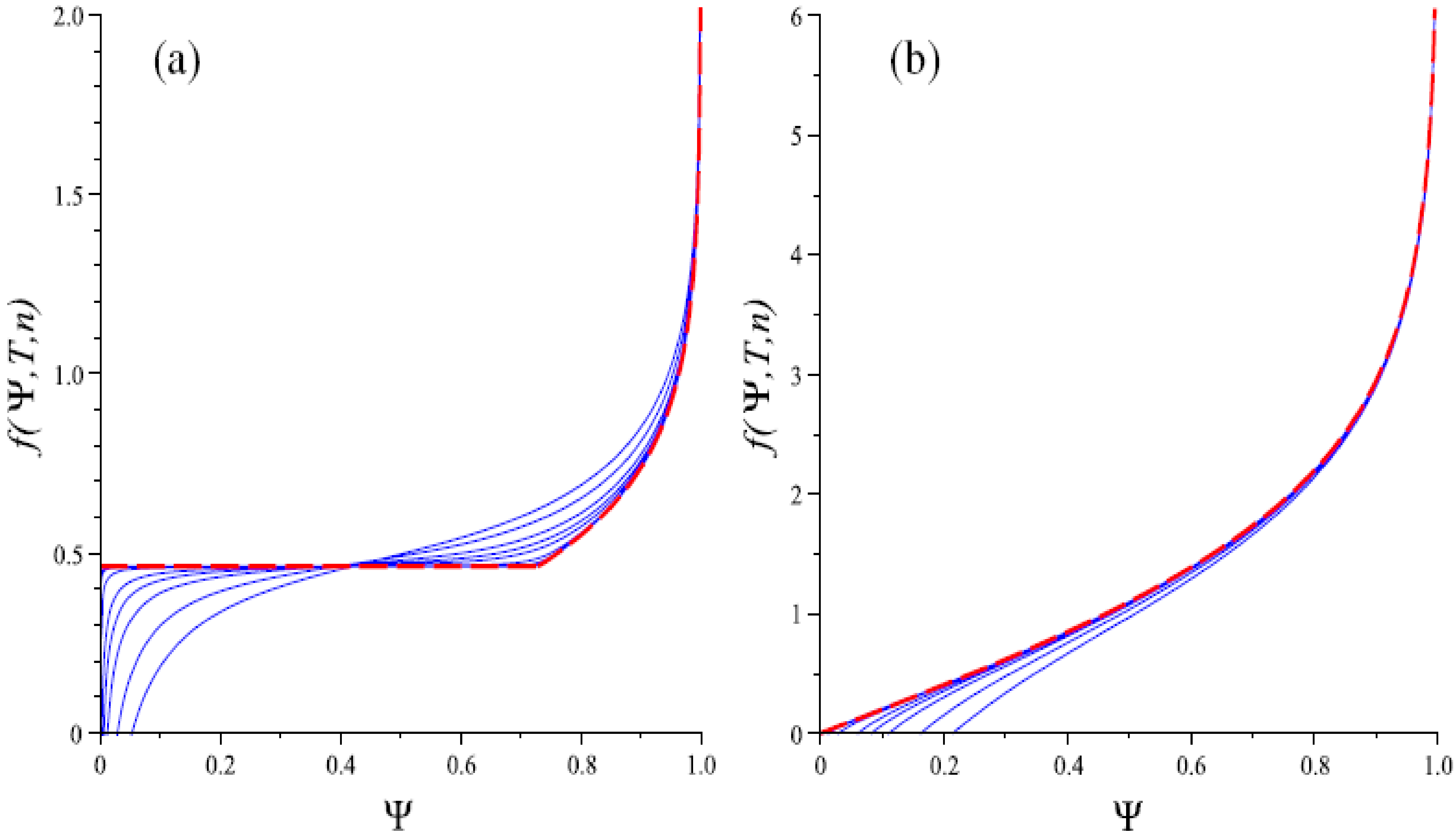
$$\sigma(\Psi,T)=\begin{cases}\frac{1}{2}\frac{e^{1/T}-2}{e^{1/T}-1}-\frac{1}{2}\frac{e^{1/T}}{e^{1/T}-1}\Psi & 0\le\Psi<1-2e^{-1/T}\\ 0 & 1-2e^{-1/T}\le\Psi<1\end{cases}\qquad 0\le T<T_c$$

