CECAM Workshop on Modeling and Simulation of Entangled Polymeric Liquids

July 18 – July 21, 2005
Lyon, France

This workshop was the first on the topic of entangled polymer dynamics held at CECAM. It was organized by Frank Peters and Jay Schieber. CECAM (Centre EuropÈen de Calcul Atomique et MolÈculaire) is an institute based in Lyon that is supported by 14 European research organizations. CECAM aims at facilitating dissemination and networking activities in the area of molecular simulation. For example, each year, 20-25 workshops are being organized at CECAM by world experts in computer simulations. The fact that modeling of entangled melts is discussed at an institute focused on molecular simulations marks a change in this field of research that has occurred the past decades.

The workshop with 22 participants had a highly informal character. The attendants represented a nice mix of senior scientists and young faculty, post doctoral researchers and PhD students. The first part of each day was reserved for one hour research talks, the final part of the day for a big discussion session. There proved to be a real need for discussion since these turned out to be very animated. Many of the young scientists were happy to meet the faces corresponding to the papers they had read. The discussions were very frank, constructive and provided valuable insights.

Within the contributions two main themes could be discerned. The first was MD simulations of entangled systems. Computers and efficient algorithms keep evolving at a startling rate. The most striking characteristic of entangled polymeric liquids is the slow dynamics. Many people might have expected that it would take a very long time before molecular simulations would be able to reach these long scales. Well, this day has already arrived.In reptation theory the slow dynamics is assigned to the presence of topological constraints that prevent quick relaxation of polymer configurations. The primitive path as introduced by Edwards is a way to characterize these constraints. Many of the MD research groups were interested in primitive-path construction from the underlying molecular configuration.

The second theme was coarse grained modeling of entangled dynamics. Although MD develops at a very high pace still a huge amount of computer power is needed to even approach the entangled configuration. There is also a consensus that closed form constitutive equations

Figure 1 (left): CECAM is situated in Lyon, which is a city with a nice old city center many big squares and a good collection of first class restaurants.

Figure 2: Yuichi Masubuchi presenting his workshop contribution on primitive chain network simulations.

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will not give full quantitative predictions for the entangled melt. The coarse grained modeling tries to balance computational effort with accurate quantitative predictions in agreement with experimental findings. One of the observations one can make from the workshop is that the slip-link modeling of entangled polymers is having a big revival.

For a list of participants and abstracts of the workshop contributions the reader is referred to the CECAM website: http://www.cecam.org (section: past workshops). To summarize the meeting I want to cite the conclusions and recommendation the participants agreed upon during the final discussion.

Conclusions:

- The last 5 years great progress has been made on the modeling of entangled polymer on melts, valid on different scales. Although the models on different scales give predictions for overlapping regions they are not well connected.
- Progress in single chain modeling allows these models to predict both properties of cross-linked systems and melts.
- Recent progress in Molecular Dynamics simulation makes it possible to simulate entangled systems for long enough times such that the results show a region of overlap with more coarse grained models of entangled systems. This progress is largely due to improved Monte Carlo methods for preparation of equilibrium states for long chain systems.
- Different research groups have proposed methods to construct a so-called primitive path from polymer configurations as obtained from a MD simulation. This construction is hoped to reveal the topological constraints on the polymers that dominate long time dynamics. We were able to clarify what the differences are between the proposed algorithms for constructing the path.
- Much of the shear data on entangled systems as published in literature is influenced by non-ideal behavior of the measurement equipment. Especially slip-phenomena and transducer compliance are complicating factors. Recent extensional experiments seem to be less influenced by these factors.
- Neutron scattering data becomes increasingly important to validate models.
- The workshop was very fruitful. The discussions were of high quality and helpful for many of the participants.

Recommendations:

- Modelers should discuss their models more in detail with each other and find out what the differences in their model-predictions are. In this way experiments can be more focused and the convergence of model-predictions with reality will speed up.
- More care should be taken to make sure that models are mathematically well characterized and thermodynamically consistent. This also applies for coarse graining procedures to go from one level of description to the next.
- In the field of primitive path construction a critical comparison of algorithms is advised. The scaling of the primitive path properties for different chemical constitutions and temperatures should be checked against experimental data for the plateau modulus.
- For the current models both data on cross-linked systems and melts should be used to validate model predictions because these two systems give complimentary information.
- Historically, experimentalists have taken great pains to make sure that strains are ideal, in the sense that rates are truly constant, or nearly instantaneous on certain timescales. However, since most theoretical models require some numerical effort, ideal strains are not necessary. It is essential that all experiments report the real strain history of the rheometer. This may require cooperation from manufacturers.
- For a critical comparison with model predictions experiments should sample a wide as possible range of time scales and entanglement density should be varied. Experiments on different scales and both in solutions and melts are desirable.
- A workshop on the same topic in a similar format should be held in two years.

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