Problems with Tubes

What is Wrong with Tube Models?

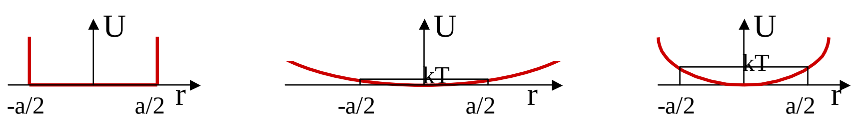
Outline

Everything You Always Wanted to Know About Tubes but Were Afraid to Ask.

1. 1001 questions about a single chain in a tube problem.
2. 1001 questions about a multi-chain multi-tube problem.
3. What is an entanglement anyway?

Single Chain in a Tube Problem

Q: What is the confining potential in the transverse direction?



Q: Is a single parameter – tube diameter *a* – enough to specify the topological confinement of a chain in a tube?

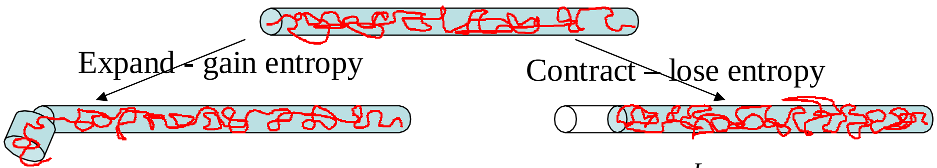
Q: Are more details of the potential needed?

Q: Why do we care?

Details of transverse confining potential may influence statistics of unentangled loops and therefore distribution of tube lengths.

Single Chain in a Tube Problem

Q: What is the longitudinal potential for tube length fluctuations?



Entropic gain is linear in tube length $F_{ent}(L) = -\psi kT \frac{L}{a}$

Elastic penalty for stretching $F_{el} = \frac{3}{2} kT \frac{L^2}{Nb^2}$

Longitudinal potential $U(L) = \frac{3}{2} kT \frac{(L - \langle L \rangle)^2}{Nb^2}$

Q: Is this the correct tube potential?

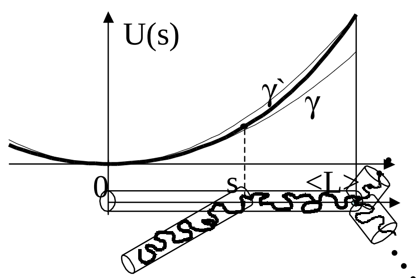
A: Yes. B: No. C: I do not know.

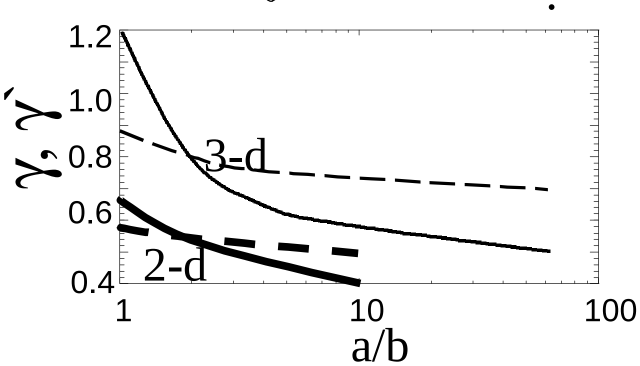
Q: Is tube potential quadratic for $|L - \langle L \rangle| \ll \langle L \rangle$?

A: Yes, but with a non-universal prefactor $\gamma/2$ instead of 3/2.

Single Chain in a Tube Problem

$U(L) = \gamma\, kT\, s^2$





Single Chain in a Tube Problem

Q: What fraction of stress is relaxed by longitudinal modes on time scale between τ_e and τ_R?

A. 1/3

B. 1/5

C. 3/7

D. None of the above.

E. I do not know.

The answer depends on the assumption made about tube deformation.

Single Chain in a Tube Problem

Q: Is 3.4 mystery resolved?

A. Yes

B. No

C. All of the above.

D. None of the above.

E. I do not know.

Q: Are there significant stress relaxation on time scale $\tau_R << t << \tau_{rep}$?

A. Yes

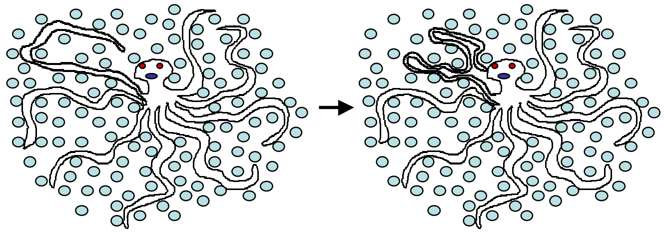
B. No

C. All of the above.

D. None of the above.

E. I do not care.

Non-linear Polymers

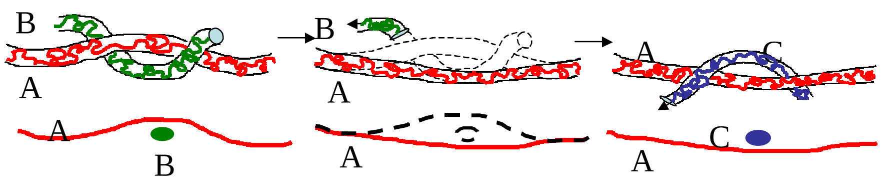


Q: What is the f-dependence of diffusion coefficient of stars in a fixed array of topological obstacles.

