Athermal Photofluidization of Glasses
or
Controlling Viscosity with Light

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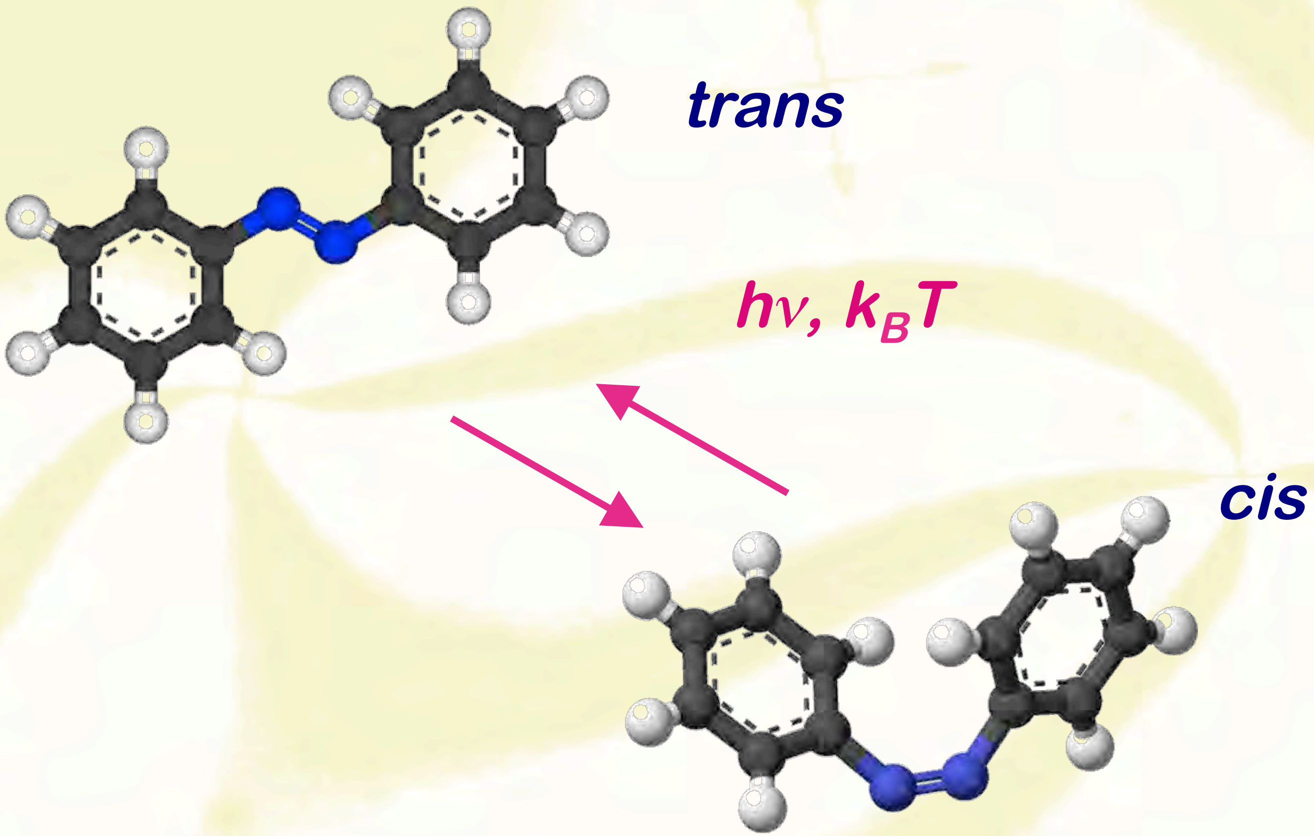
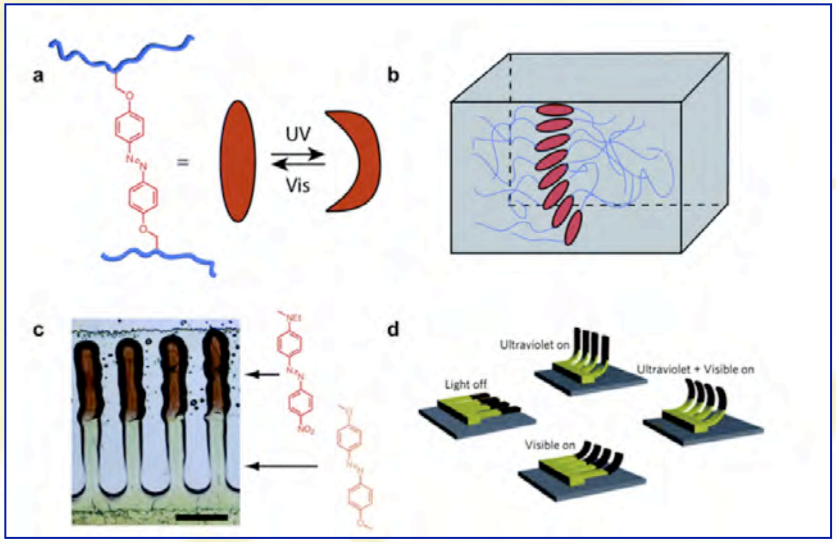
Nat. Comm. (2013)

