

Introduction to Polymer Physics
Day 2 – afternoon

Polymer Solutions (chapter 5)

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1

Polymer solutions: θ -temperature

For solutions we obtain:

$$\Pi = \frac{k_B T}{b^3} \left[\frac{\phi}{N} + \frac{\phi^2}{2} (1 - 2\chi) + \frac{\phi^3}{3} + \dots \right]$$

Near the θ -temperature (as discussed in chapter 3):

$$v = (1 - 2\chi) b^3 \approx \left(1 - \frac{\theta}{T} \right) b^3$$

At the θ -temperature:

$$T = \theta \quad \chi = \frac{1}{2} \quad v = 0$$

2

Phase diagram for solutions

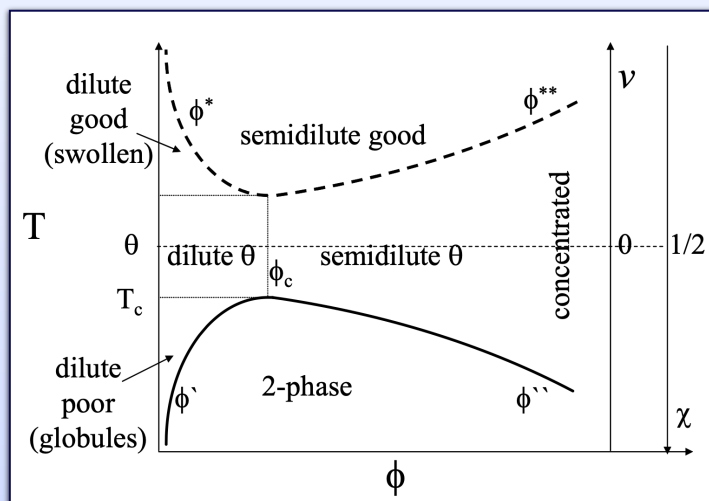
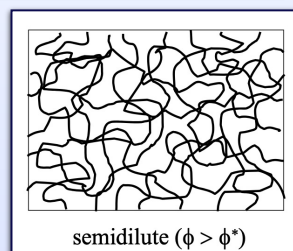
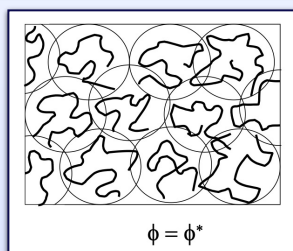
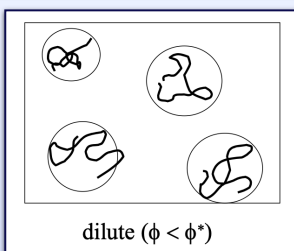


image: Rubinstein&Colby

3

Near the θ -temperature



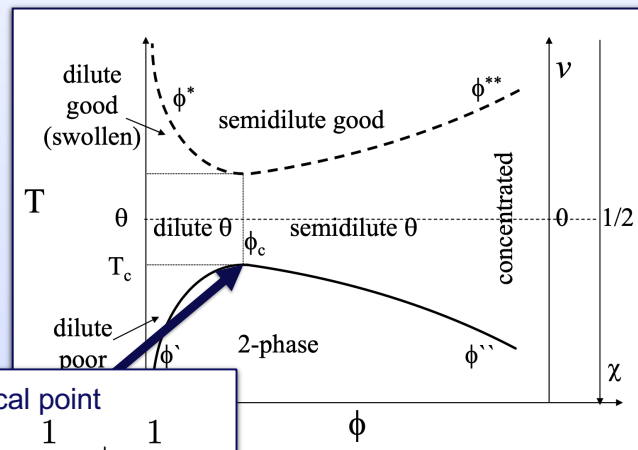
$$\phi^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}}$$

