C3: Modeling late stages of spin coating

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Supervisors: A. Blumen, J. Baschnagel

Presentations

- 3 oral IRTG
- 4 posters IRTG
- 4 oral other
- 3 posters other

Publications

[1] J.P. Wittmer, H. Xu, P. Polińska, C. Gillig, J. Helfferich, F. Weysser and J. Baschnagel, Eur. Phys. J. E **36**, 131 (2013)

[2] J. Helfferich, F. Ziebert, S. Frey, H. Meyer, J. Farago, A. Blumen and J. Baschnagel, Phys. Rev. E, **89**, 042603 (2014)

[3] J. Helfferich, F. Ziebert, S. Frey, H. Meyer, J. Farago, A. Blumen and J. Baschnagel, Phys. Rev. E, **89**, 042604 (2014)

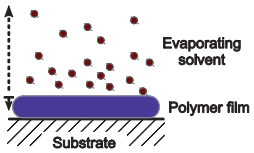
[4] J. Helfferich, Eur. Phys. J. E 37, 73 (2014)

[5] J. Helfferich, K. Vollmayr-Lee, F. Ziebert, H. Meyer and J. Baschnagel, EPL 109, 36004 (2015)

Other activities

- Member of the organizing committee: Soft skills workshop (2014)
- Participation in Master Class: Summer School 2013
- 1 Month stay in Lviv, Ukraine as part of the Marie Curie International Research Staff Exchange Scheme Fellowship within the 7th European Community Framework Program SPIDER
- 1 Week stay in Berlin

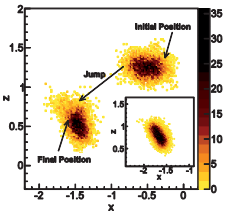
Challenges in modeling spin coating



Spin coating is a widespread technique to manufacture thin polymer films for a wide array of applications. Even though best practices and rules of thumb exist, a deeper understanding of the underlying processes is still lacking. More accurate models would greatly improve the possibilities to design tailor-made materials.

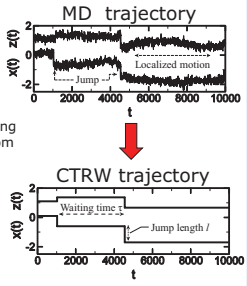
The late stages of spin coating, in particular the evaporation of solvent from the thin film, poses several challenges:

- ☑ Complex polymer dynamics
- ☑ Out-of-equilibrium configurations
- ☐ Two-component system
- ☐ Anisotropy (thin film)



On cooling towards the glass transition temperature T_g, single particle trajectories display long periods of localization interrupted by fast transitions to a new position.

The continuous-time random-walk (CTRW) approach



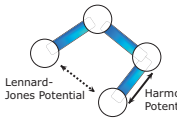
The CTRW is defined as a series of independent jumps with random time-intervals in between. In general, jump vectors ***l*** and waiting times τ are assumed to be independent random variables distributed according to

- the **jump length distribution** $f(\boldsymbol{l})$ (**JLD**) and
- the **waiting time distribution** $\psi(\tau)$ (**WTD**).

Simulation methods

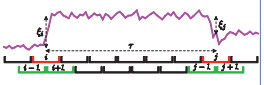
Molecular Dynamics (MD)

- Generic bead-spring polymer model
- 12288 monomers in chains of length N = 4, 16, 32 or 64
- Constant temperature close to T_c the critical temperature of mode-coupling theory
- Fully equilibrated configurations



In collaboration with Vollmayr-Lee (Bucknell University, Lewisburg, USA) we are currently analysing jump events in simulations of amorphous silica (SiO_2) [5].

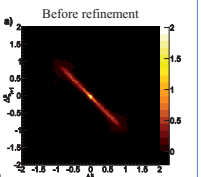
Move detection



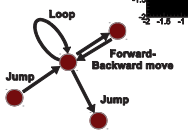
Localized motion is seperated from fast transitions by a coarse-graining algorithm. If the variance in a time-window *i* exceeds the threshold value σ_c a „move" takes place in this time-window. We have selected this threshold based on the Lindemann localization criterion.

Refinement: From moves to jumps

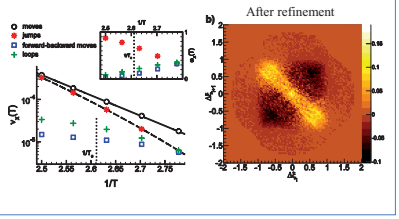
We found that not all moves comply with the conditions of a CTRW. In particular, a high propensity of loop-like events and forward-backward moves can be found. We proposed a refinement procedure to exclude these events. This result explains the large spread of parameters obtained for similar systems [2].