$$\sigma(\Psi,T)=0\qquad 0\le\Psi<1\qquad T_c\le T$$

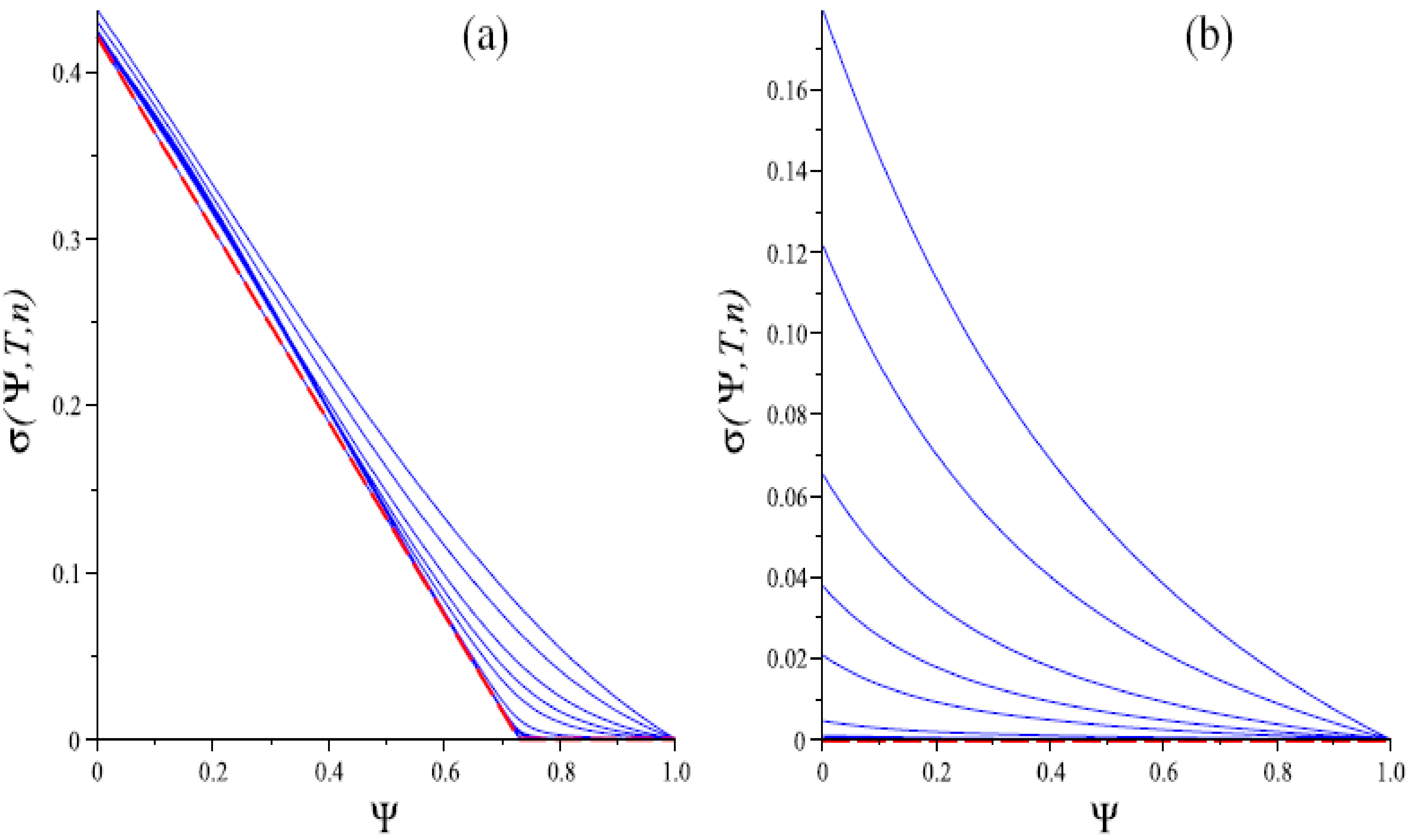
Finite average length results

$$f(\Psi,T,\bar{n}) = \begin{cases} \dfrac{T}{2}\ln\left(\mathrm{e}^{1/T}-1\right) - \dfrac{1}{\bar{n}}\dfrac{T}{\Psi}\dfrac{2-(1-2\Psi)\mathrm{e}^{1/T}}{2-(1-\Psi)\mathrm{e}^{1/T}} + \dfrac{1}{\bar{n}^2}\dfrac{T}{2\Psi^2} \\ \quad \times \dfrac{8+(3\Psi-\Psi^3-\Psi^2-1)\mathrm{e}^{3/T}+(6+4\Psi^3+6\Psi^2-12\Psi)\mathrm{e}^{2/T}+(12\Psi-12)\mathrm{e}^{1/T}}{(2-(1-\Psi)\mathrm{e}^{1/T})^3} \\ \quad + \mathrm{o}\left(1/\bar{n}^2\right) \qquad 0<\Psi<1-2\mathrm{e}^{-1/T} \\ \dfrac{T}{2}\ln\left(\mathrm{e}^{1/T}-1\right) + \dfrac{1}{\bar{n}^{1/2}}\dfrac{T}{2}\dfrac{\mathrm{e}^{1/T}}{\sqrt{\mathrm{e}^{1/T}-1}} - \dfrac{1}{\bar{n}}T\dfrac{\mathrm{e}^{1/T}}{\mathrm{e}^{1/T}-2} - \dfrac{1}{\bar{n}^{3/2}}\dfrac{T}{48}\left(\dfrac{\mathrm{e}^{1/T}}{\sqrt{\mathrm{e}^{1/T}-1}}\right)^3 \\ \quad + \dfrac{1}{\bar{n}^2}\dfrac{T}{2}\left(\dfrac{\mathrm{e}^{1/T}}{\mathrm{e}^{1/T}-2}\right)^2 + \mathrm{o}\left(1/\bar{n}^2\right) \qquad \Psi=1-2\mathrm{e}^{-1/T} \\ \dfrac{T}{2}\ln\left(\dfrac{1+\Psi}{1-\Psi}\right) + \dfrac{1}{\bar{n}}\dfrac{T}{\Psi}\dfrac{\mathrm{e}^{1/T}-2}{2-(1-\Psi)\,\mathrm{e}^{1/T}} + \dfrac{1}{\bar{n}^2}\dfrac{T}{2\Psi^2} \\ \quad \times \dfrac{8+(3\Psi^3-5\Psi^2+3\Psi-1)\mathrm{e}^{3/T}+(6-12\Psi+6\Psi^2-4\Psi^3)\mathrm{e}^{2/T}+(12\Psi-12)\mathrm{e}^{1/T}}{(2-(1-\Psi)\mathrm{e}^{1/T})^3} \\ \quad + \mathrm{o}(1/\bar{n}^2) \qquad 1-2\mathrm{e}^{-1/T}<\Psi<1 \end{cases}$$