Chains remain ideal as long as they are smaller than thermal blobs:

$$T \approx \theta \left(1 \pm \frac{1}{\sqrt{N}} \right)$$

4

Below the θ -temperature: demixing



Critical point

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N}$$

$$T_c = ???$$

Long polymers

For large N all of the following temperatures are close together

- θ -temperature: no net effect from pair interactions
- temperature where chains start deviating from ideal conformation
- critical temperature for phase separation

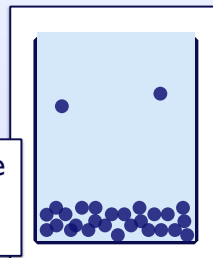
Well below T_c : phase separation

Chain conformation: collapsed globule

Flory-Huggins: $\phi' \approx 0$

Flory-Huggins works poorly in the dilute phase because

- density variations are huge
- the overlap parameter is tiny



In the dense sediment: $\phi'' \approx (2\chi - 1) = -\frac{v}{b^3}$

Inside the globules in the dilute supernatant:

$$\phi'' \approx (2\chi - 1) = -\frac{v}{b^3} \gg \phi'$$

Important aside: Polymer Melts

$$v = \left(\frac{1}{N_B} - 2\chi \right) b^3$$

In a blend of two chemically identical polymers of different lengths:

$$\chi = 0 \implies v = \frac{b^3}{N_B}$$

Flory's ideality hypothesis
Chains in a melt are nearly ideal

Phase diagram for solutions

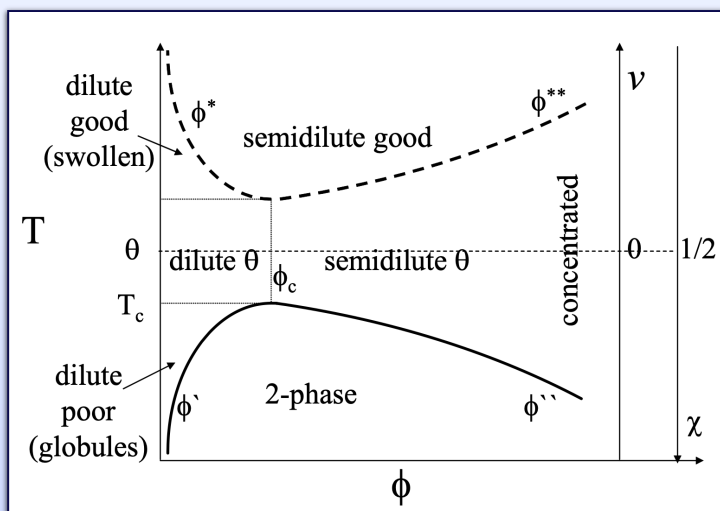
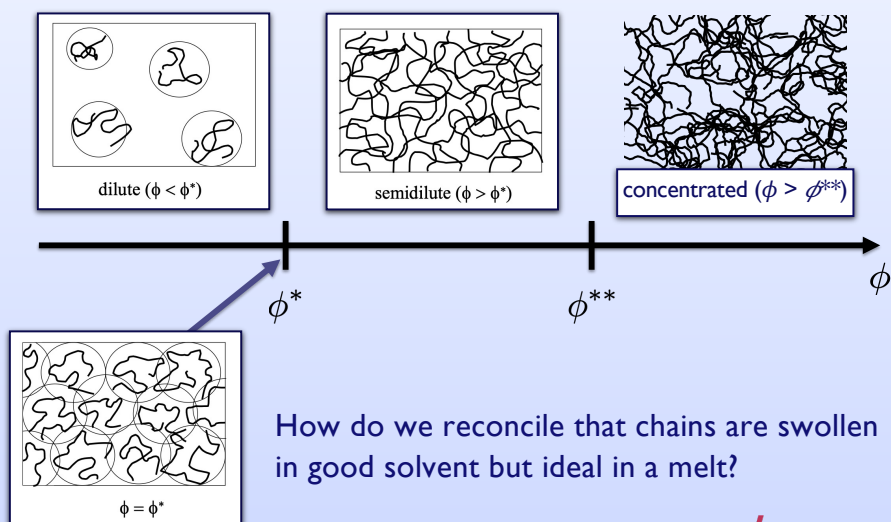