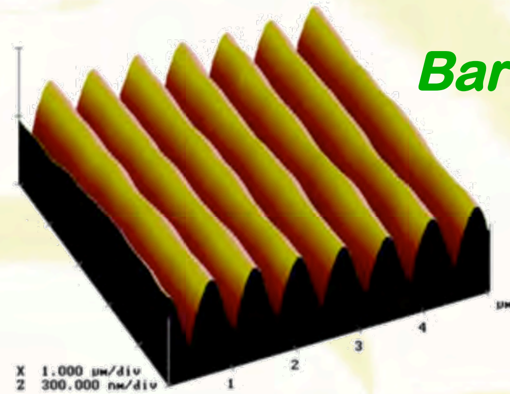
azobenzene



azo – based photo-active glassy polymers

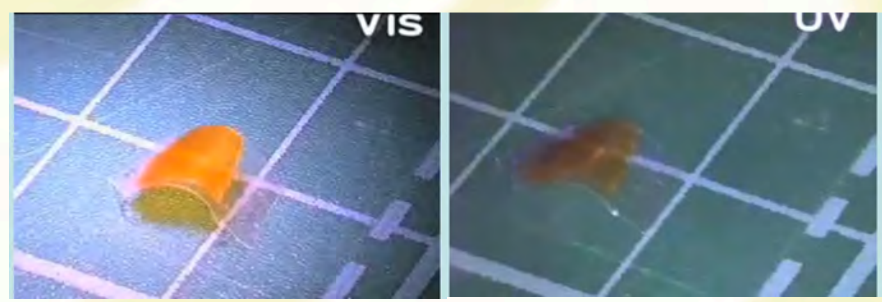


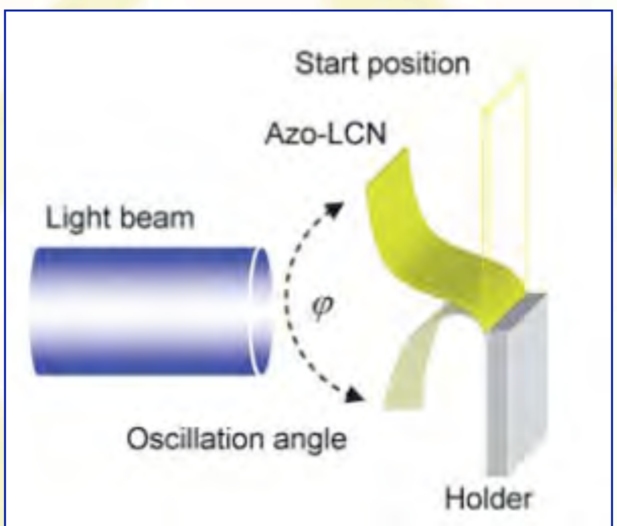
Broer



Barrett

Ikeda



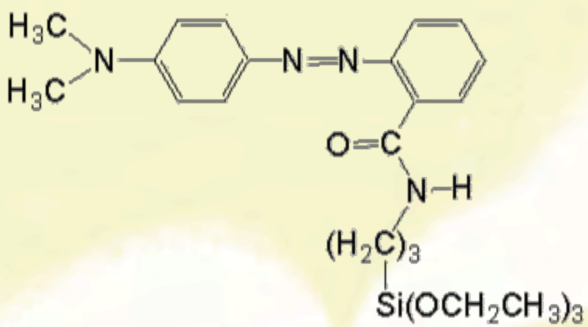


