

Osmotic Pressure of Lattice Knots

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– July 2018 –

AMS, Bowling Green



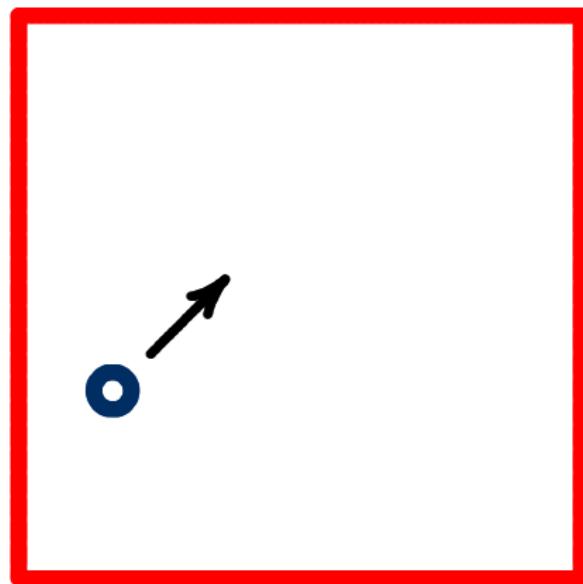




Free energy of compressed polymers

- The effects of topology on the free energy of a polymer;
- Important in biological systems
 - ▶ Koniaris & Muthukumar 1991
 - ▶ Rybenkov, Cozzarelli & Vologodskii 1993, 1997
- Entanglements in DNA and biopolymers
 - ▶ Darcy, Ernst & Sumners 1990s, Buck 2010s and more
- Conformational presentation of topology in confining spaces
 - ▶ Diao, Ziegler & Ernst
 - ▶ Rawdon, Simon, Orlandini, Cantarella & Whittington
 - ▶ Deguchi, Shimokawa & Soteros
- Statistical Mechanics and topology
- Physical environment – confinement and pressure

Entropy



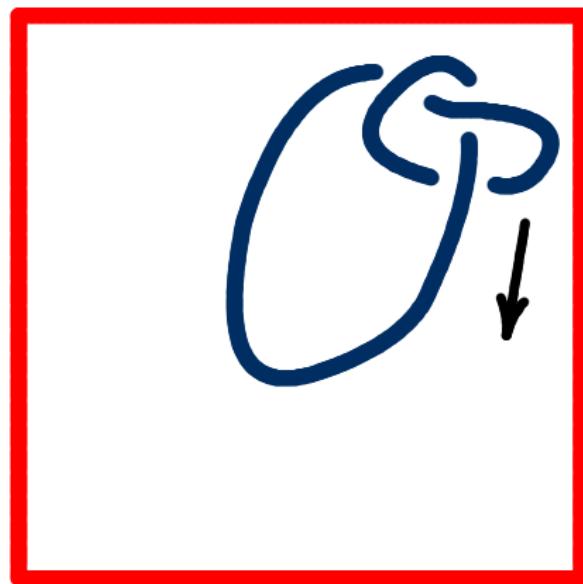
Translational degrees of freedom contribute to entropy

Entropy



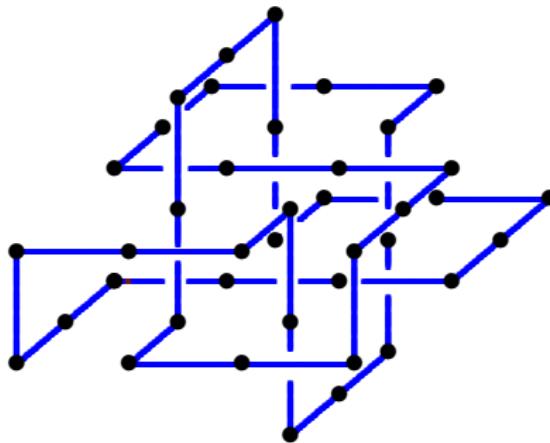
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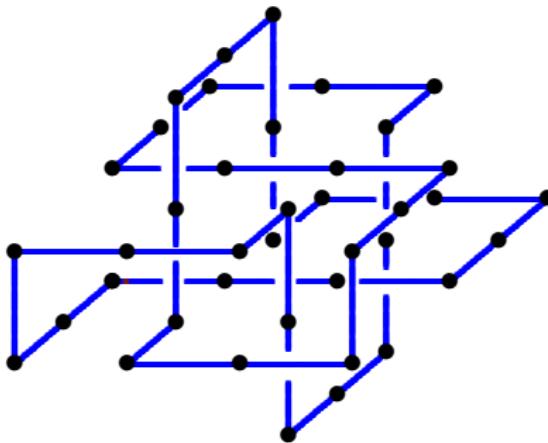
Topological constraints contribute to entropy

Lattice knots



- #Number of lattice knots of length N and type K : $p_N(K)$

Lattice knots

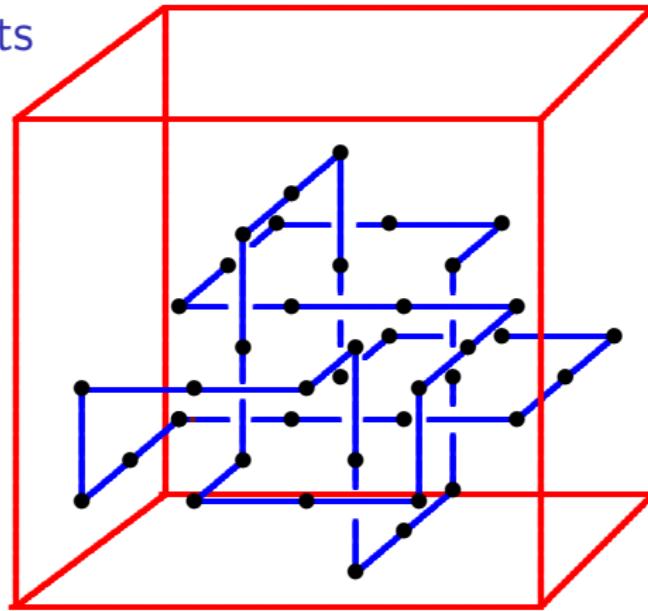


- #Number of lattice knots of length N and type K : $p_N(K)$
- The number of lattice polygons

$$p_N(K) \sim C n^{3-\alpha_K} [\mu_3(K)]^N, \quad \text{so } \log p_N(K) \sim N \log \mu_3(K) = N \kappa_3(K)$$

- – “growth constant” – $\mu_3(K)$
- – “connective constant” – $\kappa_3(K) = \log \mu_3(K)$

Lattice knots



- BFACF dynamics in cube of dimension L^3
- The confinement restricts state space
- Some states not reachable – same feature in a compressed polymer
- Work in ergodicity class containing shortest knots – “confined knots”

Ergodicity class

Lattice knots

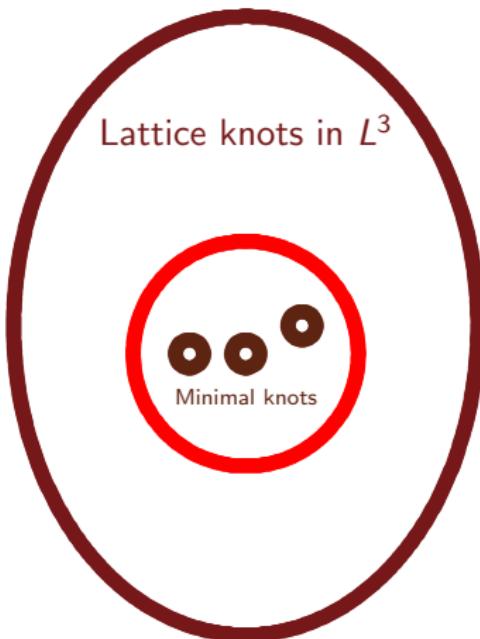
Ergodicity class

Lattice knots

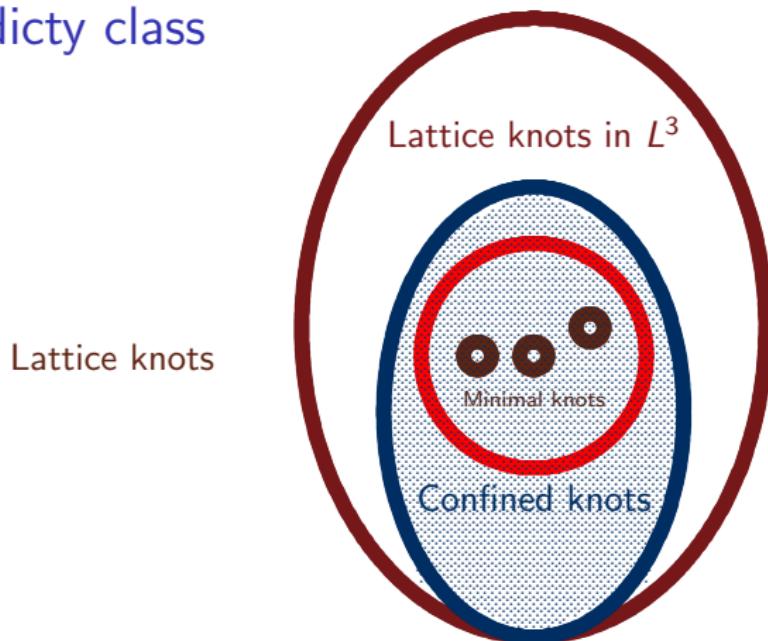


Ergodicity class

Lattice knots

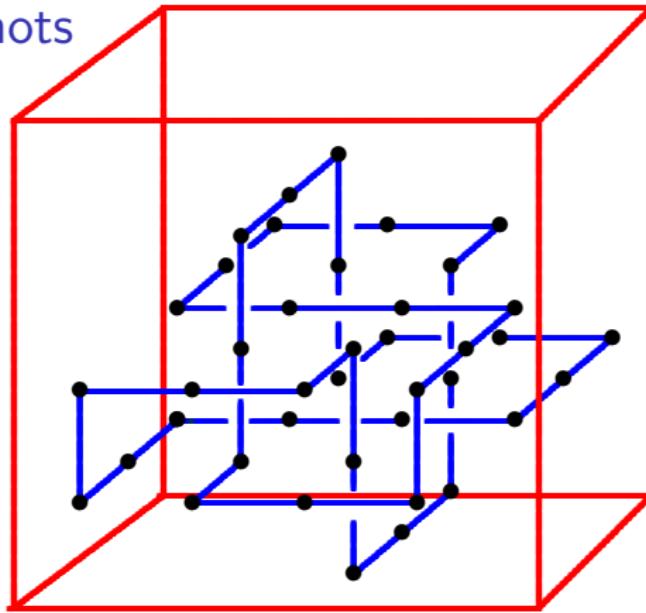


Ergodicity class



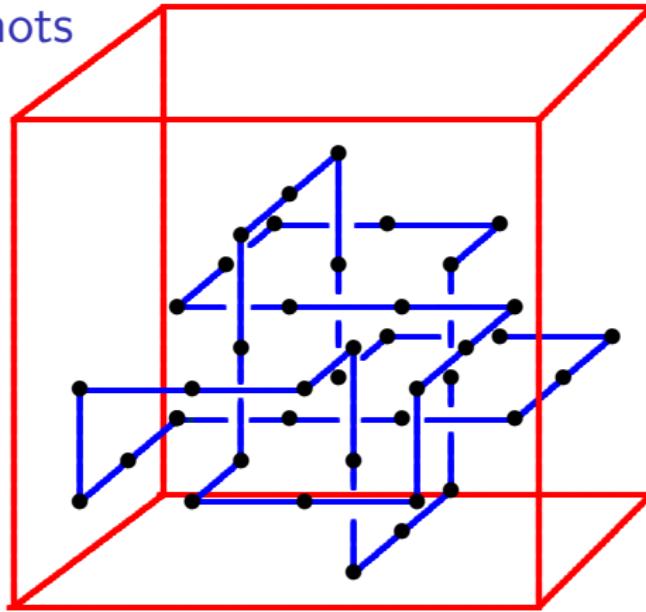
- BFACF dynamics
- The confinement restricts state space
- Some states not reachable – same feature in a compressed polymer
- Space of *Confined Knots*

Confined knots



- Confined in a volume V – translational degrees of freedom
- # confined knots in volume V : $p_{N,V}(K)$

Confined knots



- Confined in a volume V – translational degrees of freedom
- # confined knots in volume V : $p_{N,V}(K)$
- Free energy per unit volume

$$F_V = -\frac{1}{V} \log p_{N,V}(K)$$

- F_V is a function of concentration $\phi = \frac{N}{V}$

Lattice model



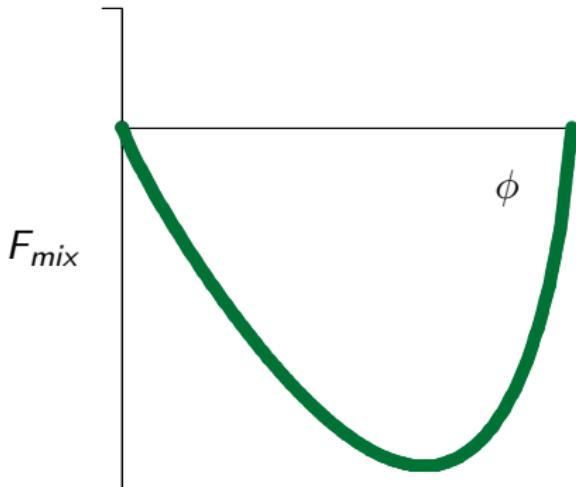
- Flory-Huggins theory for a confined polymer
 - ▶ Huggins 1942, Flory 1942, 1953
- Concentration of monomers in knot of length N in box of volume V
 - ▶ $\phi = \frac{N}{V}$
- Flory-Huggins free energy of mixing (no constant and linear terms)
 - ▶ $F_{mix} = \frac{\phi}{N} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)$

Lattice model

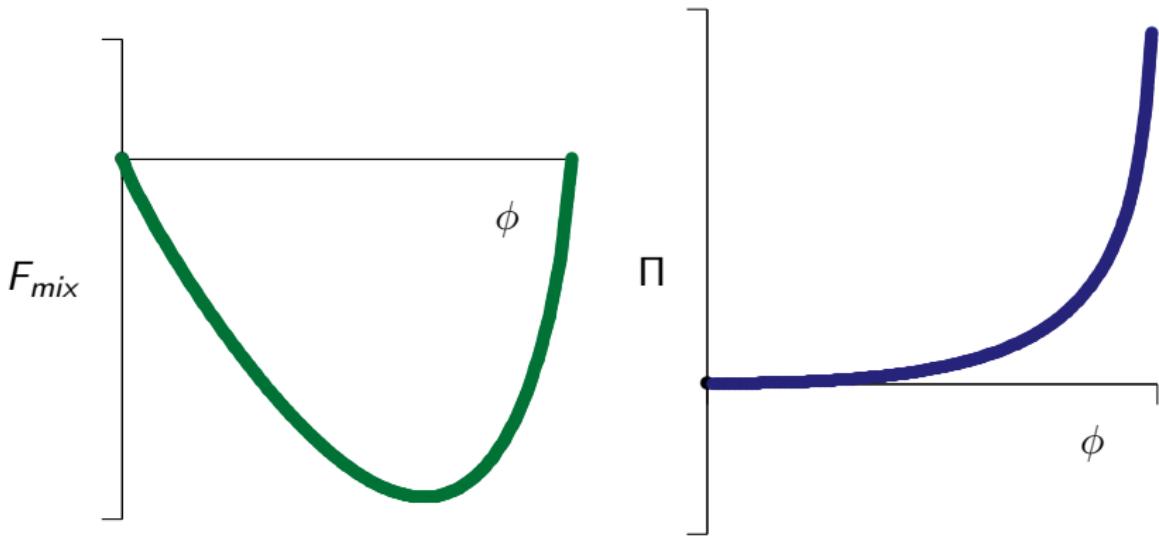


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 - ▶ $F_{mix} = \frac{\phi}{N} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)$
- Flory-Huggins interaction parameter – χ
- Osmotic pressure
 - ▶ $\Pi = \phi^2 \frac{\partial}{\partial \phi} \left(\frac{1}{N} F_{mix} \right) = \frac{1}{V} - \log(1 - \phi) - \phi - \chi \phi^2$