$$0 \le T < T_c$$

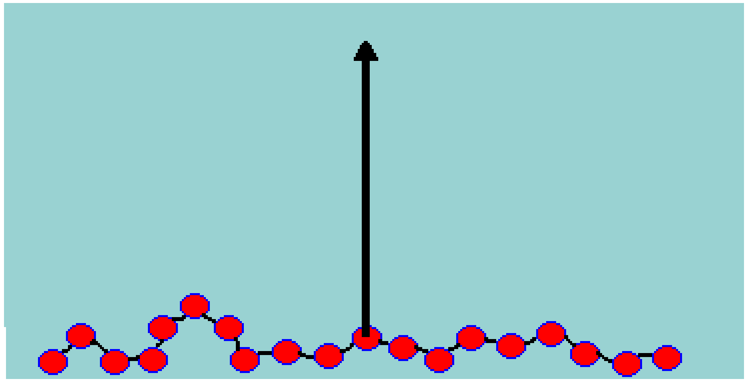


(a)
(b)
$f(\Psi, T, n)$
Ψ
0
0.5
1.0
1.5
2.0
0.2
0.4
0.6
0.8
1
2
3
4
5
6

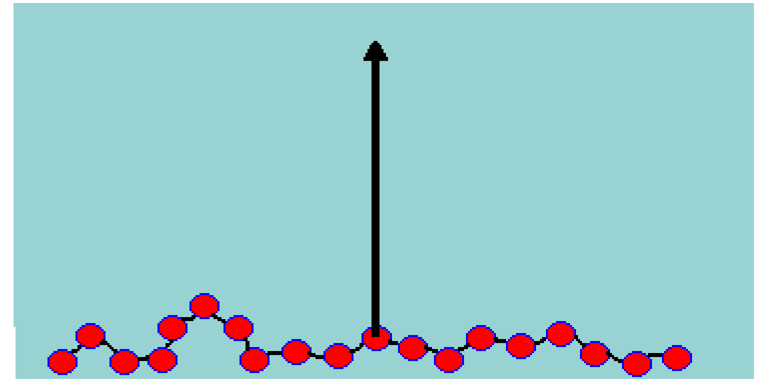


(a)
(b)
σ(Ψ, T, n)
Ψ
0
0.1
0.2
0.3
0.4
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.6
0.8
1.0

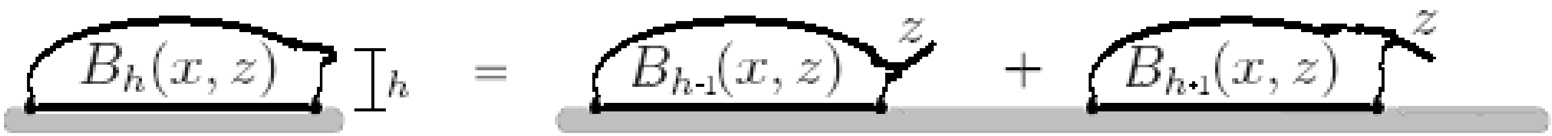