Wright- Patterson

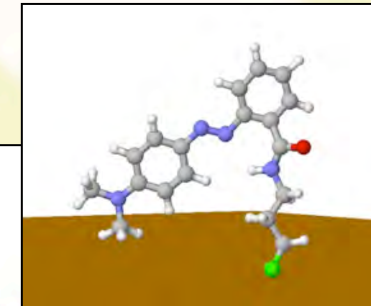
azo-based tethered molecular monolayer (dMR)

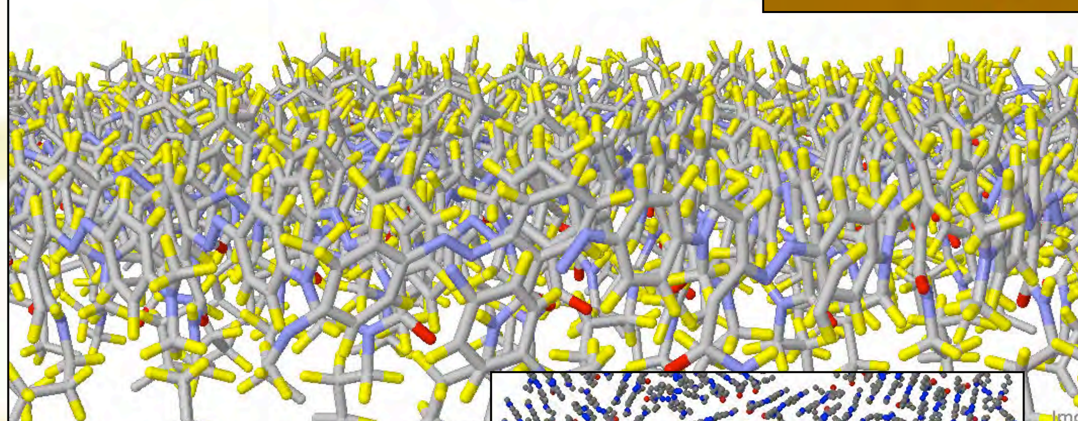
- ***precursor***

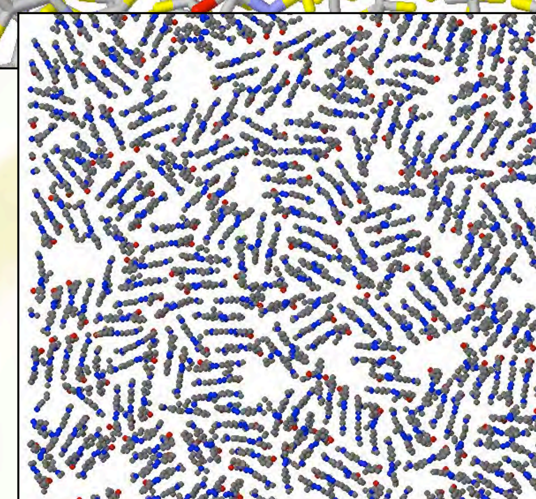
(D. Walba)



(D. Bedrov
M. Glaser)