In particular, strong forward-backward correlations are present, of which ~90% are removed during refinement. In polymer systems, however, strong correlations over several jumps persist due to chain connectivity.

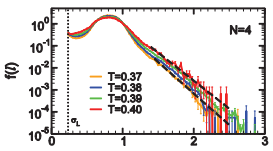


The rate of relaxation events changes from Arrhenius-like before to Vogel-Fulcher-Tamman-like after refinement. We interpret this with the bifurcation of the (high T) alpha- and beta-relaxations.

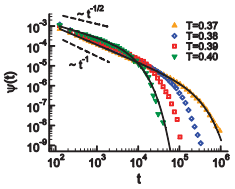


Results

Polymer Dynamics



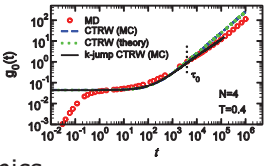
The jump lengths display clear deviations from a Gaussian distribution. Furthermore, correlations persist over many jumps in polymers.



The waiting time distribution is well described by an exponentially truncated stable distribution ETSD:

$$\psi(t) \sim t^{\alpha-1} e^{-\lambda t}$$

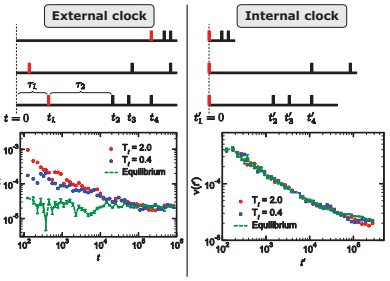
We found that macroscopic dynamics, such as the mean-square displacement, can be well reproduced by CTRW simulations, if correlations due to the chain connectivity are explicitly taken into account. We refer to this technique as the k-jump CTRW [3].



Non-equilibrium dynamics

CTRW theory states that we can define an „internal time" by starting the internal clock of a particle on its first jump (renewal property).

In the time-frame of the internal clock, the dynamics should be independent of the history of the system, i.e. its age and quench protocol.

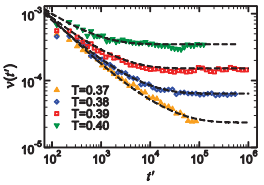


We confirmed the CTRW prediction that the single-particle trajectories can be mapped onto a well defined initial state. By this procedure, different glassy systems can be compared with each other and CTRW theory [4].

This result has further, important implications for the analysis of aging and mechanical rejuvenation. In particlar, it demonstrates that on the level of jumps no spatial correlations persist.

Relaxation rate

The number of jumps per unit time (relaxation rate), is a good measure to analyse non-equilibrium dynamics. A decaying relaxation rate was found at short times reflecting the ever slower dynamics. The jump rate remains constant once equilibrium is attained.

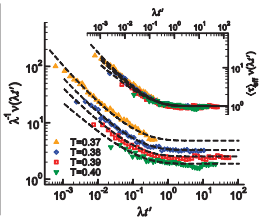


Using CTRW theory, we derived that the jump rate is given by

$$\nu(t) = \lambda^{\alpha} e^{-\lambda t} t^{\alpha-1} E_{\alpha,\alpha}[(\lambda t)^{\alpha}],$$

where $E_{\alpha,\beta}[z]$ is the two-parameter Mittag-Leffler function.

We were able to confirm that the rescaled jump rate falls onto a master curve over several timescales when multiplied with the effective mean waiting time [5].



Conclusions & outlook

We have further investigated and extended the continuous-time random-walk approach to supercooled liquids and glasses.

- We tested whether the fundamental assumptions of the CTRW are fulfilled in supercooled polymer melts. Our results demonstrate that „hops" in the trajectory may not directly be identified with „jumps" of a CTRW. To remedy this, we have proposed a refinement procedure. These refined jumps do fulfill the CTRW assumptions to a great extent.
- We demonstrated that the refined jumps may be treated as renewal events. This result could have important implications for the analysis of non-equilibrium dynamics, aging and mechanical rejuvenation.
- We have derived CTRW predictions for the mean-square displacement and the jump/relaxation rate. Comparison with MD data revealed good agreement but also significant deviations, highlighting both the prospects and limitations of the CTRW approach.

The CTRW is an apt tool for the analysis of supercooled liquids and it has seen increasing interest from several research groups. We hope our research will help advance the understanding of glass dynamics.