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10

Three concentration regimes (good solvent)



How do we reconcile that chains are swollen in good solvent but ideal in a melt?

image: Rubinstein&Colby

11

Overlap concentration (good solvent)

Ideal chains start overlapping at

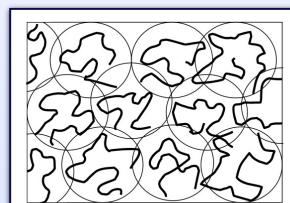
$$\phi^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}}$$

In good solvents, chains swell to

$$R \approx \xi_T \left(\frac{N}{g_T} \right)^\nu \approx b \left(\frac{v}{b^3} \right)^{2\nu-1} N^\nu$$

so that

$$\phi^* \approx \frac{Nb^3}{R^3} \approx \left(\frac{b^3}{v} \right)^{6\nu-3} N^{1-3\nu}$$



$\phi = \phi^*$

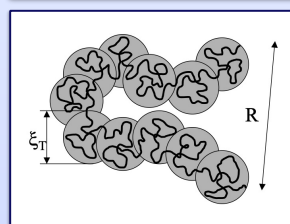


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ϕ^* depends more steeply on N : $1 - 3\nu \approx -0.76$

Correlations in semidilute good solutions

What happens when volume fraction is increased beyond overlap?

Think about...

- what drives swelling?
- what to expect as $\phi \rightarrow 1$?

New length scale:
correlation length ξ

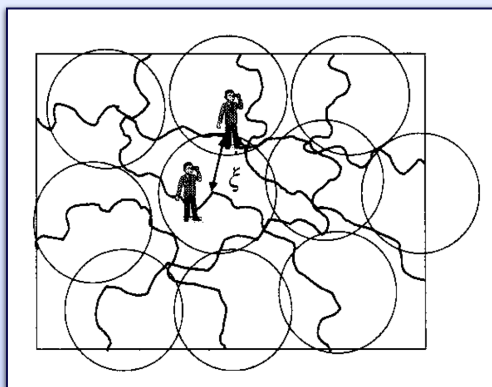


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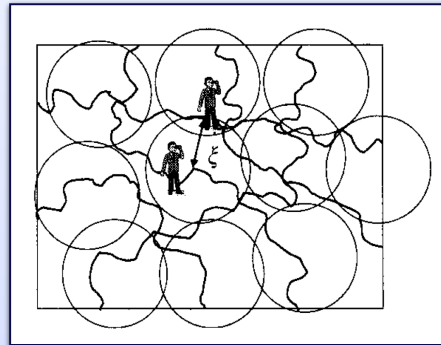
Beyond the correlation length

correlation length

$$\xi \sim \phi^{-\nu/(3\nu-1)} \approx \phi^{-0.76}$$

Swelling

“take up more space to have more distance between monomers”



Screening

“swelling doesn't serve any purpose if a chain also feels the monomers of other chains”

14

Screening in semidilute good solvents

screening of excluded volume interactions on scales beyond ξ

Conformation: random walk of correlation volumes:

$$\begin{aligned} R &\approx \xi \left(\frac{N}{g} \right)^{1/2} \\ &\approx b \left(\frac{v}{b^3 \phi} \right)^{(\nu-1/2)/(3\nu-1)} N^{1/2} \end{aligned}$$

