OBSERVING THE TWINKLING FRACTAL THEORY (TFT) OF THE GLASS TRANSITION

J.F. Stanzione III (Ph.D. Candidate), R.P. Wool (Ph.D.), and K.E. Strawhecker (Ph.D., ARL)

University of Delaware . Center for Composite Materials . Department of Chemical Engineering

Introduction[1]

- Conceptual approach to understanding T_g.
- Provides new insight to the physical properties of glass forming liquids by giving precise physical meaning to related concepts of:
  - Dynamic heterogeneity,
  - Cooperativity, and
  - Fractal structure.

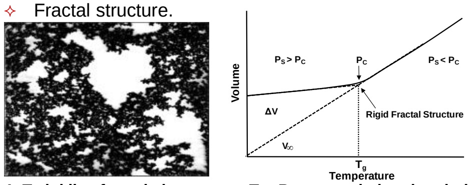

Figure 1. Twinkling fractal cluster near T_g; P_C = percolation threshold ≈ 0.5.[1]

- In Fig. 1, liquid white regions in dynamic equilibrium with solid black fractal clusters.
- T_g occurs when solid fraction P_s percolates at P_c.

Motivation

- The goal of this research is to conduct experiments that prove the TFT for traditional, amorphous polymers, in particular polystyrene (PS).

Overall Concept[1-2]

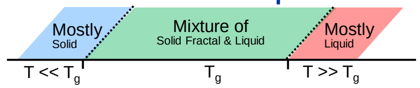

Figure 2: Conceptual illustration of the TFT.

- TFT spatio-temporal fluctuations described by a temperature dependent "twinkling" relaxation function or global autocorrelation function, *C(t,T)*:

$$C(t,T)=\int_{\omega_o}^{\omega_v=1/t}\omega_v^{df-1}\exp\left\{-\omega_v t\exp\left(-\frac{\beta\left(T^{*2}-T_g^2\right)}{kT}\right)\right\}d\omega_v$$

  - ω_v = vibrational frequency & β = universal constant = 2 x 10^{-24} J/K^2. [3]
  - $T^* \approx 1.2T_g$ & d_f = fracton dimension = 4/3. [2]
- Exact analytical solution:

$$C(t,T)=\frac{\omega_o^{1/3}}{3\alpha t}\exp(-\alpha t\omega_o)+\frac{1}{3(\alpha t)^{4/3}}\left(\Gamma\left(\frac{1}{3},\alpha t\omega_o\right)-\Gamma\left(\frac{1}{3},\alpha\right)\right)-\frac{1}{\alpha t^{4/3}}\exp(-\alpha)$$

$$\alpha=\exp\left(-\frac{\beta}{kT}\left(T^{*2}-T^2\right)\right)$$

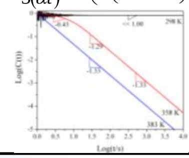

Figure 3. Behavior of *C(t,T)* for $1 < t$ (s) $< 10^4$ for *T* = 25°C, 85°C, & 110°C.

Method of Observing "Twinkles"

- Tapping-mode AFM experiments of PS thin film.[1,4]
  - M_w ~ 2 x 10^5 Da, PDI ≤ 1.07, & $T_g \approx$ 100°C.
  - Film thickness: ~ 1.0 μm; Roughness: ~ 1.0 nm.
  - Isothermal below, above, and near T_g.
  - 1-D scans: ~ 700 nm ; Time interval: ~ 1.0 s.
  - Light tapping forces employed .
  - FESP probe with *k* ~ 1-5 N/m and f_o = 70-100 kHz.
  - Capture solid fractal clusters in dynamic equilibrium with surrounding liquid.

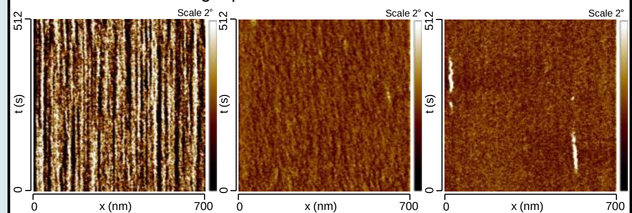

Figure 4. PS phase images at 25°C (left), 85°C (middle), & 110°C (right).[1,4]

- In Fig. 4, segmented streaklines exist indicating percolation and dynamic behavior.

Cluster Widths & Lifetimes

- Representative sample of "twinkling" fractal clusters selected.
- Theory of dynamic fractal networks: [2]
  - $t \sim r^d$.
  - $d = D_f/d_f$ = 1.42.
  - D_f = 2-D fractal dimension = 1.89.
  - d_f = fracton dimension = 4/3.

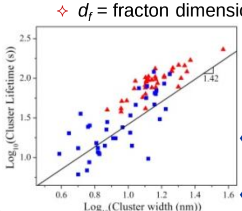

Figure 5. Cluster lifetimes as a function of cluster width for 85°C & 110°C; black line from theory.

- Cluster lifetimes ↓ as cluster sizes ↓.
- Cluster sizes ↑ as *T* ↓.

Experimental *C(t)*

- AFM X-t phase data:
  - 1st ordered flattened.
  - 1 x 3 boxcar average of each position.
- *C(t)* is calculated at each position and then averaged over all positions.
- Box & Jenkins *C(t)* employed.[5]
  - Strictly stationary stochastic process.
  - TFT AFM data meets criteria.

$$C(t)_k=\frac{c_k}{c_o}\qquad c_k=\frac{1}{N}\sum_{t=1}^{N-k}\left(x_t-\bar{x}\right)\left(x_{t+k}-\bar{x}\right)$$

  - c_k = value of autocorrelation at k^{th} lag.
  - c_o = value of autocorrelation at 0^{th} lag.
  - x_t = value of data at time *t*.
  - x_{t+k} = value of data at time *t+k*.

C(t) Comparison Near T_g

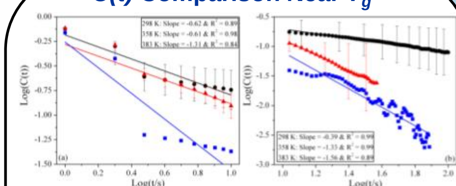

Figure 6. Log-log plot of the experimental $C(t)_k$ as a function of lags *t* between *t* = 1 – 10 s (a) & *t* = 10 – 100 s (b) for 25°C (black), 85°C (red), and 110°C (blue).

- 85°C and 110°C data in fair agreement with the TFT (see Fig. 3 above).
- 25°C data has poor agreement with the TFT
  - Slopes six orders of magnitude difference.
  - Experimental *C(t)k* sensitive to the frequent twinkles of the surrounding liquid (P_L = 1-P_C ≈ 0.4 at *T* = 25°C).

Ongoing & Future Work

- Comparing theoretical and experimental *C(t)*'s for PS at various temperatures.
- Extracting other stochastic information from current PS AFM data.
- Improve AFM technique for better "twinkling" visualization.

References

(1) Wool, R.P. *J. Poly. Sci. B.: Polym. Phy.* **2008**, 46, 2765-2778.
(2) Orbach, R. Science, **1986**, 231, 814-819.
(3) Campanella, A.; Wool, R.P. work in progress.
(4) Russell, E.V.; Israeloff, N.E. *Nature* **2000**, 407, 695-698.
(5) Box, G.E.P.; Jenkins, G.M. *Time Series Analysis: Forecasting and Control* **1976**, 23-36.

Acknowledgements

This work is supported by the Army Research Laboratory through the Composite Materials Research program under Cooperative Agreement # W911NF-06-2-011.