F_{mix} and Π



F_{mix} and Π



Animation: high concentration



Animation: low concentration



Lattice model

- Number of states
 - ▶ $p_{N,V} = \#\{\text{confined knots of length } N, \text{ type } K, \text{ in cube } L^3 = V\}$
- Free energy per unit volume
 - ▶ $F_V = -\frac{1}{V} \log p_{N,V}$
- F_V is related to F_{mix} by
 - ▶ $F_V = a_0\phi + F_{mix} + \text{higher order terms}$

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- F_V is related to F_{mix} by
 - ▶ $F_V = a_0\phi + F_{mix} + \text{higher order terms}$
- Flory-Huggins expression for F_V
 - ▶ $F_V = a_0\phi + \frac{\phi}{N} \log \phi + (1-\phi) \log(1-\phi) + \chi \phi(1-\phi)$
- Free energy per unit length f_t
 - ▶ $f_t = -\frac{1}{N} \log p_{N,V} = \frac{1}{\phi} F_V$

Flory free energy

- The Flory approximation to the free energy is

$$f_t(K) = a_0 + \frac{1-\phi}{\phi} \log(1-\phi) - \chi \phi$$

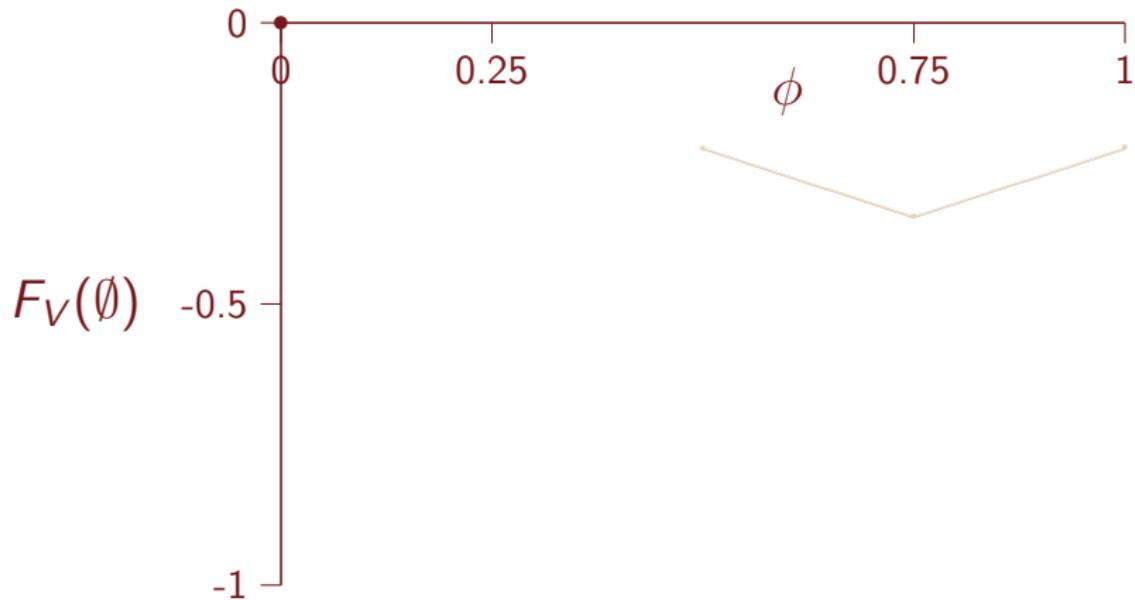
$$F_V(K) = f_t(K) \times \phi = a_0 \phi + (1-\phi) \log(1-\phi) - \chi \phi^2$$

- The parameter a_0 is estimated by noting that

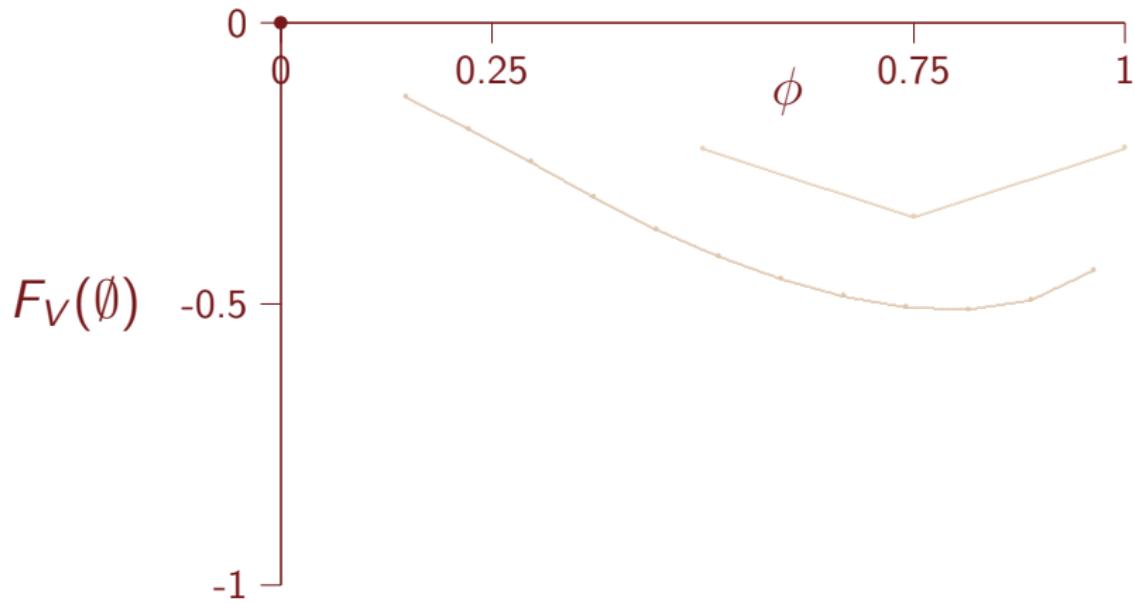
$$\lim_{\phi \rightarrow 0^+} \lim_{L \rightarrow \infty} f_t(\phi) = a_0 - 1 = -\log \mu_3(K)$$

- This approximation is given by red dashed curves

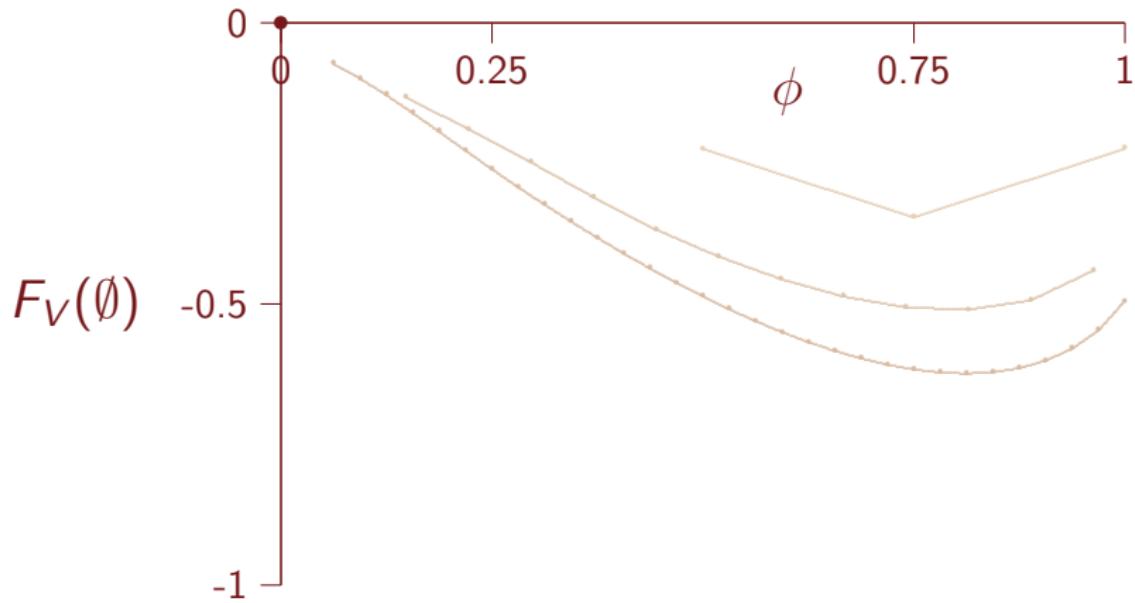
Free energy F_V per unit volume (unknot)