15

Three regimes

Chains in good solvents only swell on intermediate scales

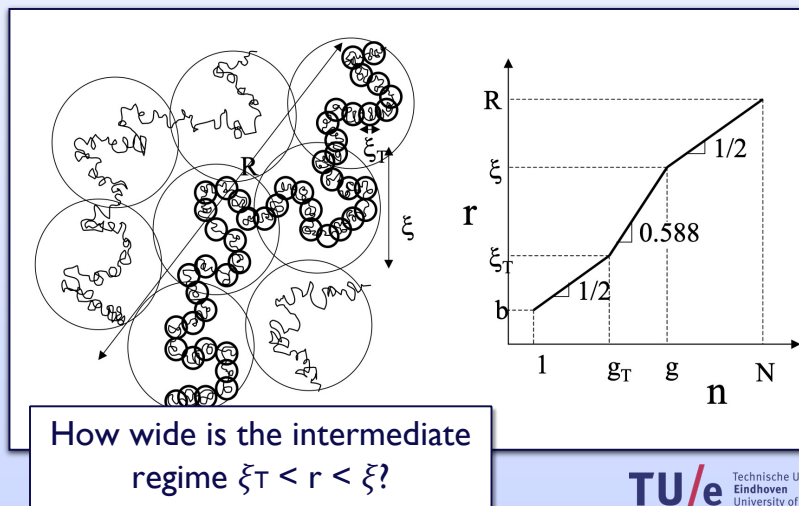


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16

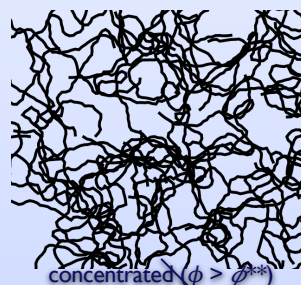
Concentrated solutions

Intermediate regime disappears when $\xi_T = \xi$

The correlation length ξ goes down as ϕ increases, equalling ξ_T at

$$\phi^{**} \approx \frac{v}{b^3}$$

This marks the crossover to concentrated solutions in which all chains are ideal



17

Sizes and correlation lengths as function of ϕ

The three regimes

$\phi < \phi^*$ dilute
 $\phi^* < \phi < \phi^{**}$ semidilute
 $\phi^{**} < \phi < 1$ concentrated

We will discuss why $\xi \sim 1/\phi$ in the concentrated regime later.

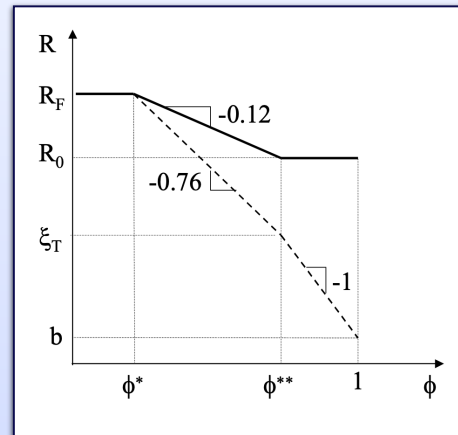


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18

Osmotic pressure near overlap concentration

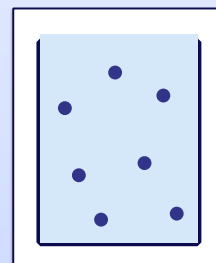
In mean-field theory we obtained, for small ϕ

$$\Pi = \frac{k_B T}{b^3} \left[\frac{\phi}{N} + \frac{v}{2b^3} \phi^2 + \frac{w}{b^6} \phi^3 + \dots \right]$$

In good solvents, the quadratic term beats the linear term when

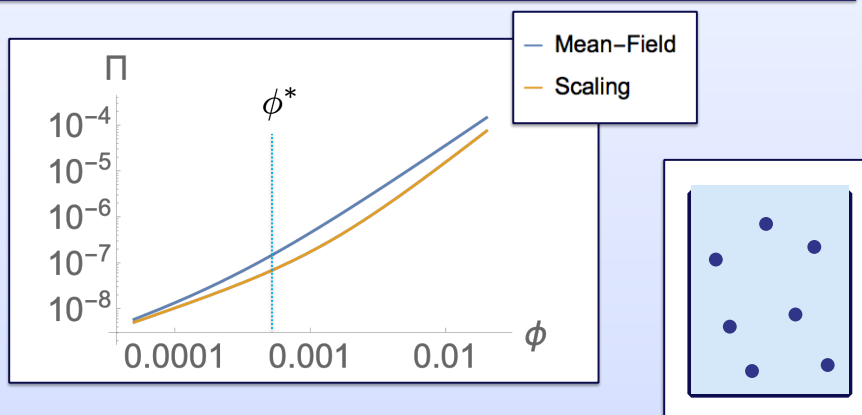
$$\phi \approx \frac{2b^3}{vN} \ll \phi^*$$

Why is that bad? What does that mean?



