

### Preview

Is the concept of entanglement of polymer chains well described, in your opinion, by:

### Answer Choices:

- a bowl of spaghetti?
- a knot of electrical wires entangled in a suitcase?
- temporal cross-links that can form and melt out (slip)?
- the de Gennes, Doi-Edwards Tube model?
- any other model that you subscribe to?

**JPI: my answer was # 5**

**I realize that the classical answer would be # 4, but no tubes have ever been seen. Besides, the closest analogy with my Dual-Phase model model of entanglements would be a network of pipelines or river channels constantly in motion. Under stress, the motion of those “phase-lines” changes from a diffusion mode, at very low stresses to an activation-relax cooperative mechanism (“cooperative blinking”) describing shear-thinning, followed by the orientation of the phase-lines (entanglement network), followed by the instability of the network and the involvement of enthalpic contributions to the deformation (yielding).**

<sup>1</sup> The link to the quiz and to the class recording<sup>2</sup> are found in the footnote

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<sup>1</sup> <http://www.wiziq.com/online-tests/22446-the-entanglement-quiz>.

<sup>2</sup> <http://www.wiziq.com/online-class/430878-the-need-for-a-new-understanding-of-entanglement-in-polymer-physics>

**Preview**

Is the Objective of the New School of Polymer Physics to present a new understanding

**Answer Choices:**

- that makes entanglements thermodynamically and kinetically controllable?
- to be able to manipulate them and improve processing?
- to provide the industry with new disentangled resins that can flow better?
- All of the above

**JPI: the last answer (#4) is the good choice**

### Preview

When a melt is "disentangled", can it be frozen into pellets that will be showing, on reheating, decrease benefits of the melt?

### Answer Choices:

- YES, but many questions remain to be resolved. I understand that it might mean that we need to reconsider established views on the p-entanglements.
- NO, the current established theories DO NOT ALLOW such a benefit to occur. TAU<sub>0</sub> is preserving melt orientation beyond that time is an erroneous concept.

**JPI: my answer was #1.**

**The reptation protagonists will disagree, but they should read The Great Myths of Rheology part II (downloadable in the MY CONTENT of the WIZIQ courses) and provide another answer that edge fracture for the triggered viscosity time dependence at strain starting around 15%. for PS.**

### Preview

If the state of non-equilibrium of the entanglement network controls and modulates the response of a melt, what are the chances that the reptation model remains the dominant description of the properties of melts (viscoelasticity, molecular weight dependence, etc)?

### Answer Choices:

- REPTATION MODEL DOES NOT SEEM APPROPRIATE TO DESCRIBE DYNAMICS EN
- REPTATION needs not be abandoned, it needs to be modified
- The reptation model has many successes, one does not need to address new uncertainties would require to think differently.

### JPI: My answer was #1

**The tube itself has become another giant “macromolecule”, see de Gennes “scaling concepts in polymer physics”. The fixed obstacles to define the envelope for local motions (Rouse type) are frozen for the time of reptation ( $t_d$ ). All these concepts must be easily defined from the inter-intra molecular bonding forces, and, in a sense, it is much easier to define a network of tubes and its diffusive motion (or activated cooperative deformation mechanism) by the Dual-Phase concept. Besides, the dual-phase understanding of entanglement is compatible with the spectroscopic data above and below  $T_g$ , and explains all various types of deformation mechanisms as stages of collaborative processes**

## Preview

How long can ORIENTATION survive above  $T_g$  for an amorphous linear polymer melt?

## Answer Choices:

- Relaxation takes place according to  $\tau_{Uo}$ , the longest relaxation time
- IT DEPENDS ON THE STABILITY OF THE NETWORK OF ENTANGLEMENT, WHETHER NOT
- I am getting more and more confused about what I know or don't know about polymer p  
Isn't  $\tau_{Uo}$  the longest relaxation time?

**JPI: my answer was #2**

**Answer #1 would be correct under no stress, for a stable entanglement state which is at equilibrium. Lots of counter-examples can be shown. The stability of the network of entanglement can be modified by thermal-mechanical history. It would be like creating a new set of tubes for the reptation model, with a different topology. In order to link the network pipeline topology with the state of the conformers interactions, one needs to abandon the ad hoc framework of the reptation tubes and adopt the concept of Dual-Phase which allows a living link between the scales , permitting to define time relaxation of the entanglement network in a kinetic fashion. In other words, the re-scaling between the local motions and the motion of the entanglement network is integrated kinetically as well as energetically.**

**The entanglement manipulation consists in unlocking the kinetic dependence to influence the energetic structuring, and vice-versa.**

### Preview

IS ORIENTATION OF A POLYMER MELT THE RESULT OF DISENTANGLEMENT/RE-ENTANGLEMENT/RE-ORGANIZATION?

### Answer Choices:

- NO
- YES
- I am getting confused

### JPI: my answer was #1

This is where the reptation model diverges with my understanding of disentanglement/re-entanglement. It is my opinion that the network of continuous rivers and pipelines described by my phase-lines, a consequence of the Dual-Phase concept, is not a description of the whereabouts of a single chain. The Doi Edwards considers the tube as the space of confinement for a single chain motions. The rms end to end distance of a single chain does not change at all from its value in the Newtonian and the shear-thinning region, according to L. Noirez's recent SANS data. The statistics should not focus on the single chain, but on the evolution of the mechanism of diffusion of the dual-phases. This may very well make the chain rotate around its gravitational axis as it is being displaced by diffusion. The local interactions are constantly being formed and deformed (say this would be the equilibrium local Rouse description), but the localization of the Dual-Phases is either randomly the same, or it is changing. This is the point of focus, in my opinion. And the definition of the reptation time by  $1/\omega_x$ , without relating it to the stability of the network, makes it as flawed (incomplete) view.

**Preview**

Can one modify the Equilibrium Entanglement state of a polymer melt?

**Answer Choices:**

- YES, but I would not know HOW
- NO, IT IS CONTRARY TO OUR PRESENT UNDERSTANDING OF THE CONCEPT OF EN

**JPI: the correct answer was # 1**

**It is my purpose to teach in this course the bases that will enable the polymer community to modify the state of entanglement of plastic melt in a controllable and designed fashion**

### Preview

Does a melt with greater than equilibrium entanglement density have GREATER modulus equilibrium melt?

### Answer Choices:

- No, it's impossible
- YES, but the melt will lose it as it returns to its thermodynamic equilibrium entanglement
- The question is irrelevant to our present understanding of melt behavior. The melt spring

**JPI: My answer was #2.**

**I have produced melts with boosted viscosity increase, the reverse of disentangled melts. They are also unstable and try to return to a thermodynamically stable state.**

**Preview**

Can we produce polymer melts which exceed their equilibrium entanglement state (the reverse of disentanglement)?

**Answer Choices:**

- YES
- NO
- Irrelevant question, a melt is stable for times greater than  $\tau_{AU0}$

**JPI: my answer was #1 (see my previous answer)**

**Preview**

Does a disentangled melt (driven by thermodynamic reasons) try to recover its EQUILI when it is annealed?

**Answer Choices:**

- NO, a melt is always at equilibrium
- YES
- the question is irrelevant, a melt cannot change its entangled state

**JPI: my answer was #2**

**Preview**

Is it possible to modify the kinetics of re-entanglement of a disentangled polymer?

**Answer Choices:**

- YES and I know how to do it
- NO
- YES, but we still need to control the science behind the process
- NO, it is controlled by TAU<sub>0</sub> which is too fast to control anything

**JPI: my answer was #3**

**Once the complete answer is known theoretically, we will have established the understanding of a true time dependent renormalization group theory, bridging with Prigogine non-equilibrium concepts of instability. Scaling and universality are defined for steady states, they should be modified to apply to transients, for which universality must incorporate a dissipative component, in my opinion. I once called a very intuitive attempt to do this “ the Interlock Band Model.”, but realized that “IBM” was the focus of attention for doing something else...**

**Preview**

When a polymer melt is disentangled (even partially), how long does it take to "re-entangle"?

**Answer Choices:**

- TAUo (terminal time)
- A little longer than TAUo, but same order of magnitude
- 100,000 times TAUo or more

**JPI: my answer was #3.**

**The real time of recovery depends on the state of non-equilibrium achieved for the melt. I have observed for PMMA, 24 hours at  $T = T_g + 130^\circ\text{C}$ , whereas TAUo at that temperature was less than 1 sec.**

**Preview**

The kinetics of re-entanglement of an unentangled polymer varies with Molecular weight

**Answer Choices:**

- M
- $M^{2.4}$
- $M^3$
- $M^{3.4}$

**JPI: my answer was #3**

**There is perhaps a difference between “re-entanglement” originating from fully unentangled polymers (such as produced by Prof. Rastogi) and the return to equilibrium of melt whose entanglement network has been modified. We suspect that in gap structuring (gradient of entanglement modification) plays a different role than Molecular weight. In conclusion, the answer above is based on the re-entanglement of the Rastogi’s PE sample.**

**Preview**

Can only BRANCHED polymers be disentangled mechanically?