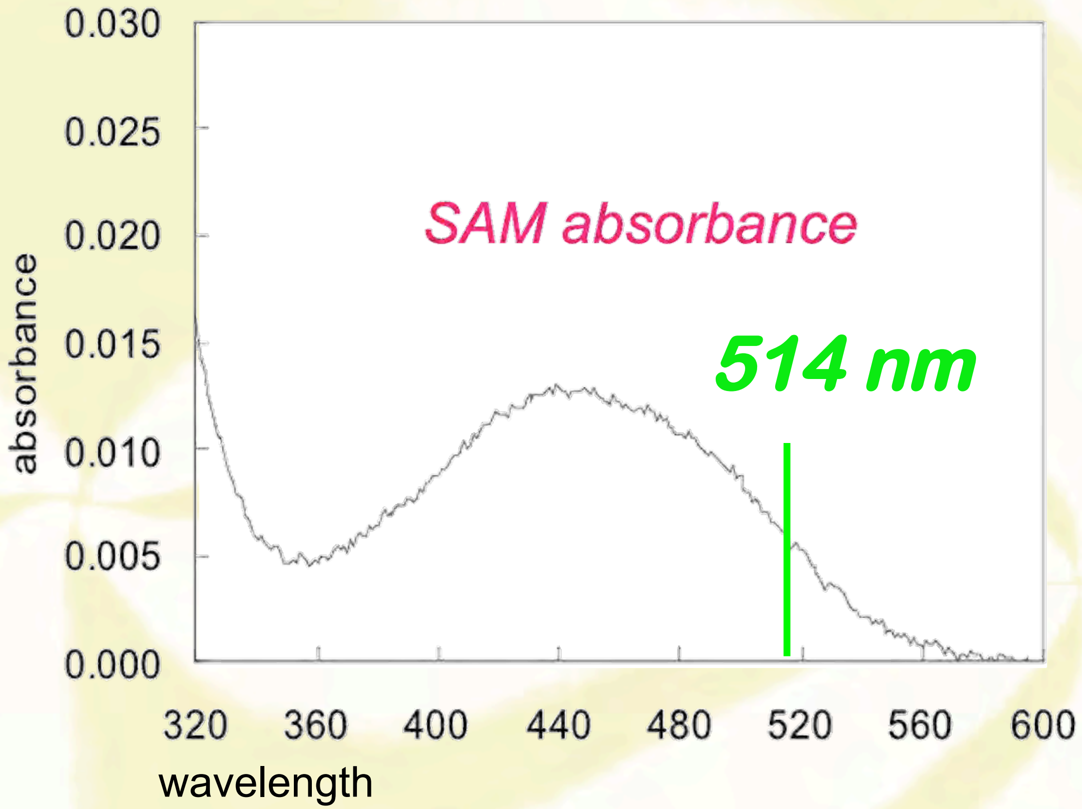


- ***covalently bonded to glass surface***
- ***photo-orients in-plane***

Weigert mechanism:

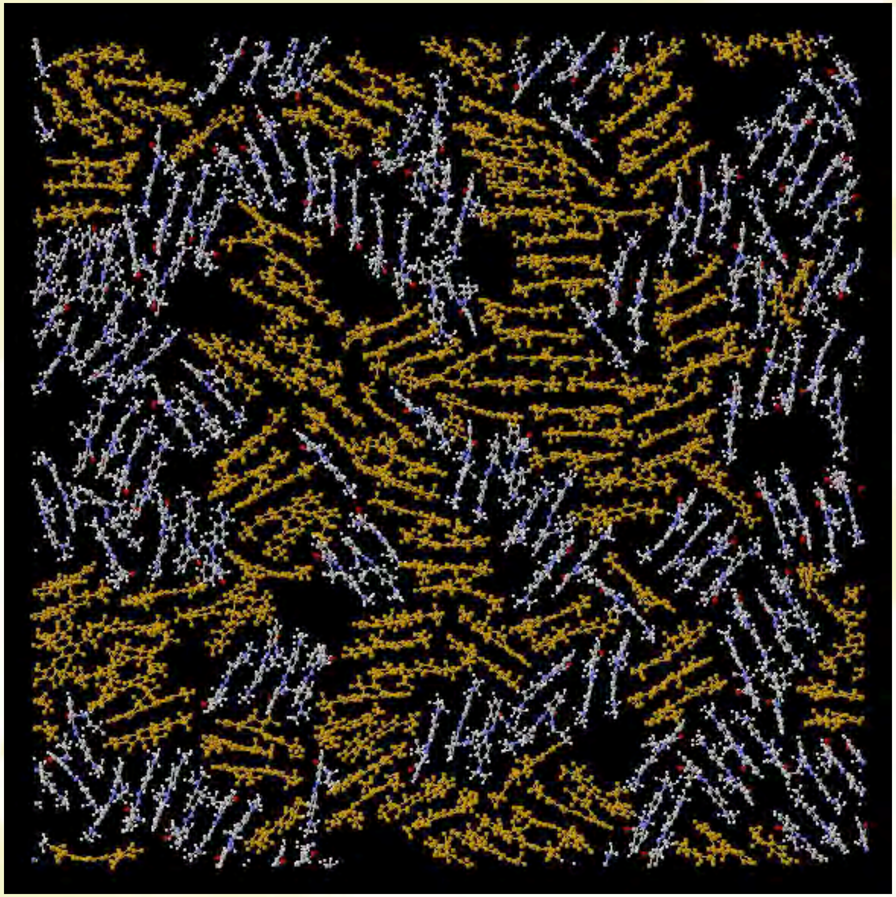
- ***photo-orientable 2D XY system***

optical absorbance of the dMR monolayer

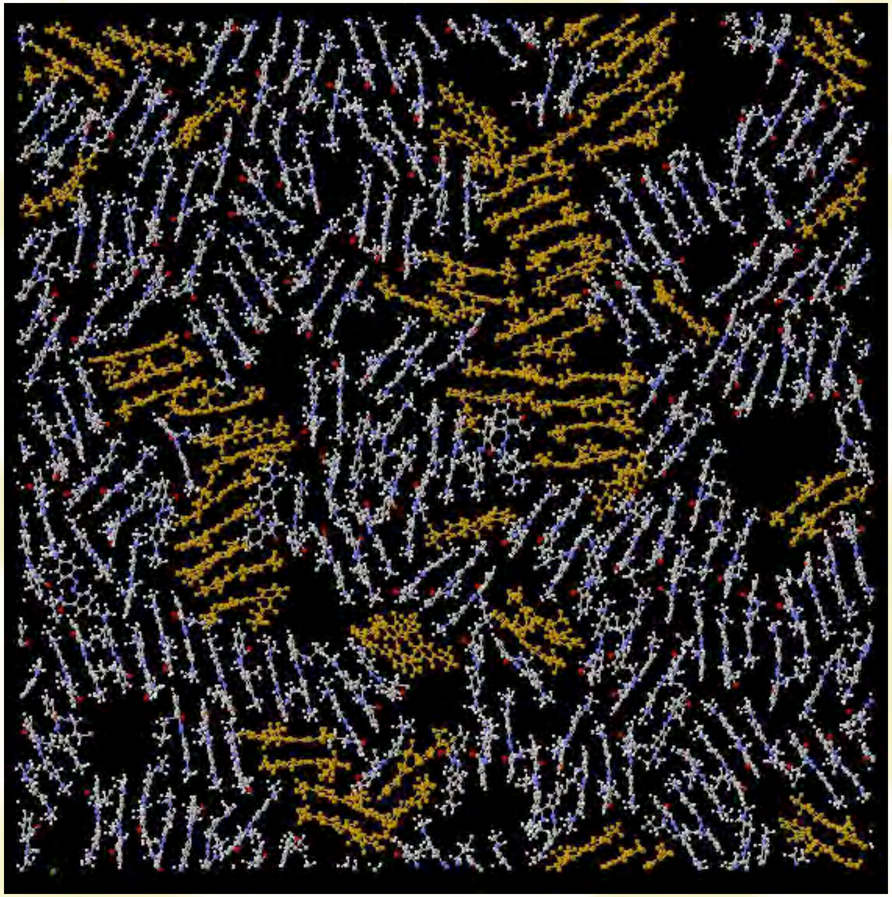


- ***compare to solution** (monolayer ~70% coverage)*
- ***a fluence of** 20mJ/cm^2 **gives** 1photon absorbed/molecule (pa/mol)*