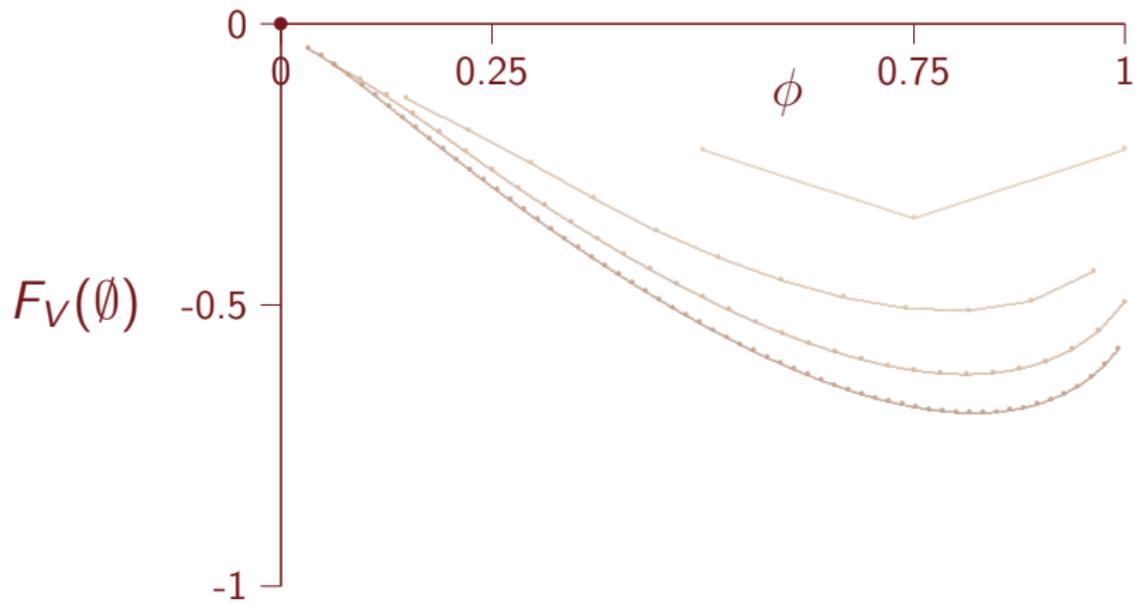
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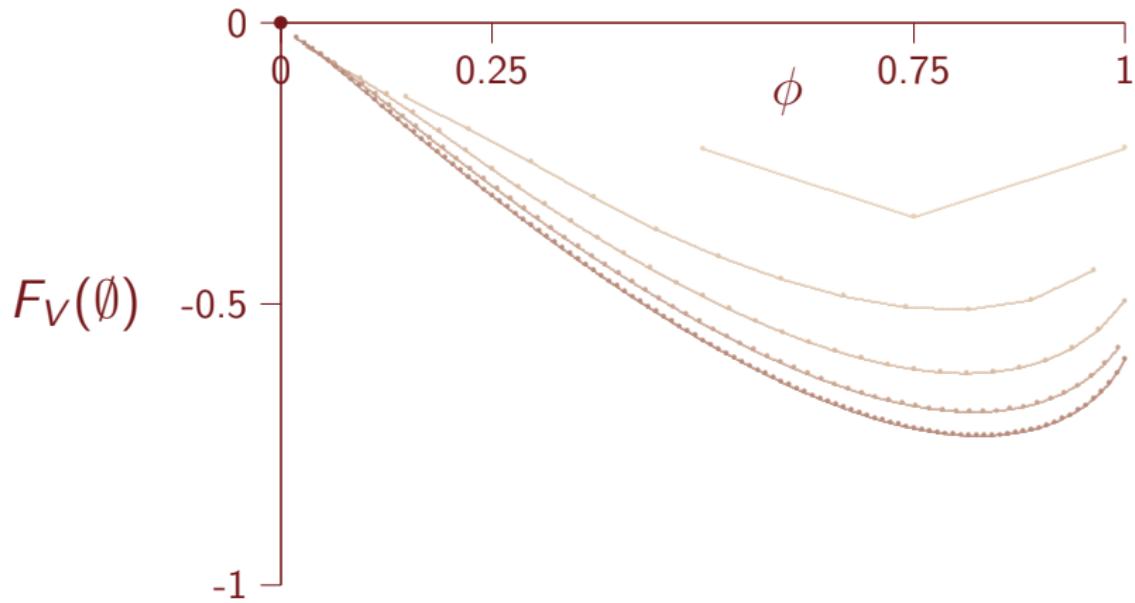
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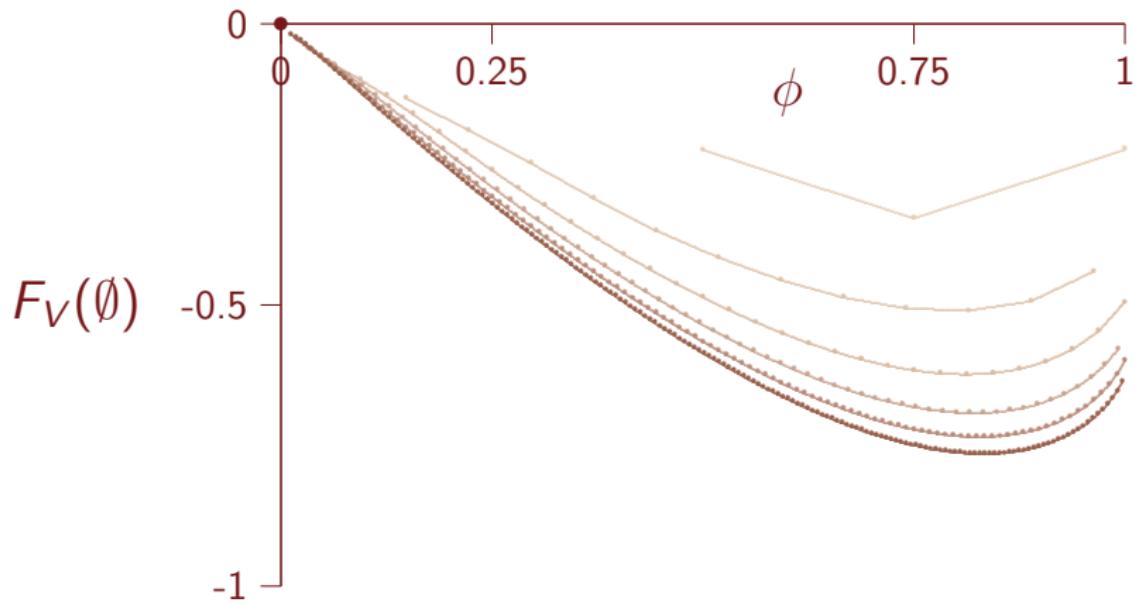
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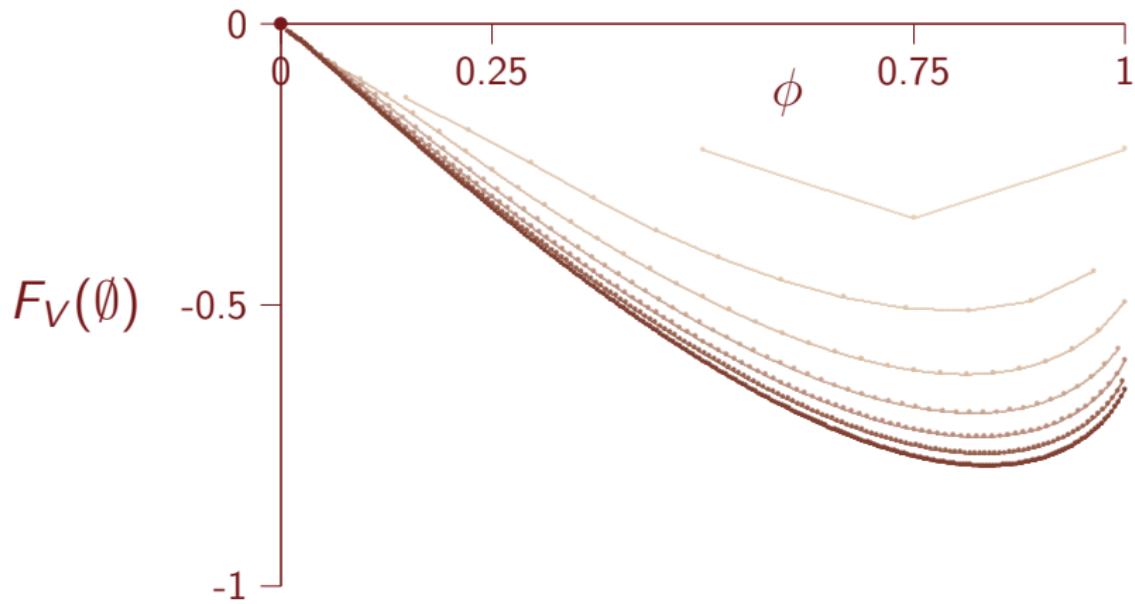
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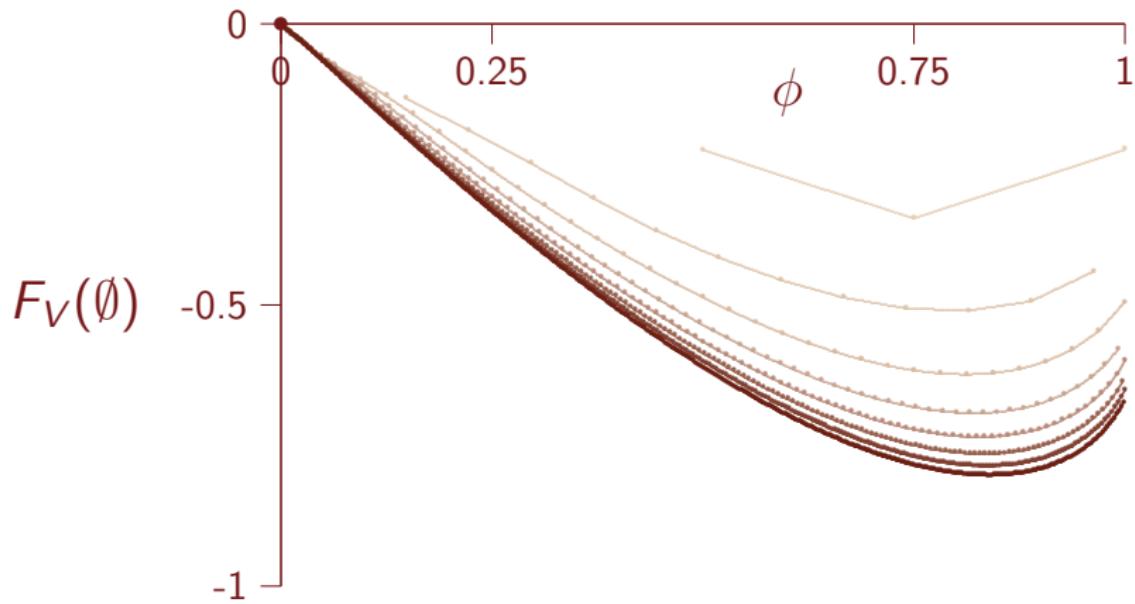
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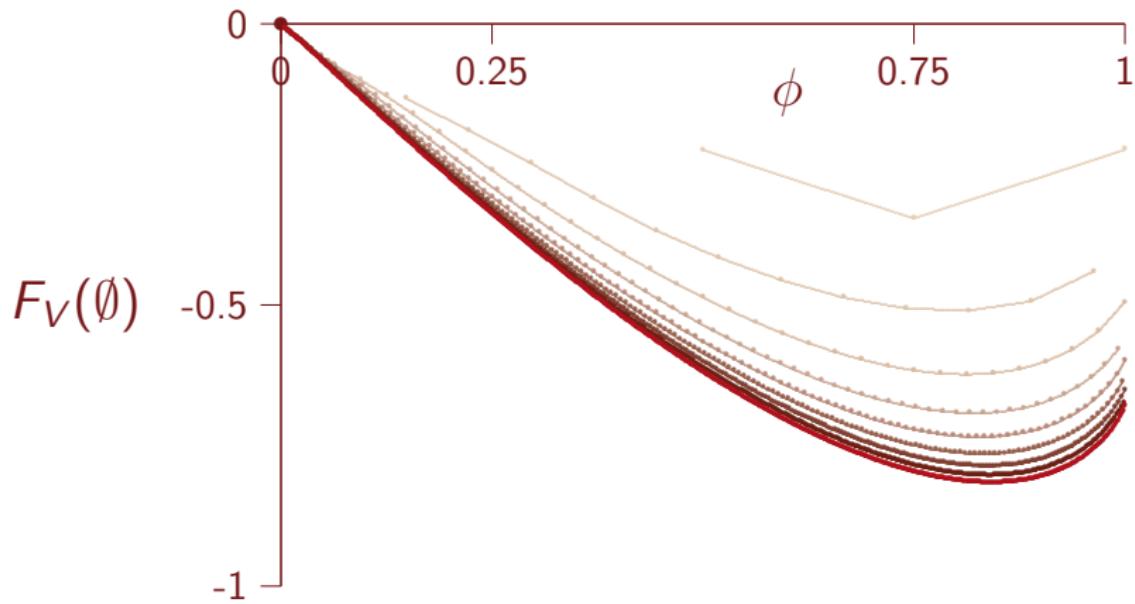
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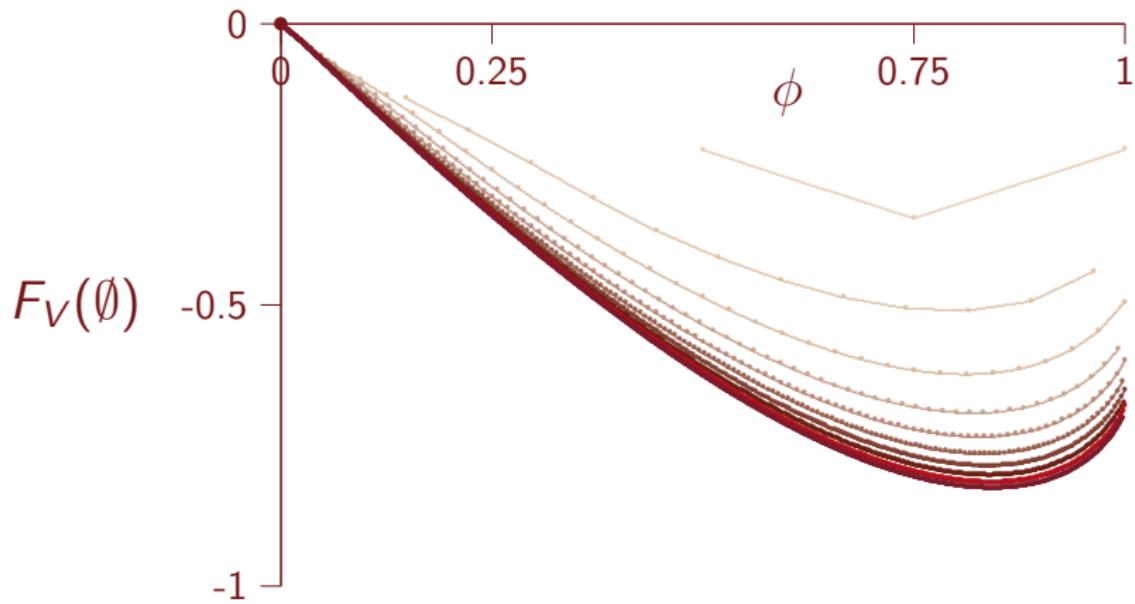
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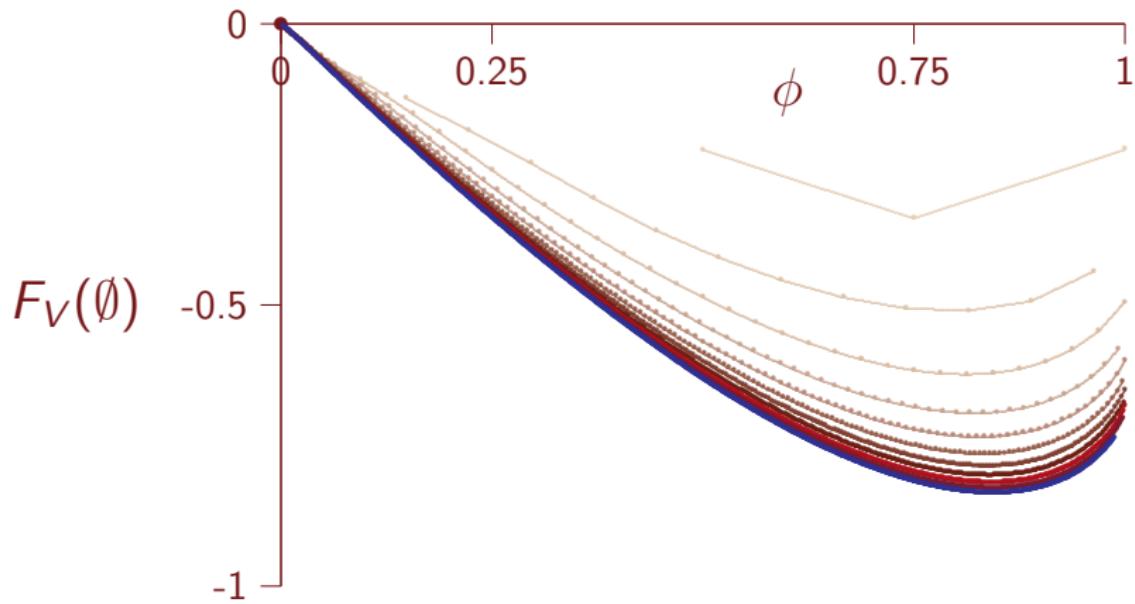
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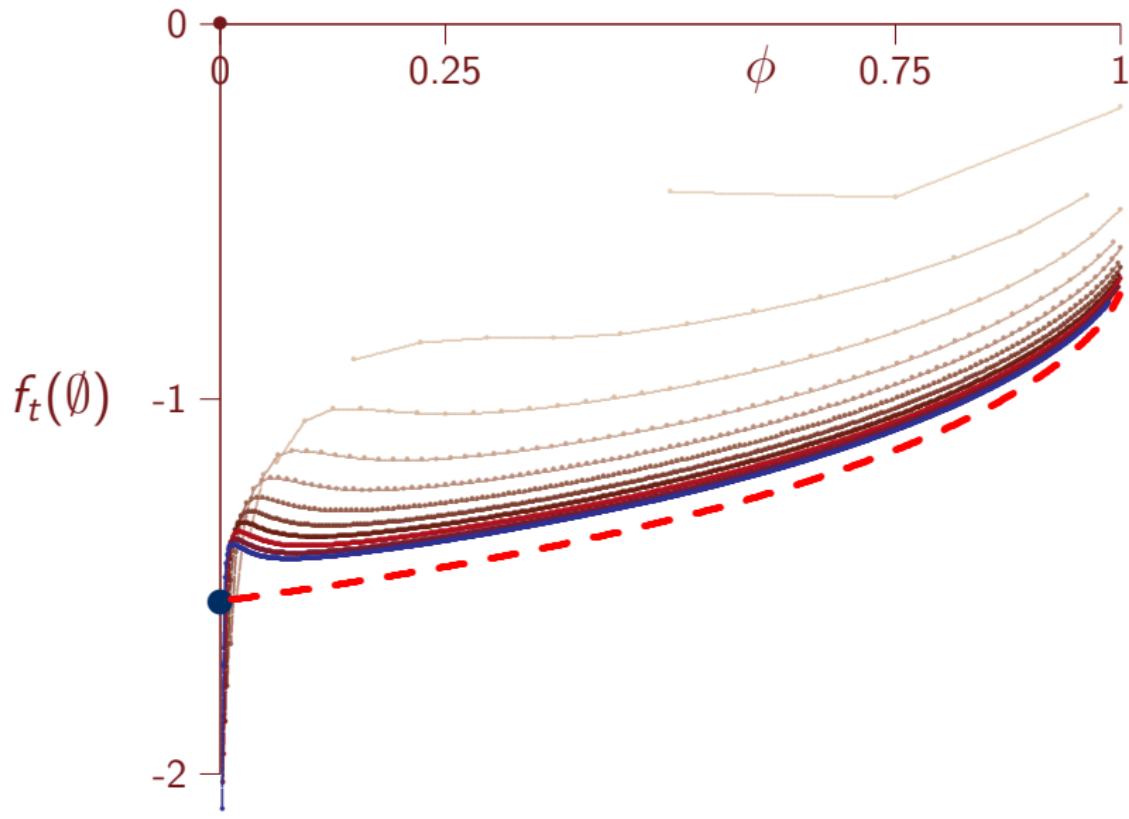
Free energy F_V per unit volume (unknot)