Pulling from a central location



Pulling from a central location



- Dyck paths ending at height *h*: $B_h(x,z) = \sum_{n,v} b_n(v,h) x^v z^n$



$$B_h(x,z) = zB_{h-1}(x,z) + zB_{h+1}(x,z)$$

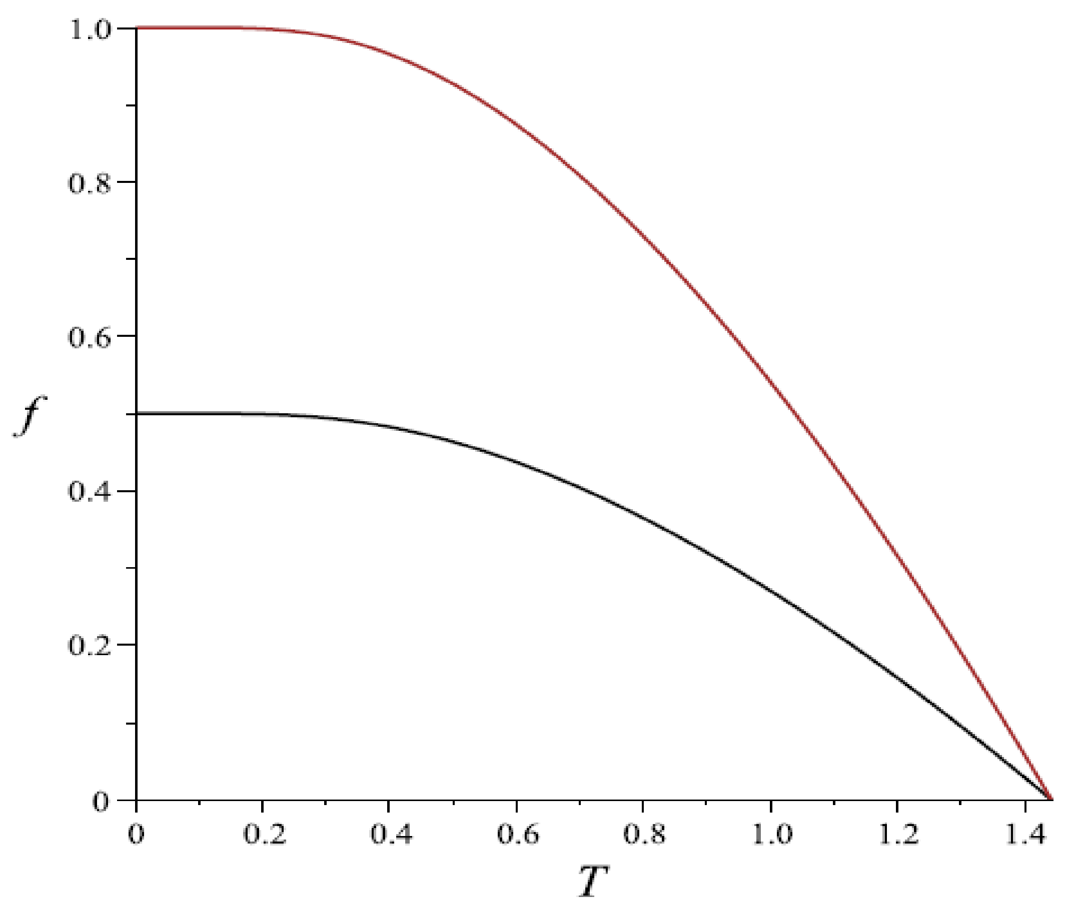
$$B_h(x,z) = \frac{2\left((1-\sqrt{1-4z^2})/2z\right)^h}{2 - x\left(1-\sqrt{1-4z^2}\right)}$$