Q: How are the rheological predictions for stars sensitive to the choice of γ and γ` in arm retraction potential?
For a/b~5 lattice models predict prefactors γ=0.63 and γ`=0.75.
For stars with M/M_e=20 the arm retraction time in a fixed topological net differs by factor of 3.3.

Q: Are predictions of viscosity and diffusion coefficient for a melt of stars consistent with each other?

Many-Chain Problem
Constraint Release

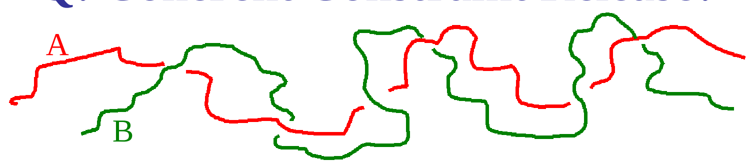


Q: Duality assumption: does reptation away of chain B leads to a local displacement of chain A by *a*?
Is there a parameter needed that is related to the collective nature of entanglement?

Q: Distribution of constraint release rates is modeled by a Rouse chain with distribution of bead mobilities.
In the Rouse model mobilities are quenched, while constraint release rates should be annealed.

Many-Chain Problem

Q: Coherent Constraint Release?



There are many topological constraints between a pair of neighboring chains.

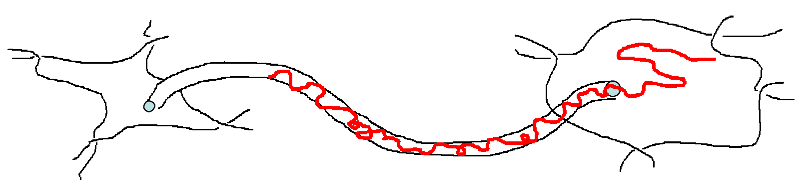
Reptation of chain B leads to a disappearance of many constraints for chain A.

There are correlations of constraint release events making it more effective.

Coherent constraint release is one of possible explanations of molecular weight dependence of the tracer diffusion coefficient in binary blends.

Many-Chain Problem

Q: Collective Reptation?

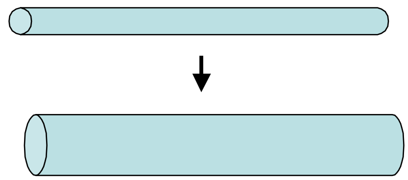


Q: Are collective reptation effects important?

$$\eta \sim \tau \sim \exp\left(const \frac{v_0^2}{b^3} \frac{N^{2/3}}{N_e^2} \right)$$

Need an accurate estimate of *const* to predict the cross-over length for quenching of reptation.

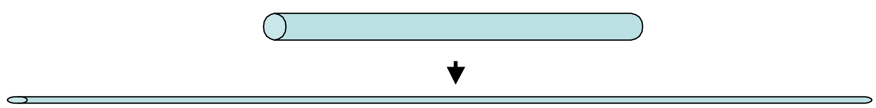
Many-Chain Problem
Q: Tube dilation?



Q: In what cases is there any tube dilation?

Q: What is the friction coefficient of a chain in a dilated tube? Compare it with reptation of a chain in a supertube in binary blends.

Deformation of Tubes



Q: How do tubes deform?

A. Tube diameter does not change upon deformation.
B. Tube diameter deforms affinely.
C. Tube diameter deforms non-affinely.
D. I do not know.
E. Why should I care?

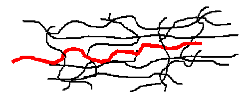
It is important for deformation of networks and non-linear flow.

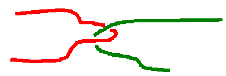
Q: What is an entanglement?

A: It is a topological constraint imposed by surrounding chain on a given one.

Q: Is it collective or pairwize?

A1: It is collective
because of Kavassalis-Noolandi conjecture:
constant number of sections of other chains overlapping with an entanglement strand.
Works well in melts, but not in θ-solutions.





A2: It is pairwize:
density of entanglements ~ density of pairwize contacts.

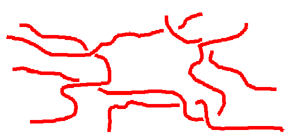
Works in solutions, but requires a large prefactor.

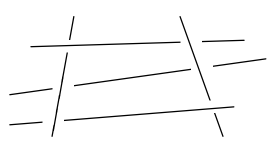
Need a unifying picture for both melts and solutions.

Q: What is an entanglement?

Q: What is the effect of chain flexibility?

Q: Is the nature of entanglement different for flexible vs. stiff chains?





Q: Is this difference related to the problem of solutions vs. melts?

Need a unifying model of an entanglement.

Summary

We are still a long way from a quantitative theory. **(Unless we are lucky and there is a magic cancellation of errors.)**

There are more questions than answers.

It is a great time to work in the field.

Well-designed computer simulations and experiments may lead to answers to some of the questions.

Q: Why is this man grinning?

A. He believes that "All theories are wrong by definition".

B. He still holds the record for measuring viscosity of a melt with highest M/M_e.

C. He put all the answers into his textbook.

D. He enjoys macro-rheology in shear-rate-control mode on his boat.

E. All of the above.

F. None of the above.