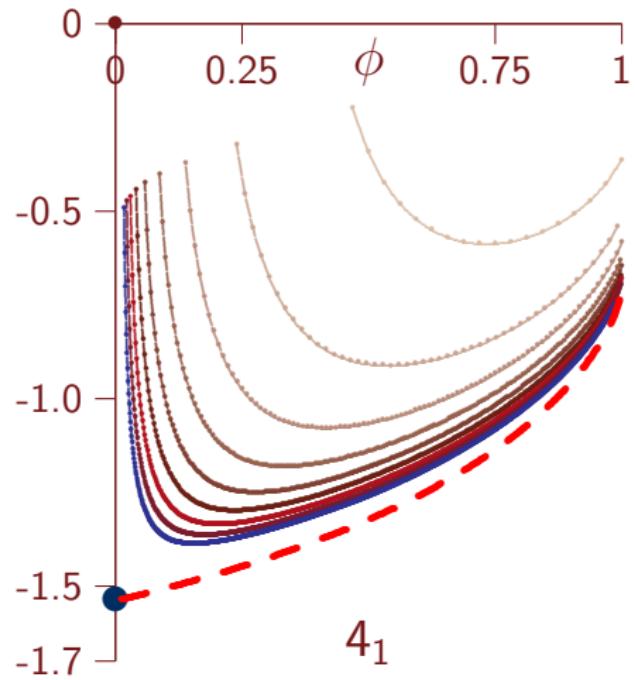
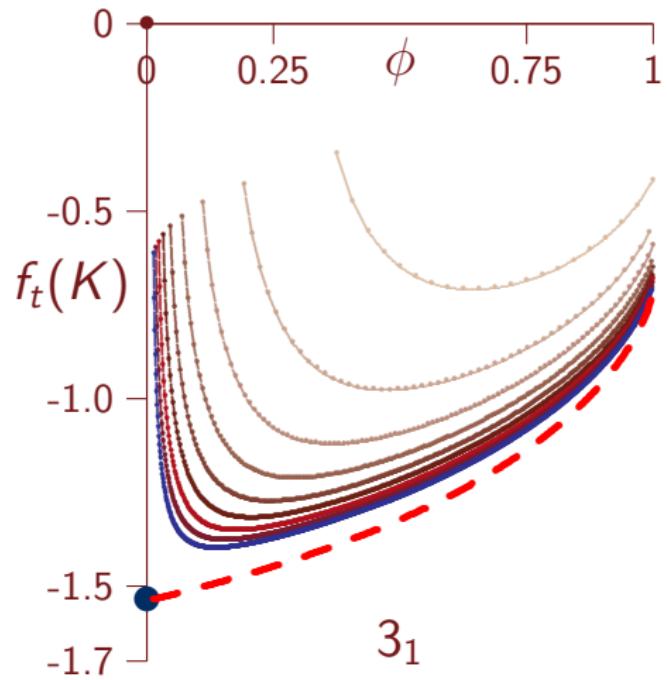
Free energy F_V per unit volume (unknot)



Free energy f_t per unit length (unknot)



Free energy f_t per unit length (3_1 and 4_1)



Flory interaction parameter χ

Estimate an effective value by fitting $f_t = a_0 + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi\phi$

L	χ_{01}	χ_{31}	χ_{41}
3	0.4265	—	—
4	0.3530	0.6906	0.8784
5	0.3046	0.4482	0.5115
6	0.2748	0.3564	0.3886
7	0.2561	0.3053	0.3265
8	0.2437	0.2760	0.2895
9	0.2370	0.2569	0.2686
10	0.2320	0.2471	0.2531
11	0.2260	0.2383	0.2450
12	0.2220	0.2325	0.2370

Table: Estimated Flory interaction parameters from f_t

$$\chi = 0.18 \pm 0.03$$

Osmotic pressure

- Total free energy: $F_{total} = V F_V$
- Osmotic Pressure

$$\Pi = -\frac{d}{dV} F_{total}$$

Osmotic pressure

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$$\Pi = -\frac{d}{dV} F_{total} = \phi^2 \frac{\partial}{\partial \phi} \left(\frac{1}{\phi} F_V \right) = \phi^2 \frac{\partial}{\partial \phi} \left(\frac{1}{\phi} F_{mix} \right)$$

- Flory-Huggins expression

$$\Pi = \frac{1}{V} - \log(1 - \phi) - \phi - \chi \phi^2.$$

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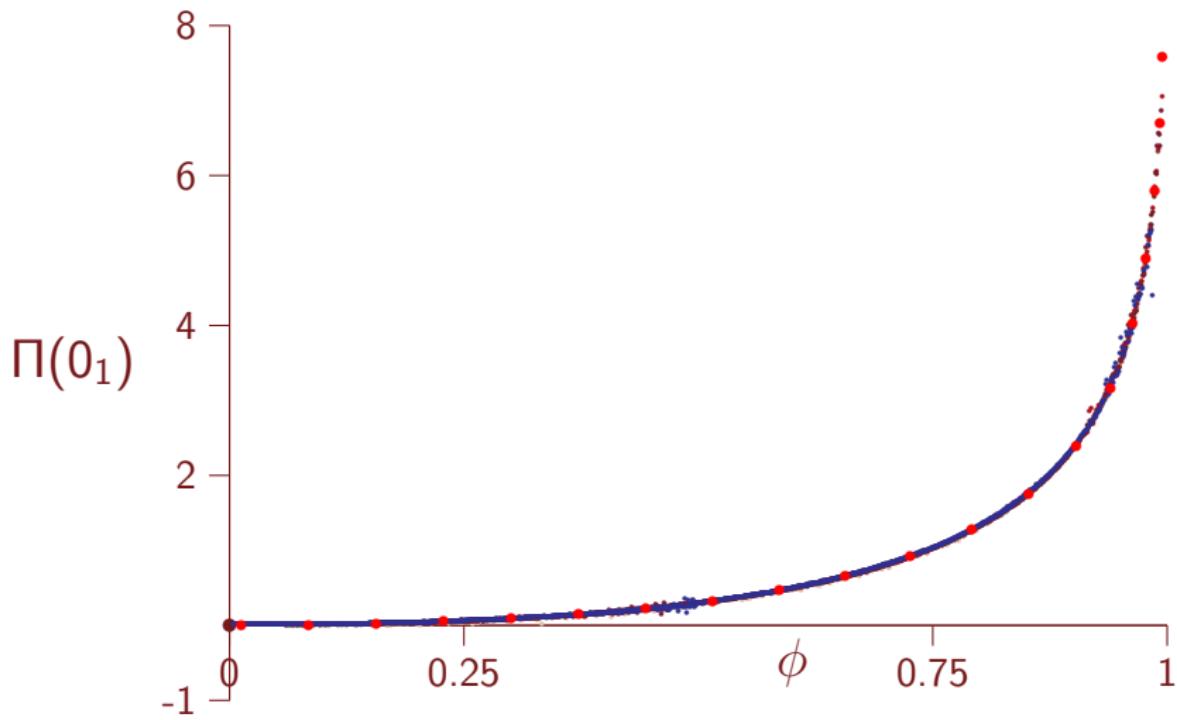
$$\Pi = \frac{1}{V} - \log(1 - \phi) - \phi - \chi \phi^2.$$

- This does not work well, modify to

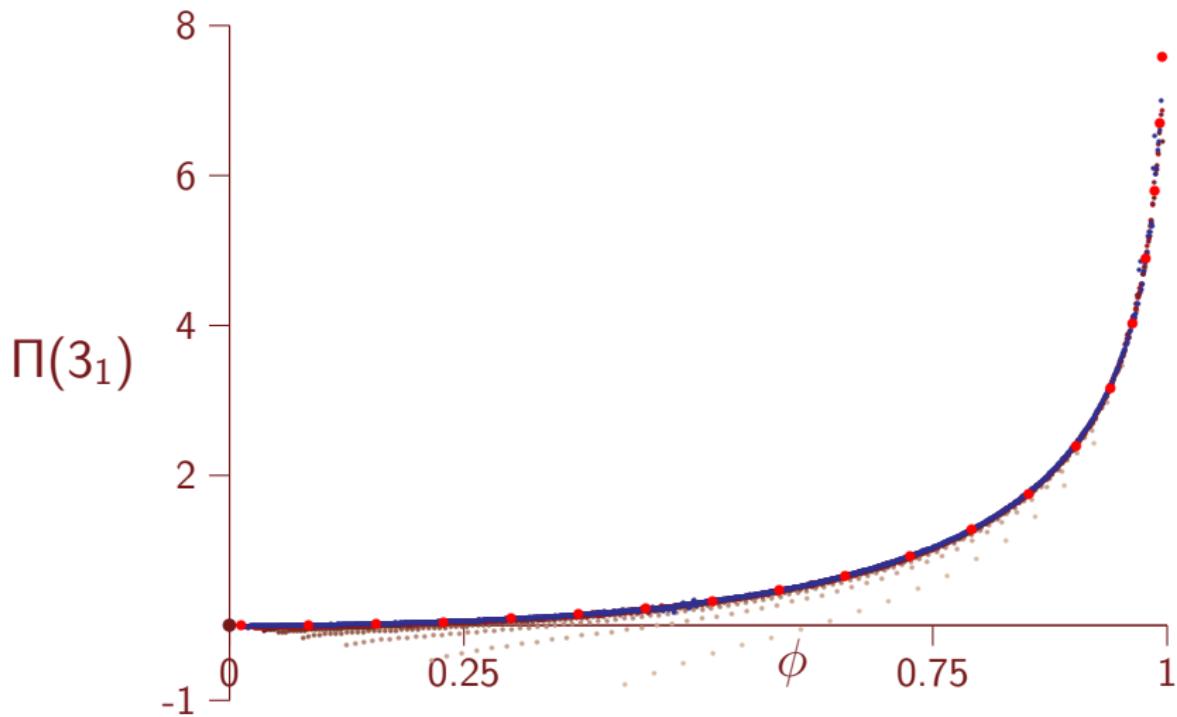
$$\Pi = -\alpha (\log(1 - \phi) + \phi) - \chi \phi^2$$

- $\alpha = 1.78\dots$

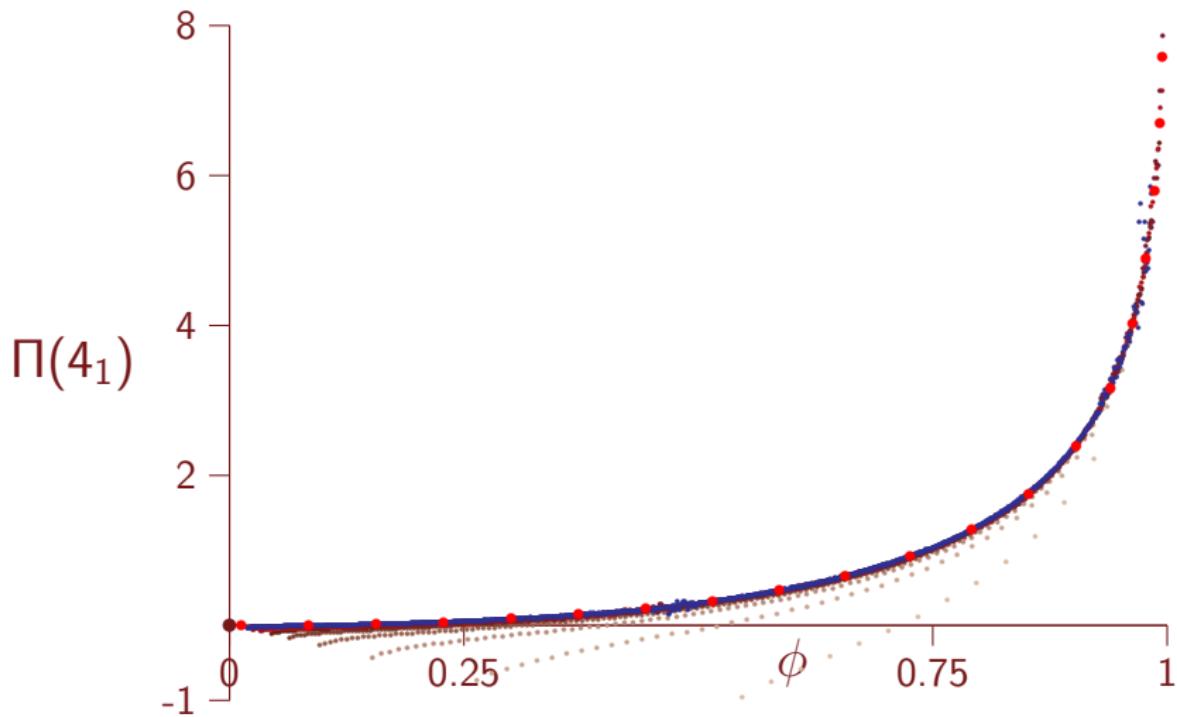
Osmotic pressure $\Pi(0_1)$



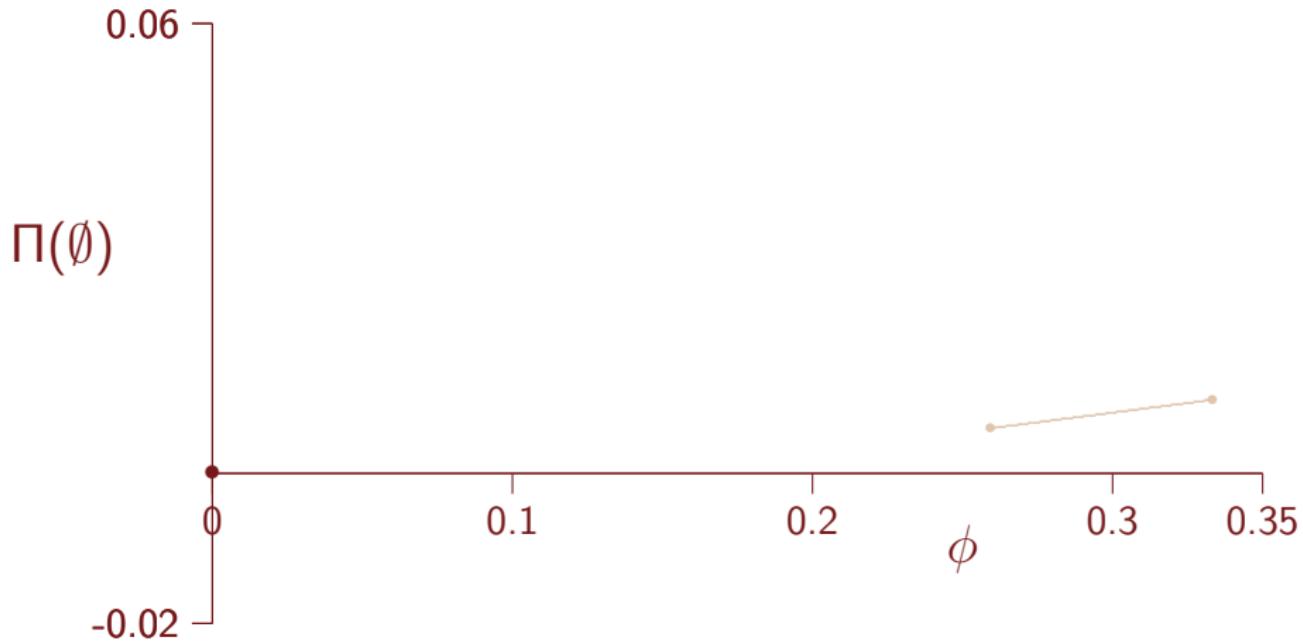
Osmotic pressure Π (3_1)