- Flip one path and *stitch* it to another with the same final height

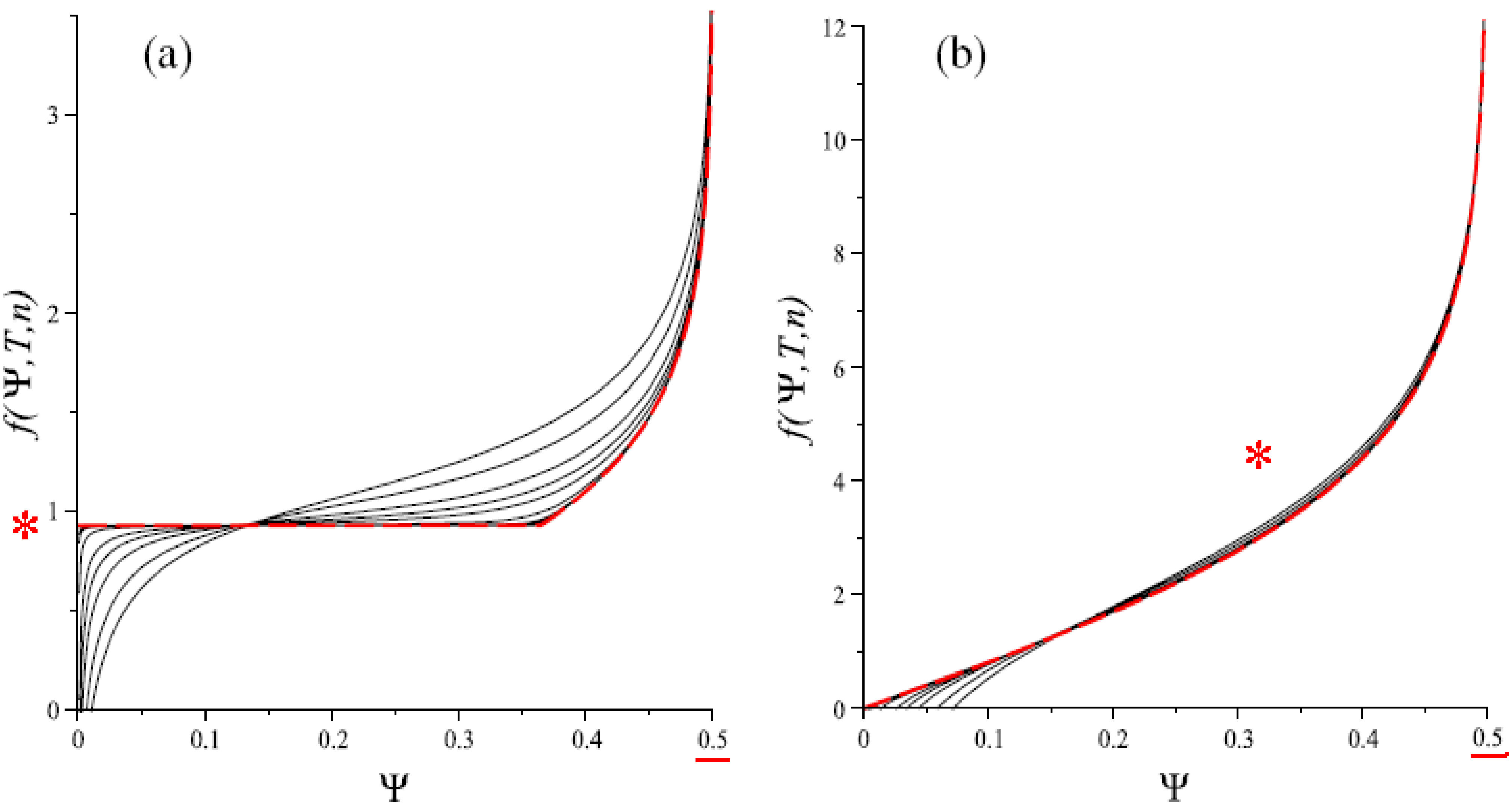
$$S(x,y,z) = \sum_h (B_h(x,z))^2 y^h = \frac{16z^2}{\left(2 - x\left(1-\sqrt{1-4z^2}\right)\right)^2 \left(4z^2 - y\left(1-\sqrt{1-4z^2}\right)^2\right)}$$