Photo-orientation

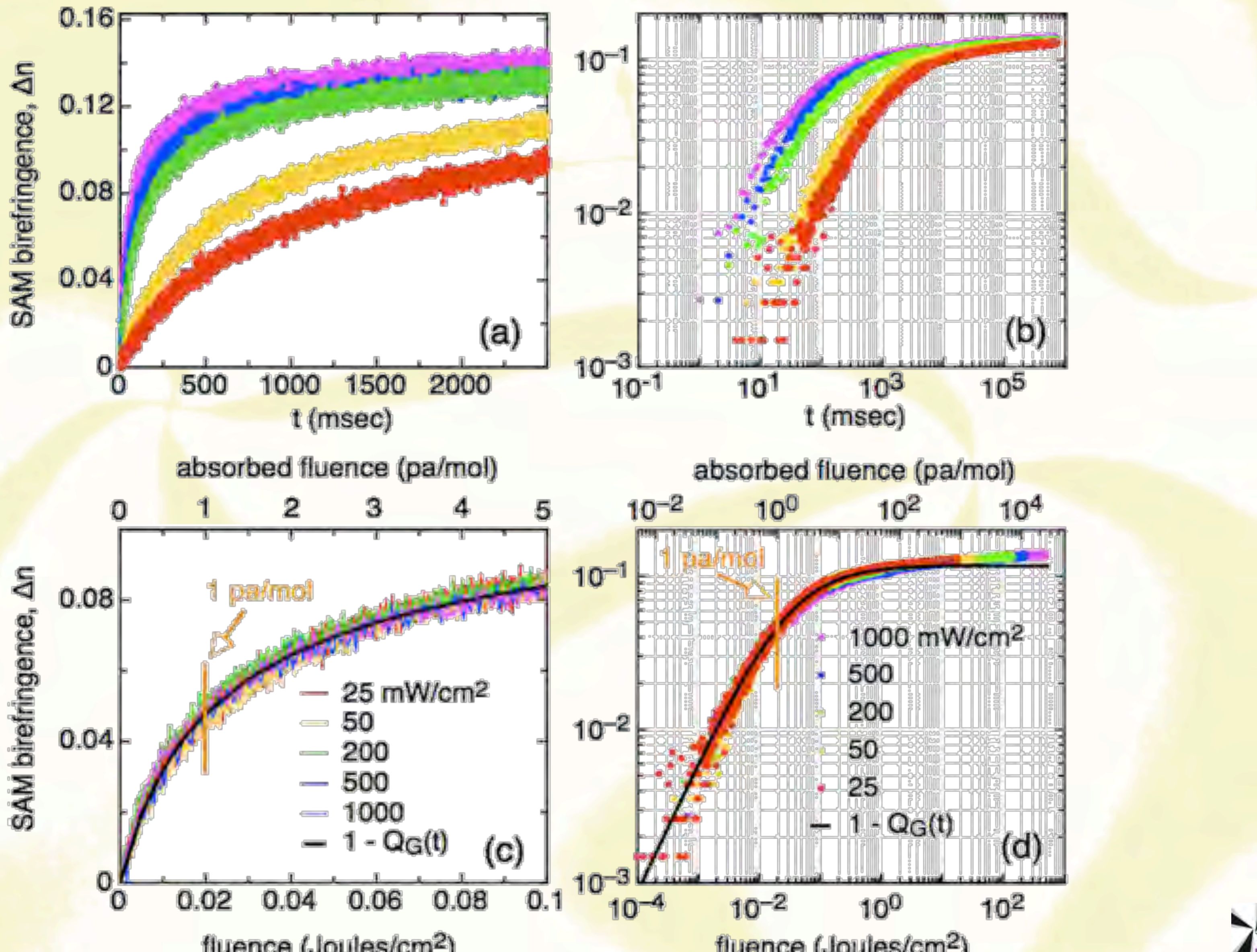


t=0



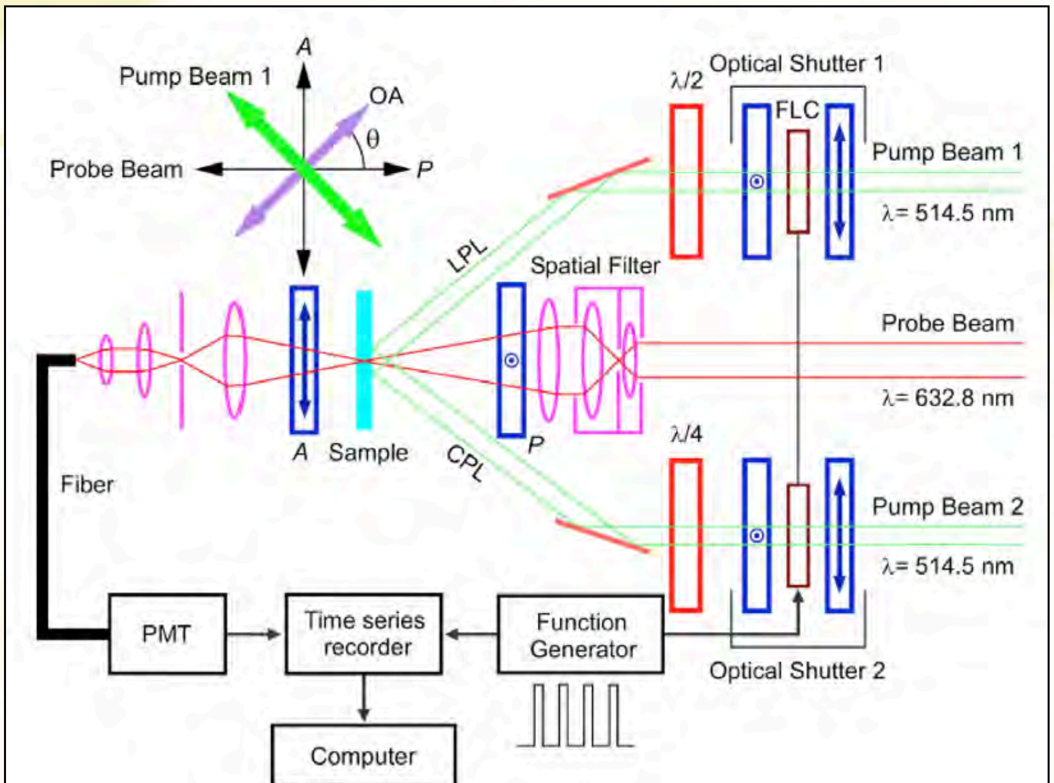
After 9ns

writing dynamics

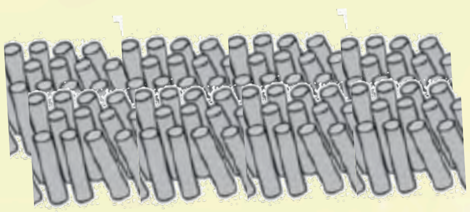


dynamic measurement of in-plane birefringence

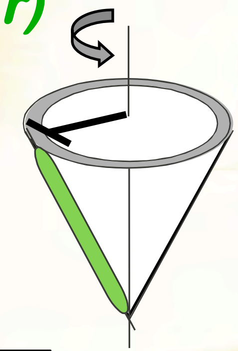
- *red probe light (632 nm, focused to 40µm)*
- *green write light (514 nm focused to 1mm)*
- *100 µsec time resolution*
- *high extinction contrast between crossed polarizers (2.4 x 10^{-10})*



a 2D nematic (smectic C monolayer)