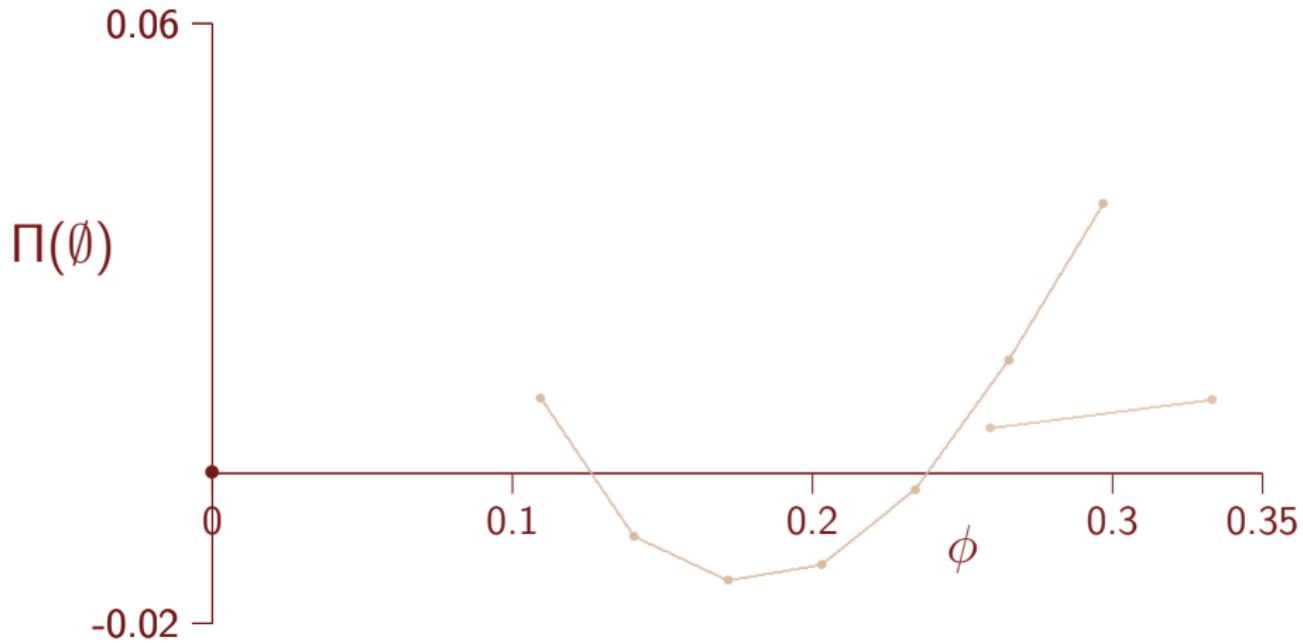
Osmotic pressure Π (4_1)



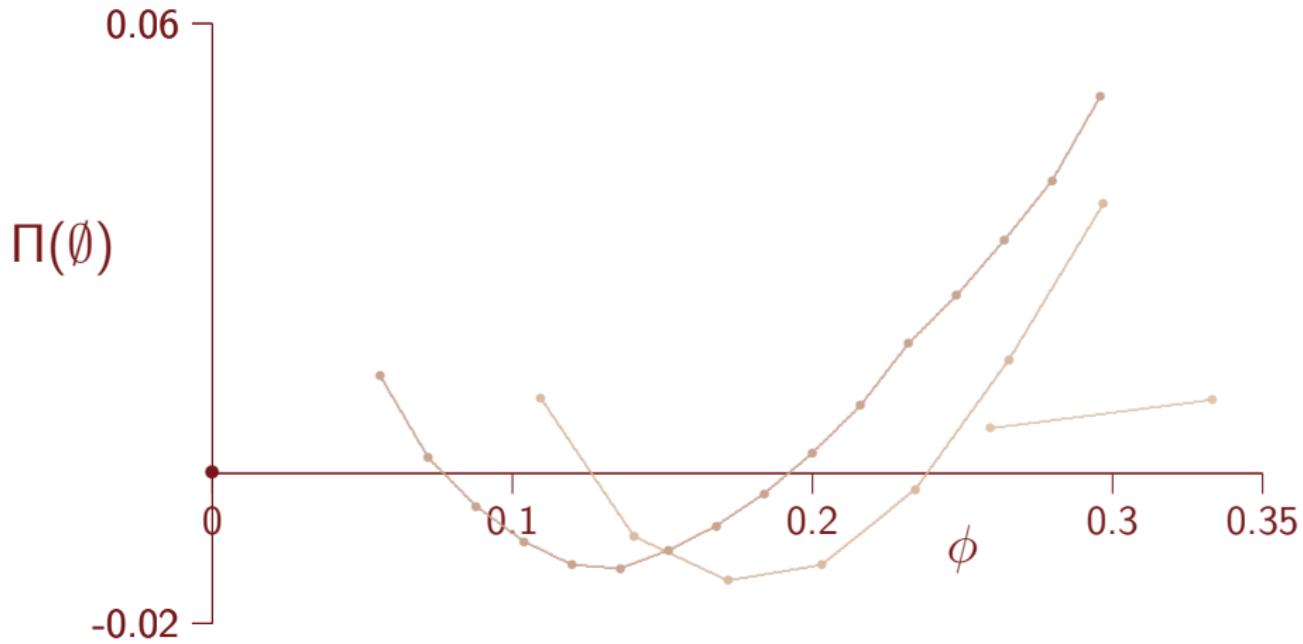
Low concentration osmotic pressure – unknot



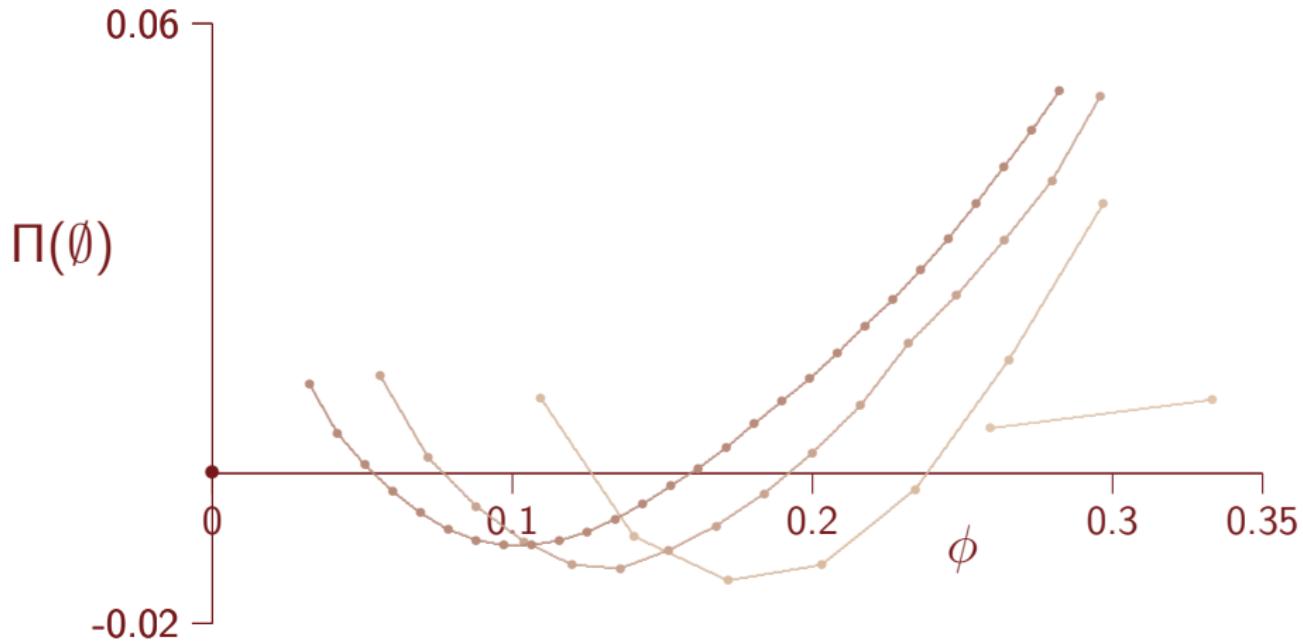
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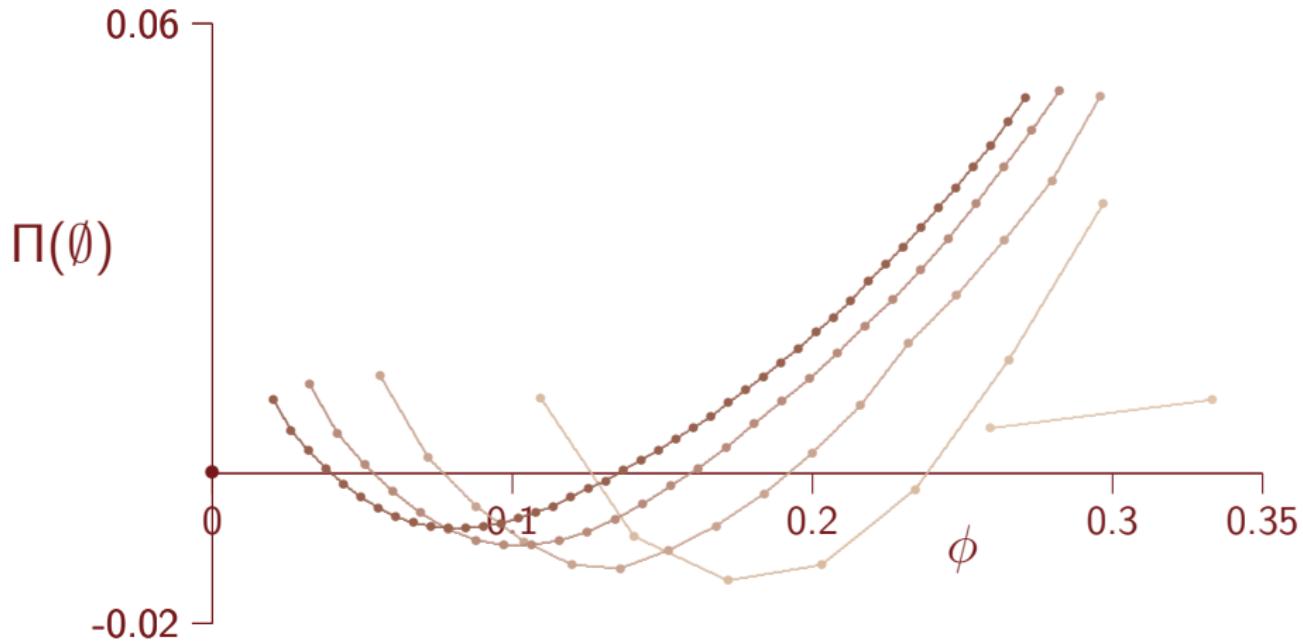
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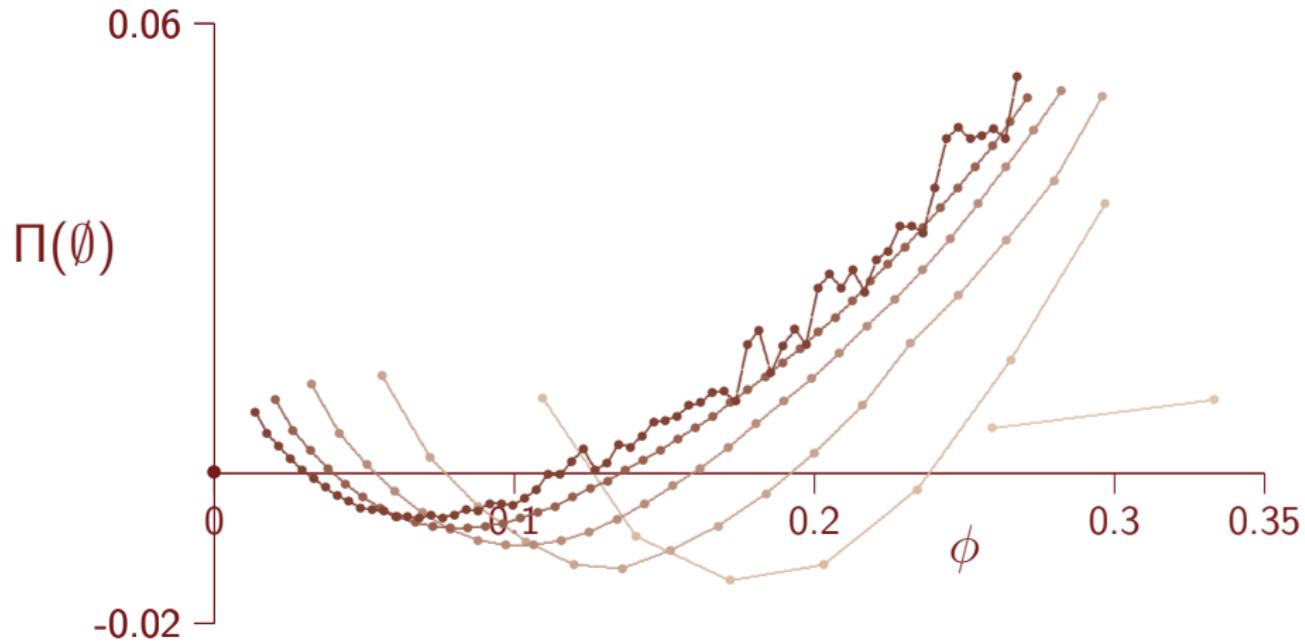
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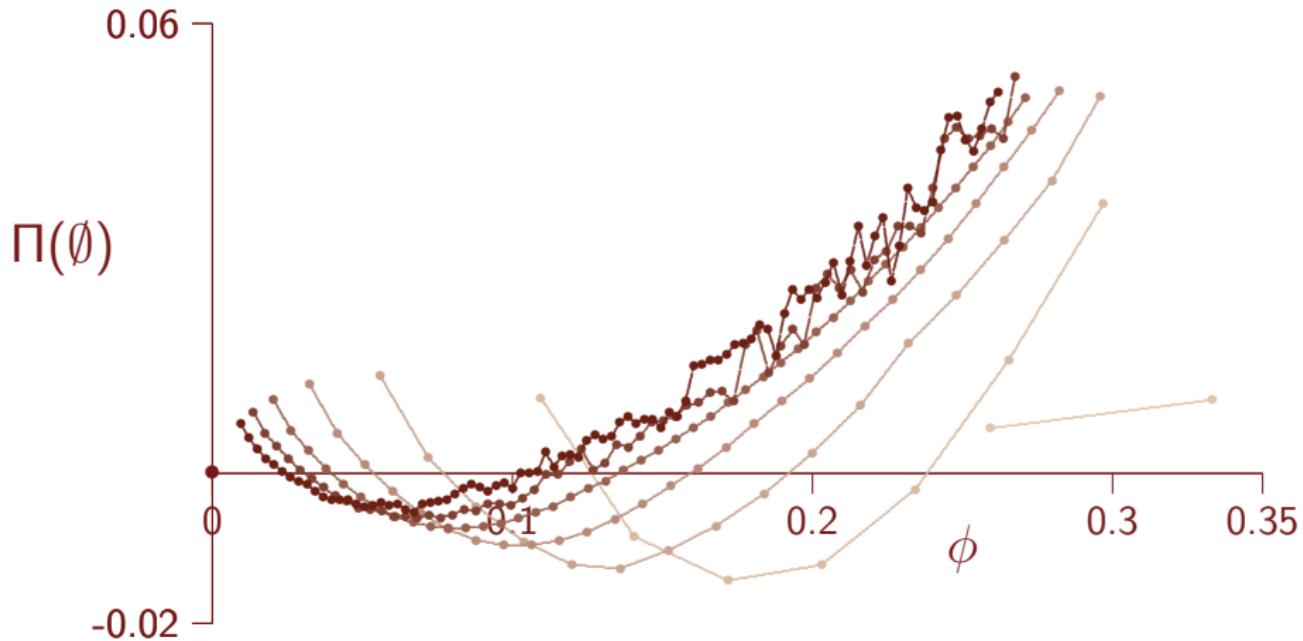
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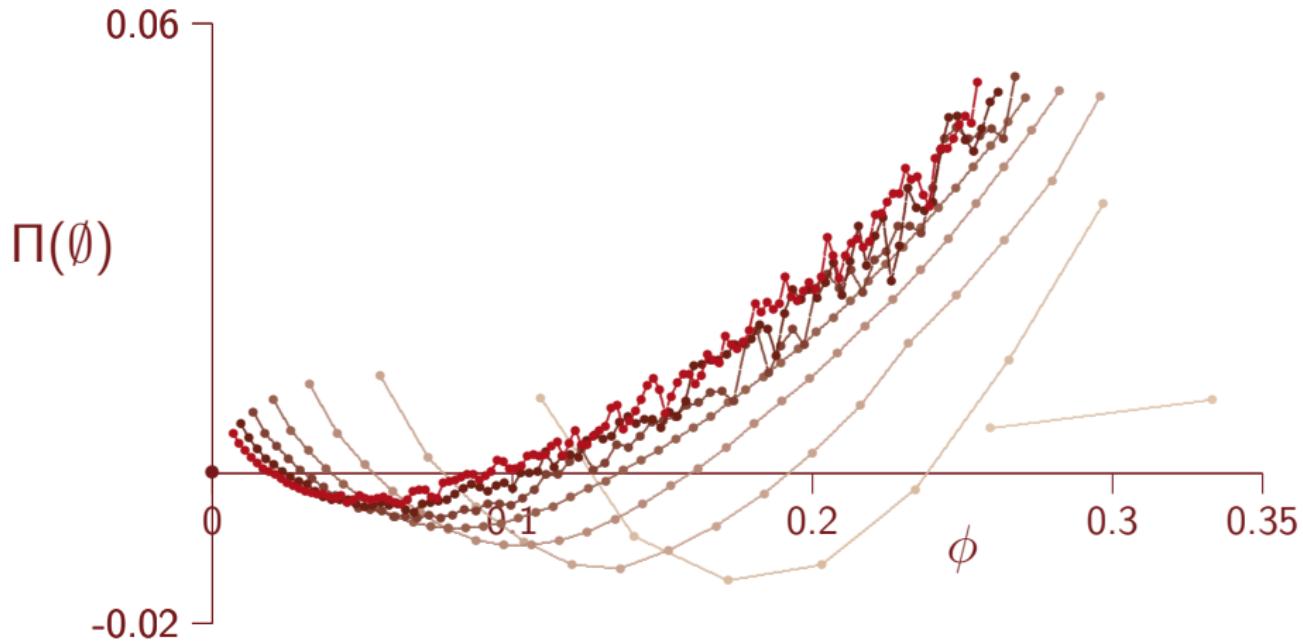
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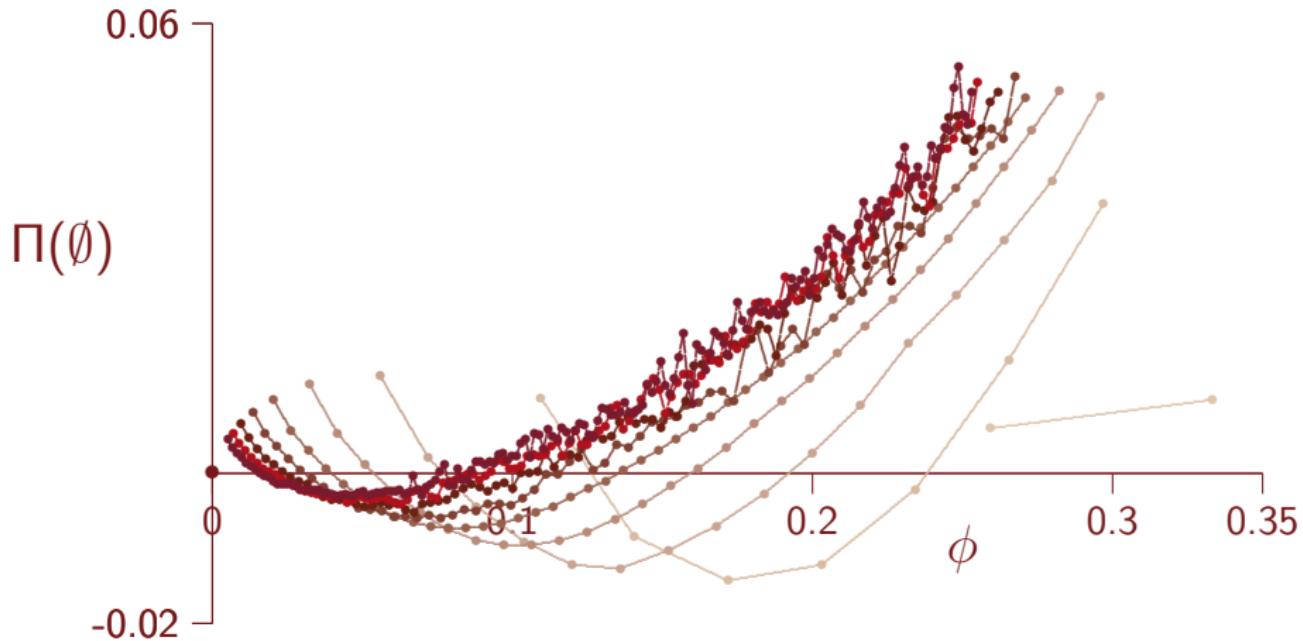
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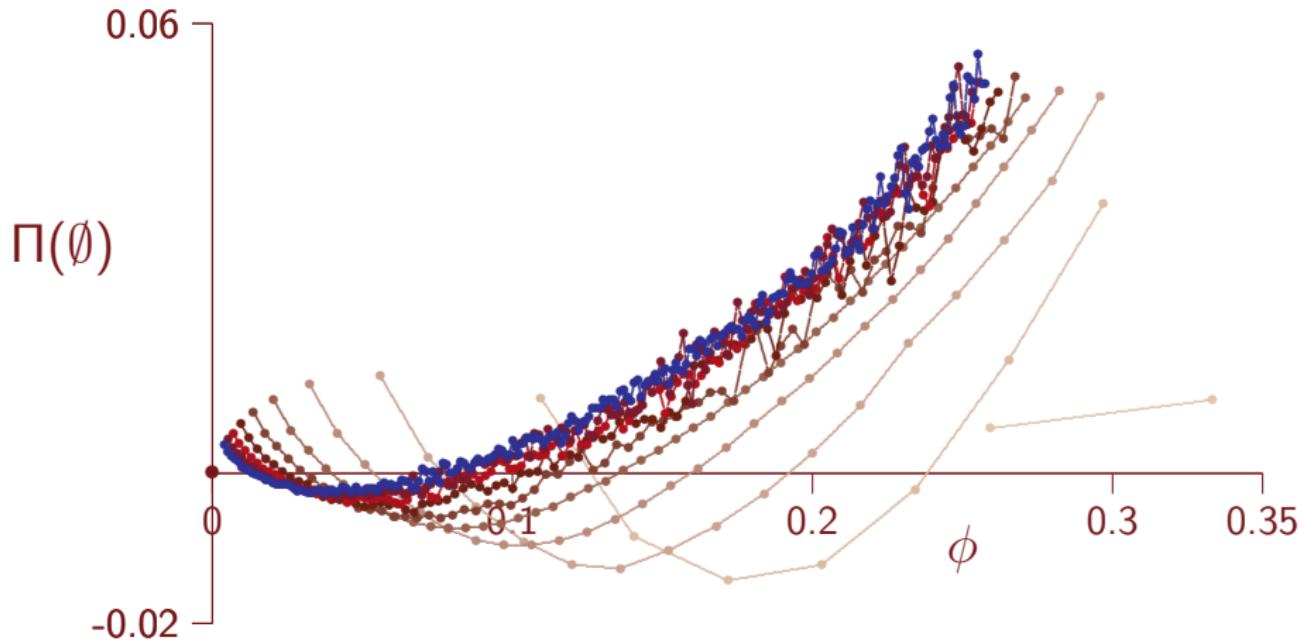
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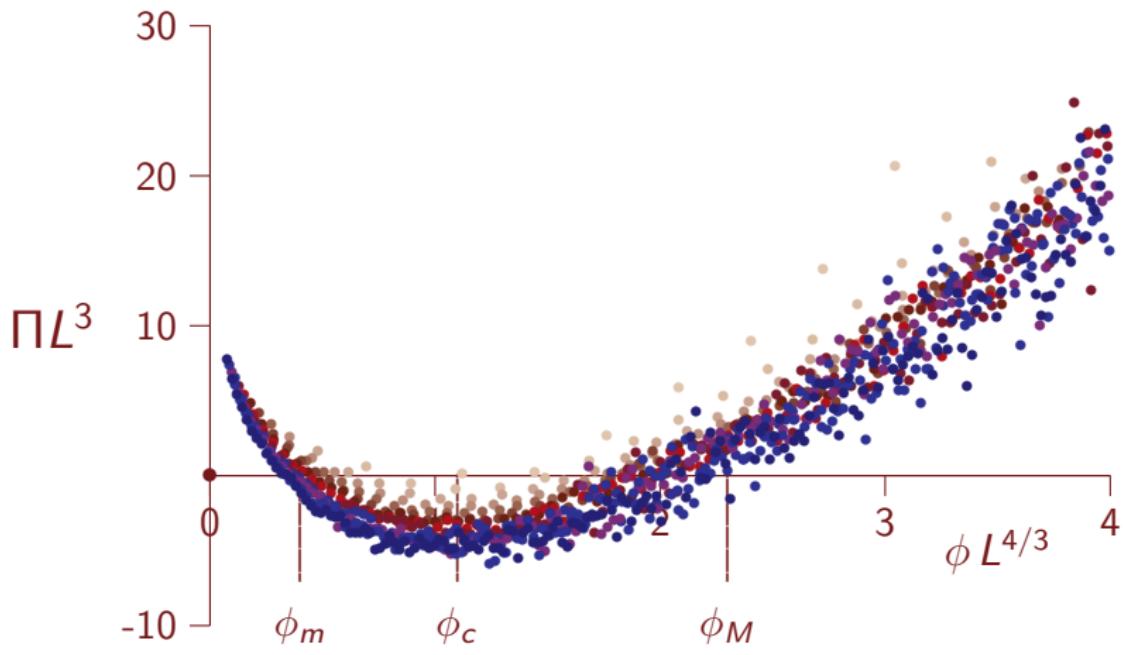
- At low concentration the osmotic pressure is negative
- Size S of a lattice knot of length $N \ll L$:

$$S = O(N^\nu)$$

- It touches walls of its confining cube when $S = O(L)$, or when $N = O(L^{1/\nu})$
- Concentration where this happens is

$$\phi_0 = \frac{1}{V} O(L^{1/\nu}) \sim L^{1/\nu - 3} = L^{-4/3}, \quad (\text{Flory value: } \nu = \frac{3}{5})$$

- Since $\Pi V = O(1)$ for $\phi \rightarrow 0^+$, plot ΠL^3 against $\phi L^{4/3}$

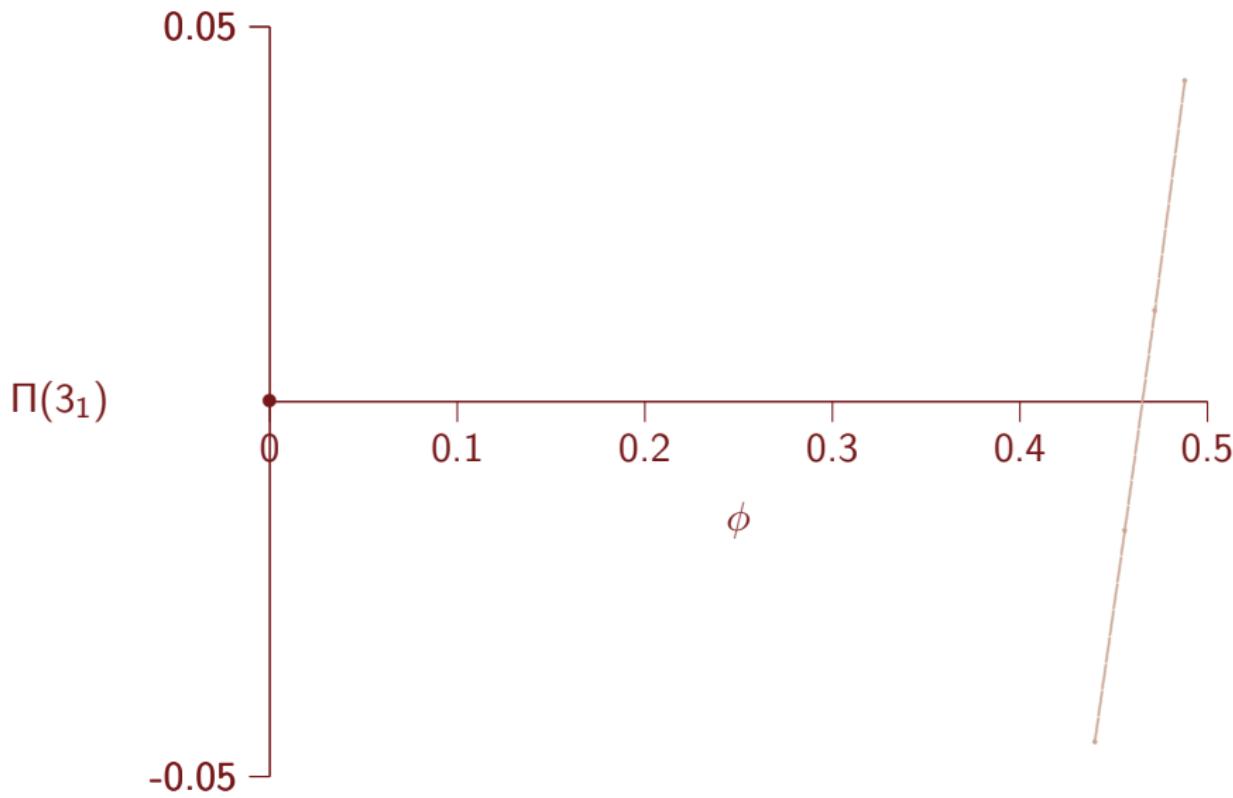


$$\phi_m L^{4/3} \simeq 0.37$$

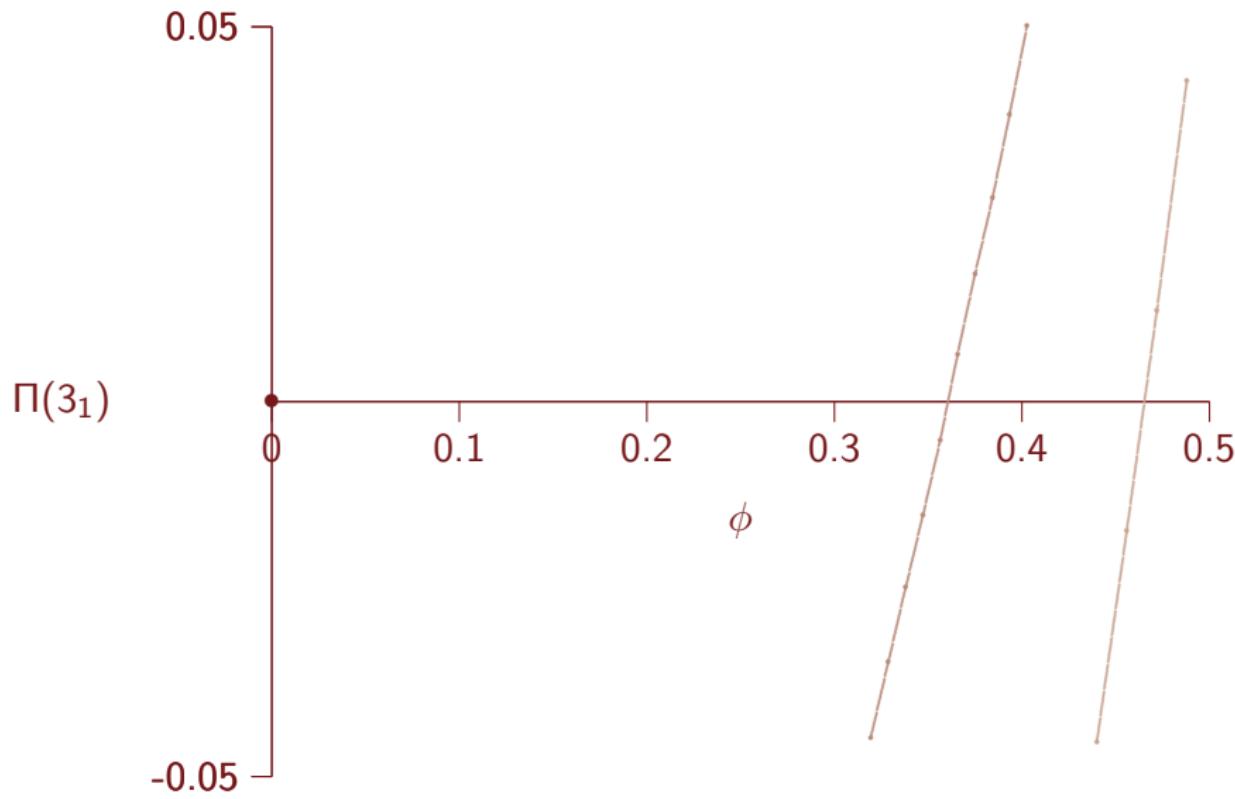
$$\phi_c L^{4/3} \simeq 1.1$$

$$\phi_M L^{4/3} \simeq 2.3$$

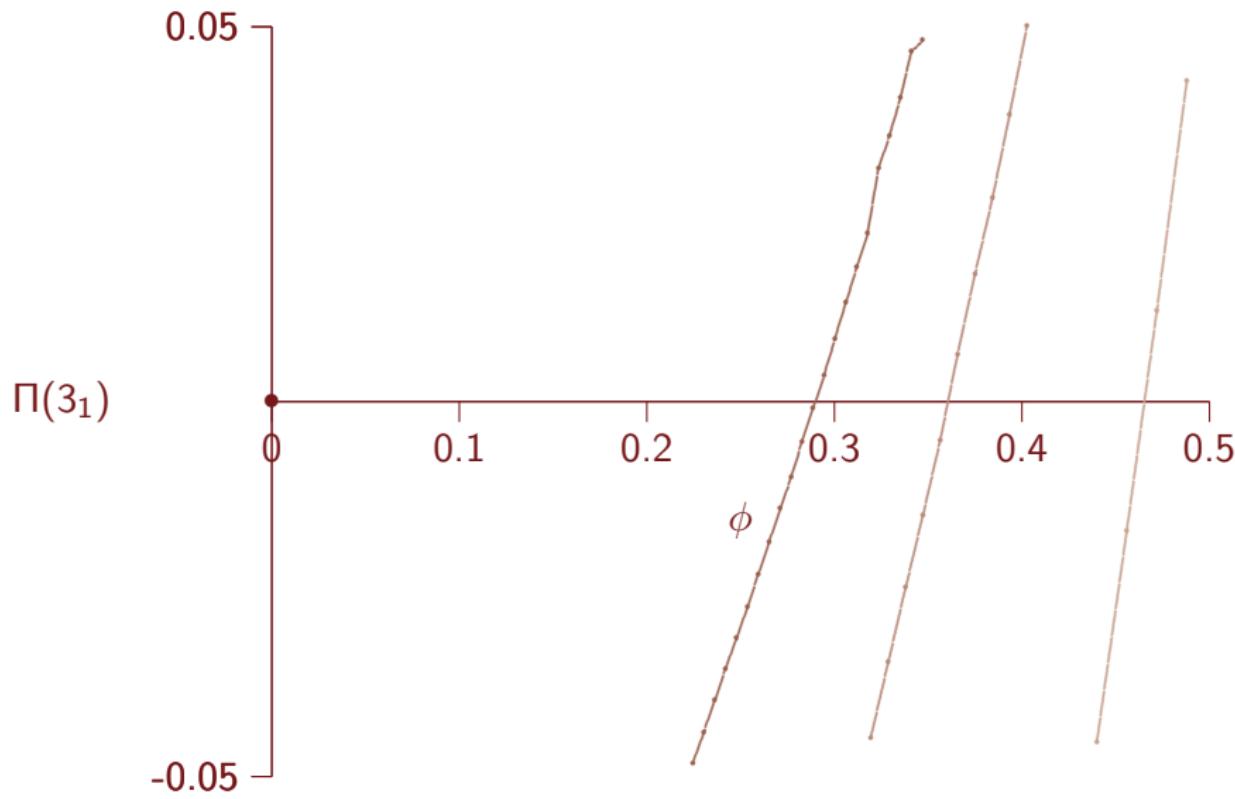