19

Mean-field overestimates Π in dilute solutions



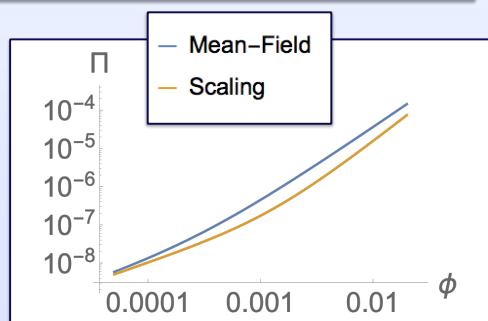
20

Scaling theory Π in dilute solutions

Interpolate between limits:

Π follows van 't Hoff up to ϕ^*

Π dominated by monomer-monomer repulsions at high ϕ



$$\Pi \approx \frac{\phi k_B T}{b^3 N} \left[1 + \left(\frac{\phi}{\phi^*} \right)^{1.3} \right]$$

21

Semidilute θ -solutions

correlation volume in θ -solutions:

$$\xi \approx \frac{b}{\phi}$$

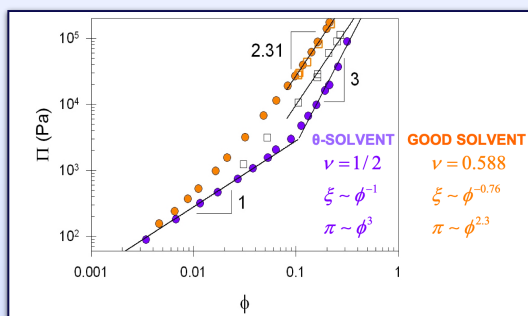
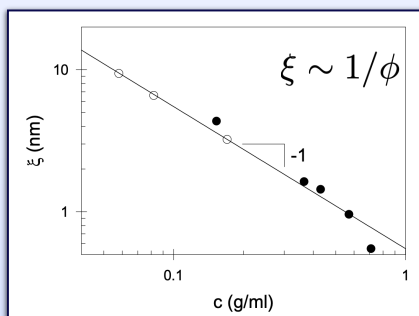
and because $\nu = 0$

$$\Pi = \frac{k_B T}{b^3} \left[\frac{\phi}{N} + \frac{w}{b^6} \phi^3 + \dots \right]$$

which is dominated in semidilute solutions by the cubic term

$$\Pi \approx \frac{k_B T}{3b^3} \phi^3$$

Experiments on semidilute solutions



Experiments on polystyrene confirm these scaling relations

Left: Correlation length (see Fig. 5.8 in Rubinstein for references)

Right: Osmotic pressure (Flory and Daoust, *J. Polym. Sci* 1957)

Summary

Chains in good solvent are swollen on lengths r when $\xi_T < r < \xi$.

In concentrated solutions all chains are ideal because $\xi < \xi_T$

Mean-field predictions perform poorly in the dilute regime, just like they do in the dilute phase of a demixed poor Solution

Chains in melts and sediments take up ideal conformations.

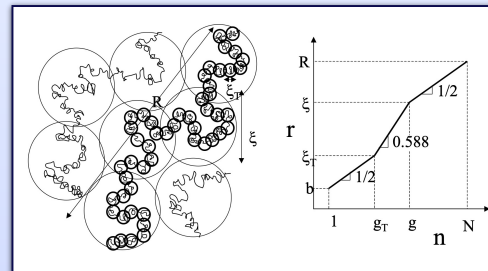


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