- Minimum force to desorb?

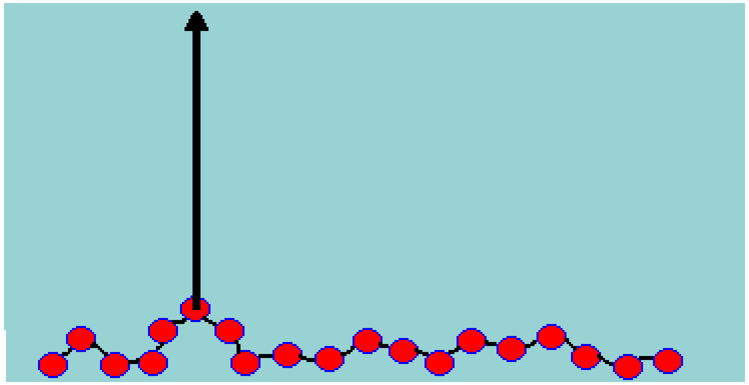
$$f_c(T) = \max\left\{0,\, T\log\left(e^{1/T} - 1\right)\right\}$$



Finite length results



Pulling off center



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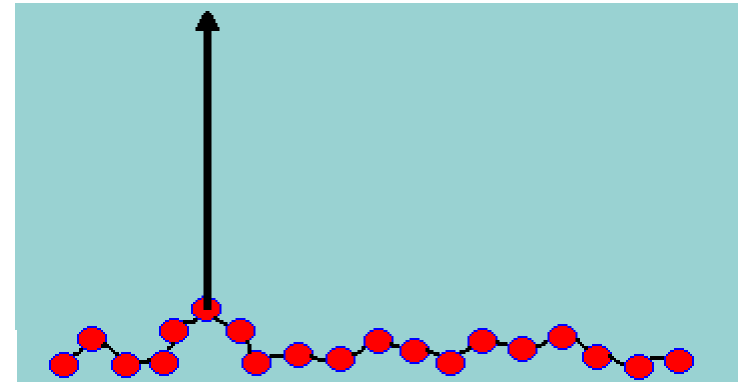
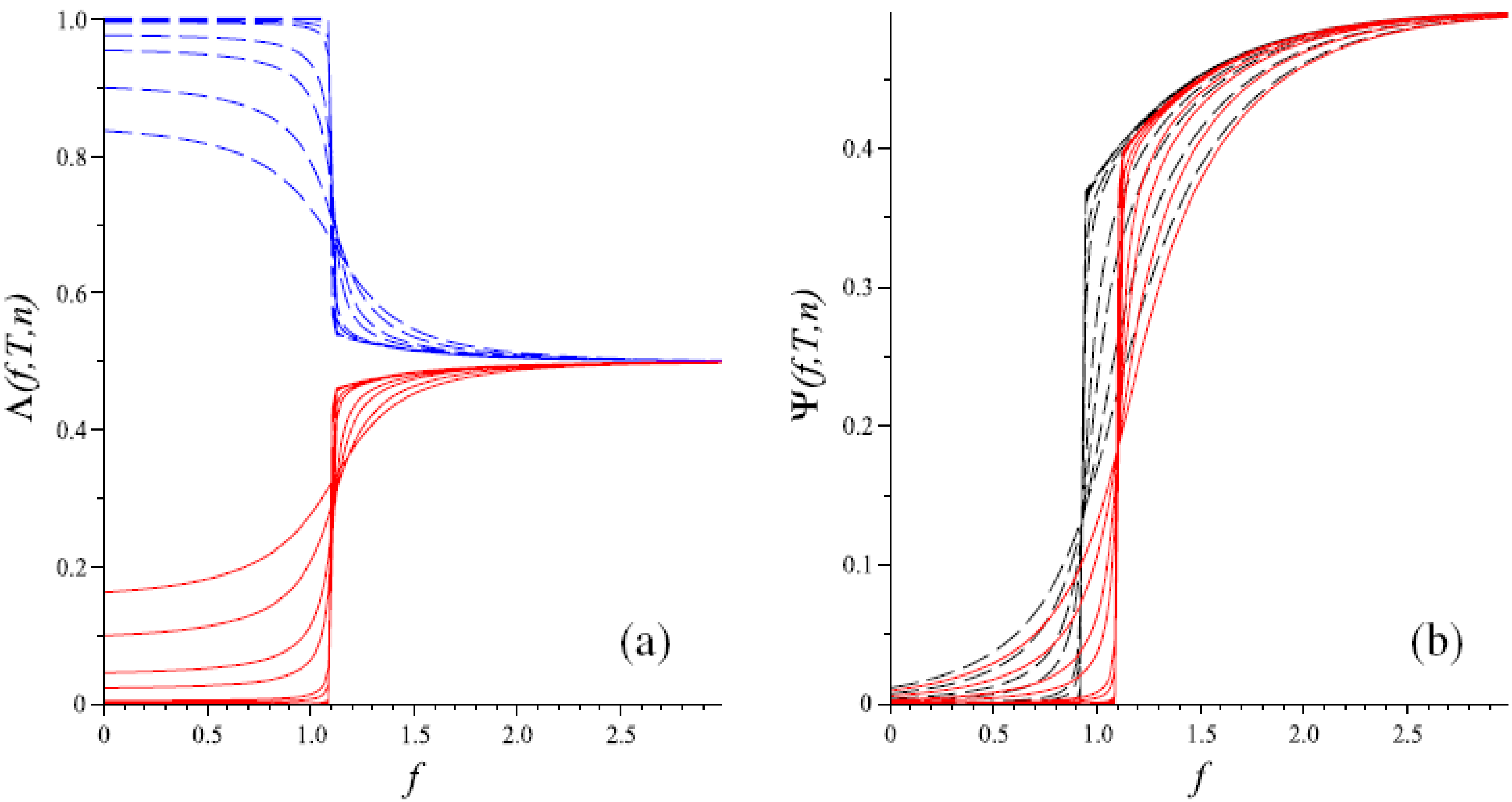


$$\hat{S}(x,y,z,w) = \sum_h B_h(x,zw)B_h(x,z)y^h = \frac{16z^2w}{(2-x(1-\sqrt{1-4z^2w^2}))(2-x(1-\sqrt{1-4z^2}))(4z^2w-y(1-\sqrt{1-4z^2w^2})(1-\sqrt{1-4z^2}))}$$



Thank you.