Low concentration osmotic pressure – trefoil



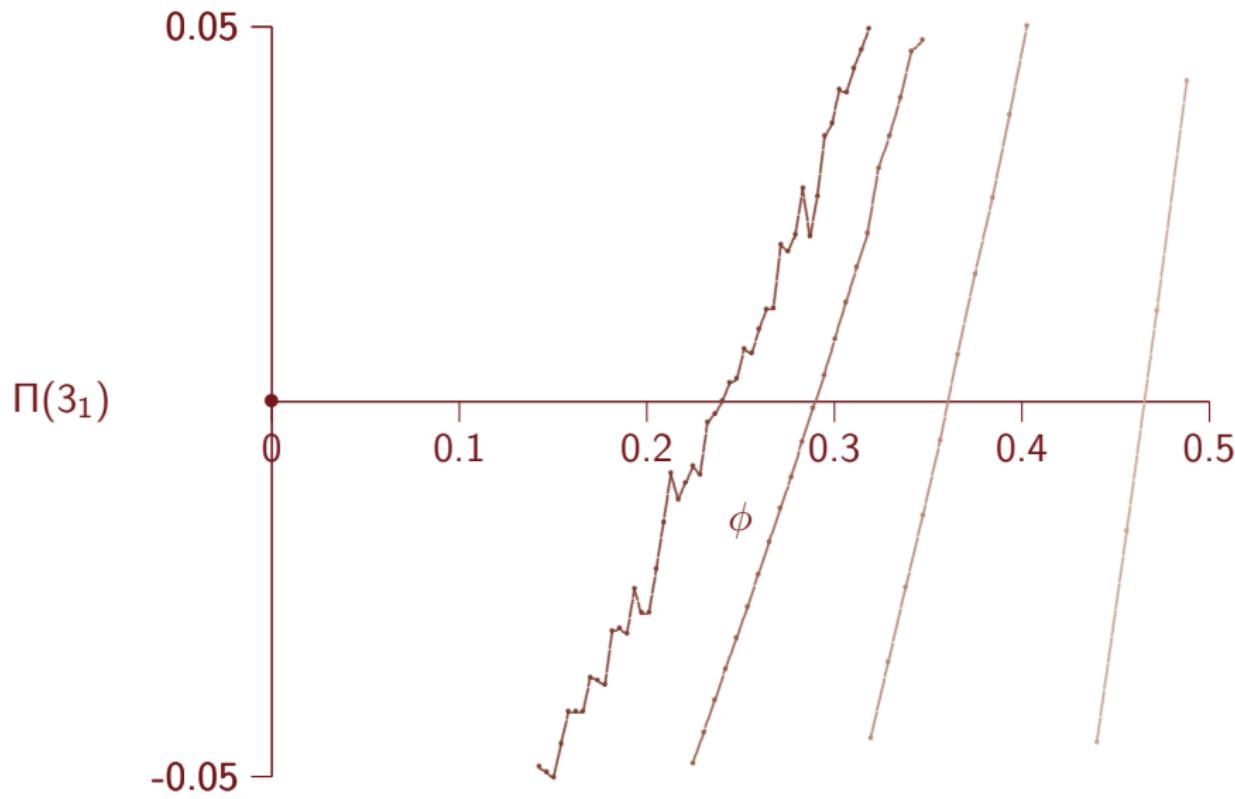
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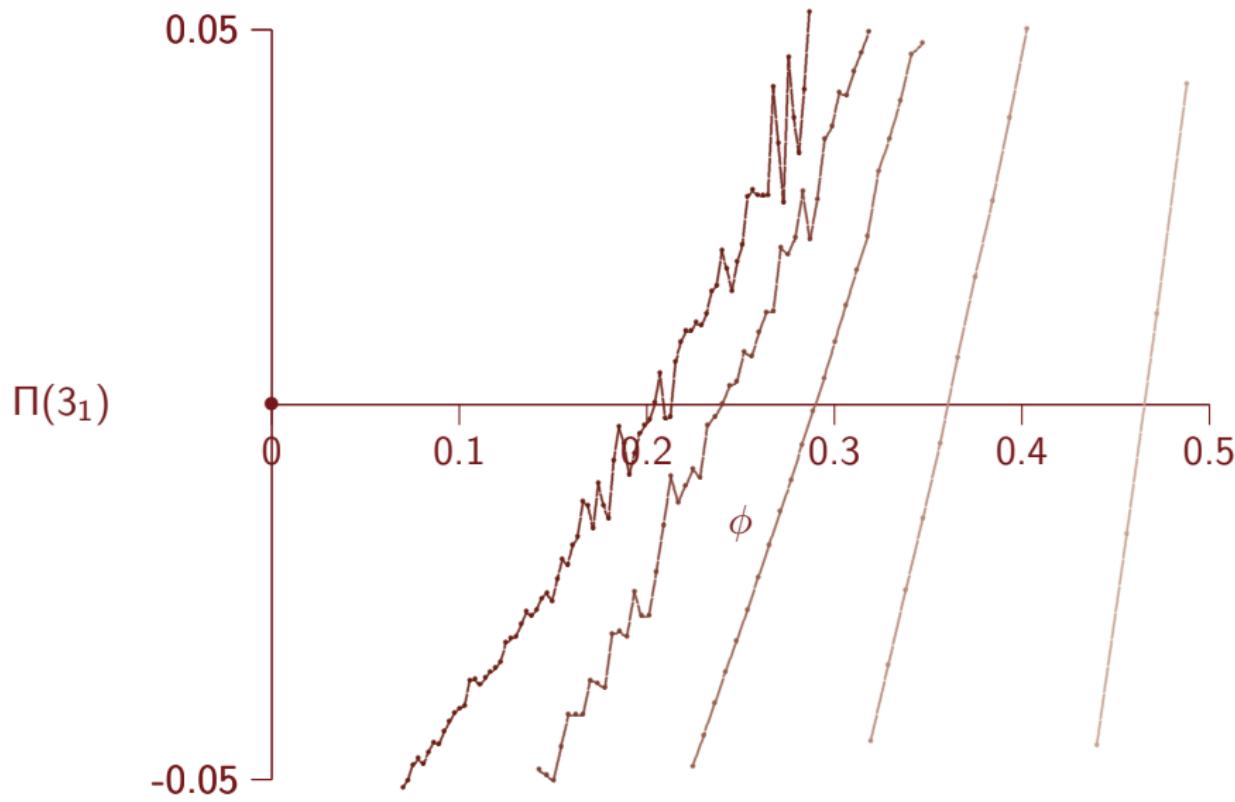
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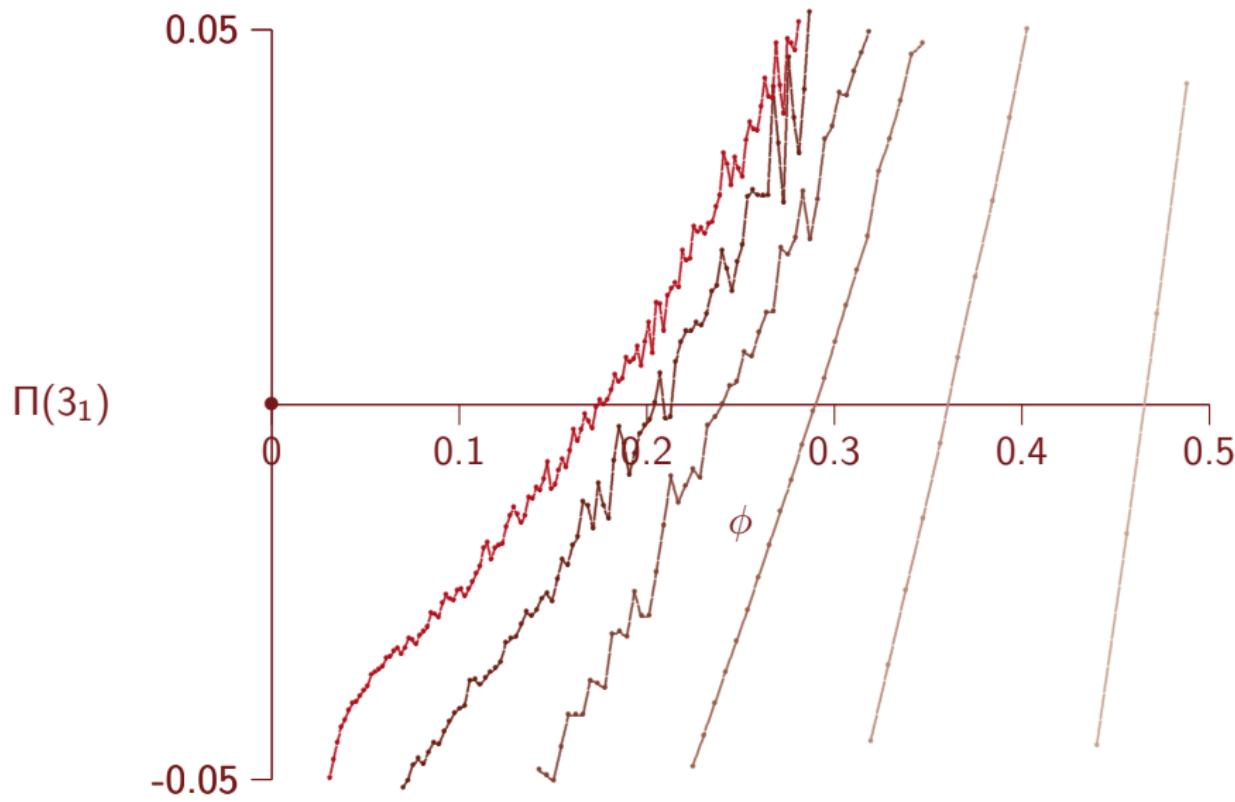
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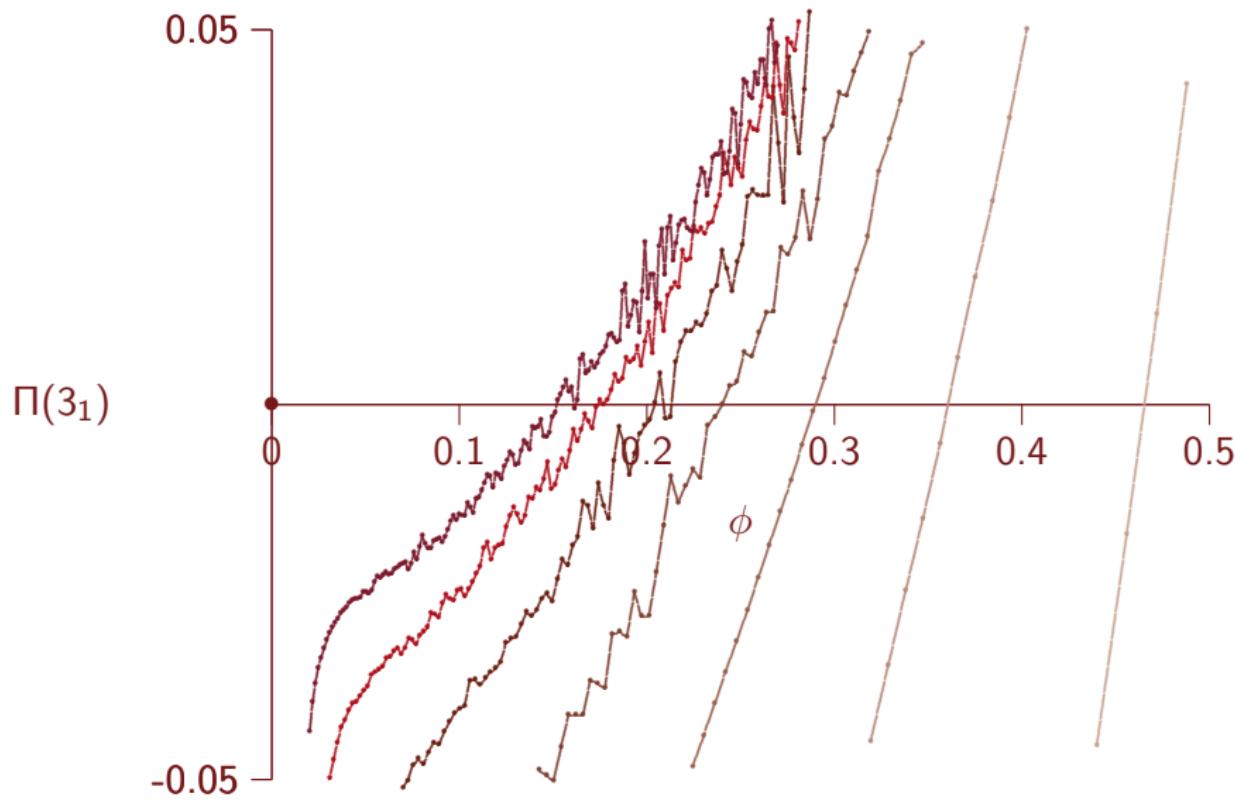
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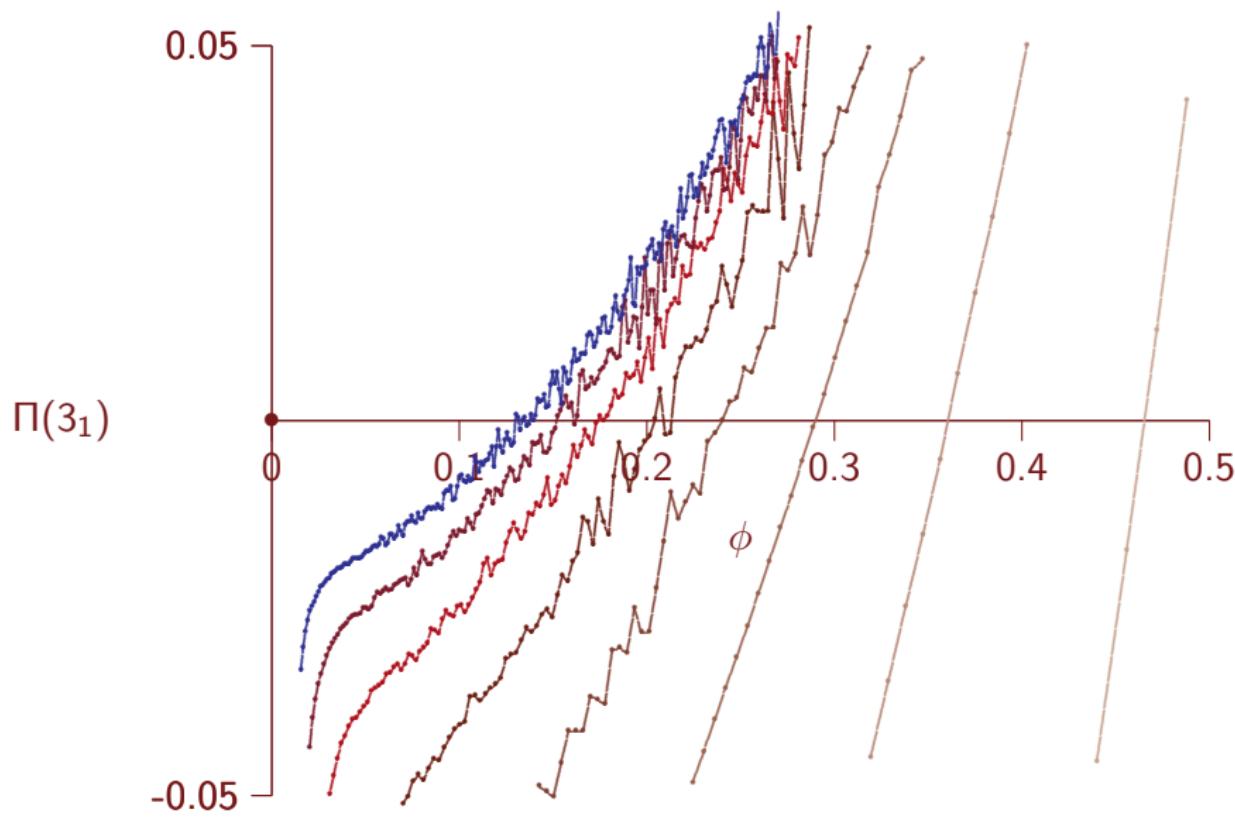
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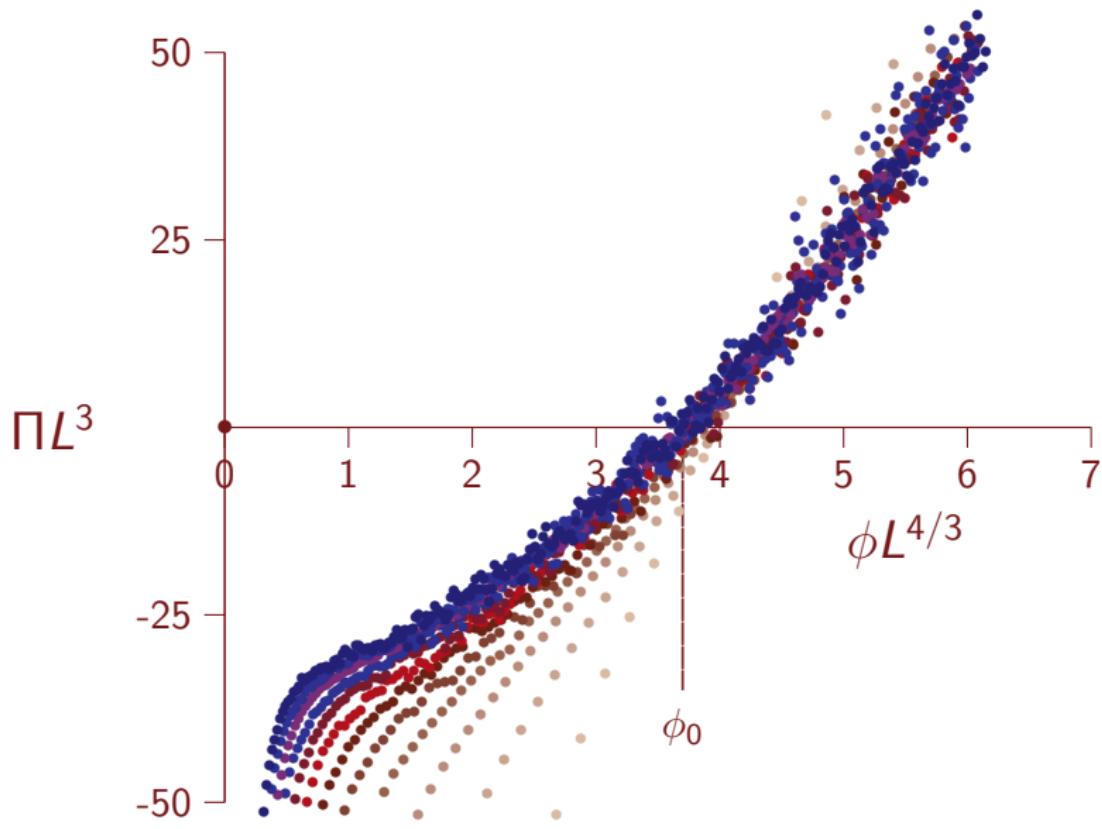