**Answer Choices:**

YES

NO, LINEAR POLYMERS CAN DISENTANGLE AS WELL

**JPI: My answer was #2**

**Previous work by others exclusively focused on branched polyolefins (to increase their TAU<sub>0</sub>) and believed that linear polymers would not work, but this turned out to be incorrect. It appears that all polymers that have an entanglement network can “disentangle”.**

### Preview

When a polymer melt is disentangled (even partially), how long does it take to "re-ent:

### Answer Choices:

- TAUo (terminal time)
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- 100,000 times TAUo or more

### **JPI: my answer was #3**

Disentanglement is not local and is not defined by the reptation time. It is a property derived from the relaxation of the network. When the network is not "oriented", say only shear-thinning is activated, then #1 answer is correct. But when "disentanglement" (distortion of the topology of the dual-phase "phase-wave") is successfully achieved, the entropic and enthalpic character of the conformer interaction coupling may result in very long time for network thermodynamic recovery.

**Preview**

For a disentangled melt, the degree of swell is:

**Answer Choices:**

- 1/3SS than for the entangled melt
- MORE than the entangled melt
- SAME
- UNRELATED

**JPI: my answer was #1. A disentangled melt has undergone strain softening, which is due to the enthalpic contribution to strain production (stress induced conformational changes, from cis-gauche to trans-conformers). Moduli of elasticity are reduced accordingly, normal stresses follow through. .**

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**Preview**

the viscosity of a disentangled polymer melt is:

**Answer Choices:**

- LESS than the entangled polymer
- MORE than the entangled polymer
- the same as the entangled polymer

**JPI: my answer was #1.**

**HOWEVER, I would strongly disagree that this could be derived from the simple concept that this is because  $M_e$  increases.**

**Preview**

Can one compare the behavior of unentangled melt and disentangled melt?

**Answer Choices:**

YES

NO

**JPI: my answer was #1.**

**Indeed, see my paper *The Great Myths of Rheology, part II* which provides many examples of such comparison. In some instances the disentangled melt has the same  $\eta_{TAo}$  (Newtonian value), but a different melt index (pseudo-plasticity), and in other cases the disentangled polymer has a lower Newtonian viscosity as well, we can be observed by measuring the Melt Flow Index (in some instances, we have observed the double for the MFI).**

**Preview**

when a melt is disentangled by mechanical means, is  $M_e$  changing evenly across the thi

**Answer Choices:**

- YES
- NO
- it depends on the mechanical stress applied

JPI: my answer was #3. At the beginning of phase-line orientation, the entanglement network may be homogeneously deformed across a gap, especially for thin gauge, but, at higher stresses, the velocity and the  $\dot{\gamma}$  influence the degree of non-equilibrium, and thus a gradient of entanglement (stratification) is expected.

**Preview**

How long does it take for a melt to fully disentangle?

**Answer Choices:**

- on the order of the longest (terminal) time  $\tau_{Uo}$
- $\tau_{Uo} (M/Me)^{2.4}$
- a very long time, unrelated to  $\tau_{Uo}$  and  $Me$
- Nobody knows

**JPI: my answer was #3, although I could have also ticked #4, since there is a lot to learn still, and it is somewhat provocative to say that  $\tau_{Uo}$  and  $Me$  do not play any role. What I mean to say is that the answer should be better described with a different analytical frame than the linear viscoelastic parameters.**

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**Preview**

Is Me changing for a melt which "shear-thins"?

**Answer Choices:**

YES

NO

IT DEPENDS on the strain

**JPI: my answer was #2.**

**Shear-thinning is not related to disentanglement, but to the increase of the number of activated systems of the network coordinating their response to the strain rate application (interactive coupling of systems). It is translated by an increase of the network diffusion frequency  $\omega'$ .**

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**Preview**

what is the maximum disentanglement ratio one can achieve if a polymer melt can be c

**Answer Choices:**

$(M/M_e)$

with  $M$  the molecular weight ,  $M_e$  the molecular weight between entanglement

$(M/M_e)^{2.4}$

$(M/M_e)^{3.4}$

none of the above

**JPI: my answer was #2**

**The ratio between the unentanglement line, proportional to  $M$ , and the entanglement line, proportional to  $M^{3.4}$**

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**Preview**

Are ENTANGLEMENTS stable in time and what would cause them to become instable?

**Answer Choices:**

- Heat?
- shear stress?
- pre-shear treatment (mechanical history)?
- melt extension?
- melt vibration at given frequency and amplitude?
- all of the above?

**JPI: my answer is last (#6).**

**This is the heart of my research This will be developed during the other lectures.**