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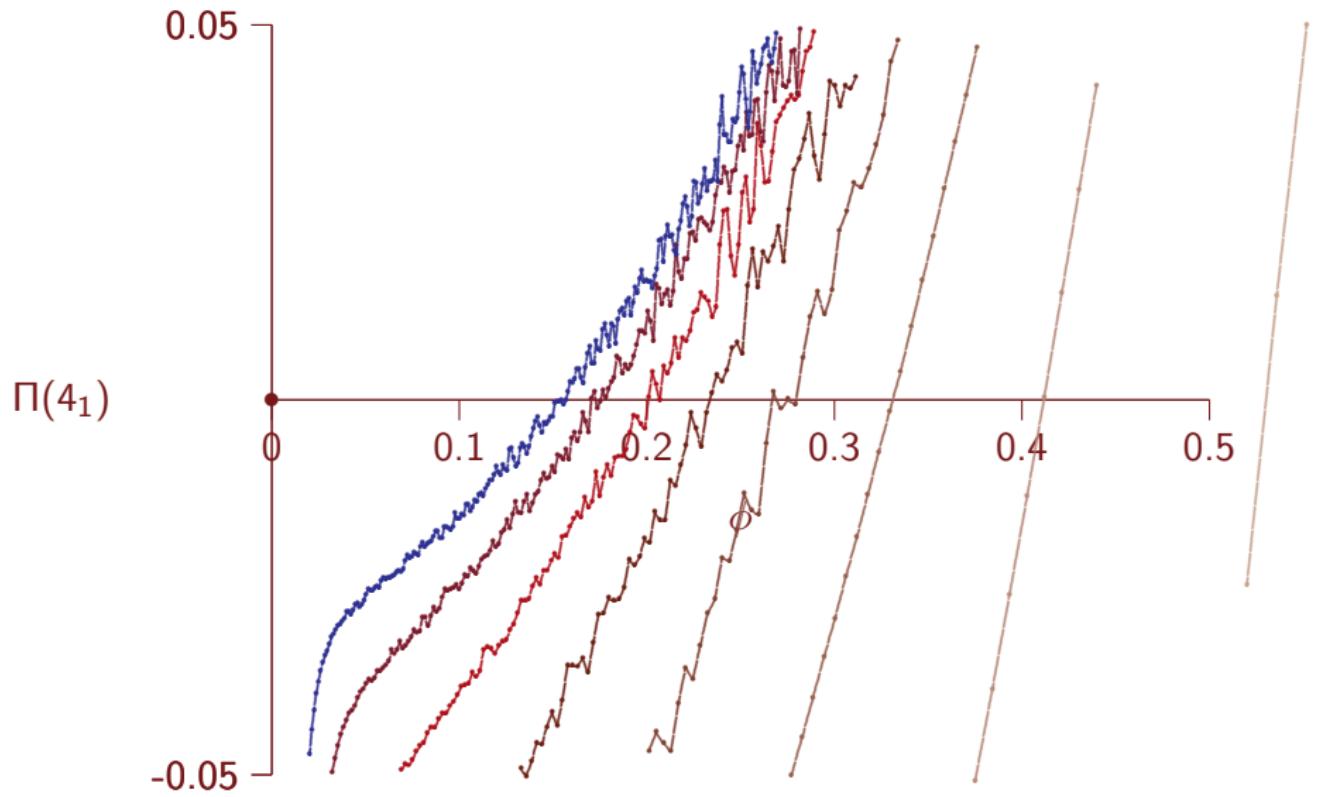
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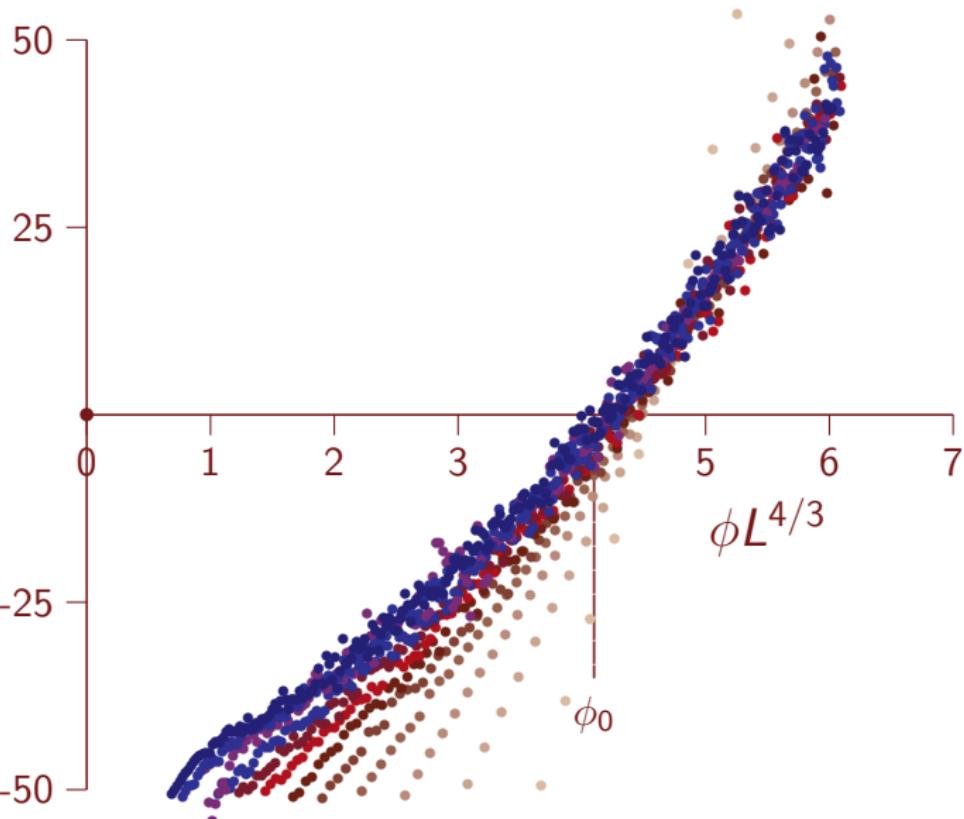


$$\phi_0 L^{4/3} \simeq 3.7$$

Low concentration osmotic pressure – figure eight



$$\Pi L^3$$



$$\phi_0 L^{4/3} \simeq 4.1$$

Conclusions

- Flory-Huggins model of F_V for confined compressed lattice knots
 - Flory interaction parameter for confined knots in 3d: $\chi = 0.18 \pm 0.03$
 - Low concentration osmotic pressure is knot type dependent
-
- Thanks Claus and Yuanan!