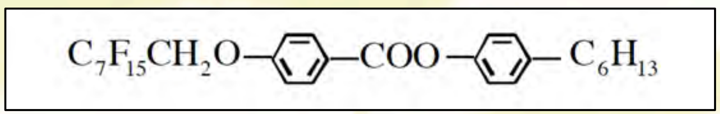


$\phi(r)$



deGennes (1972)

$$\langle \Phi_q(0)\Phi_q(\tau)\rangle = \langle |\Phi_q|^2\rangle \exp(-Dq^2\tau) = \frac{k_B T}{Kq^2}\exp(-Dq^2\tau).$$



$D = K/\gamma$

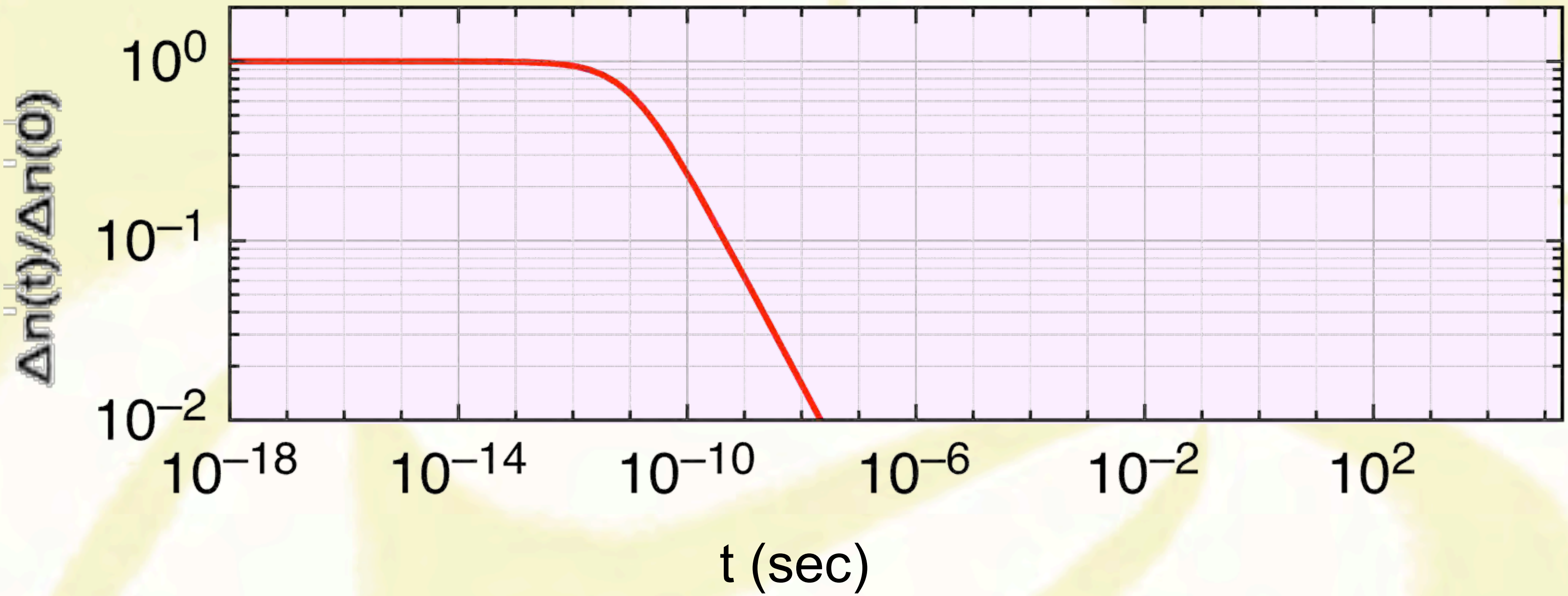
$\Delta n(t) \sim (t/\tau)^{\alpha}$

$\alpha = T/8\pi K$

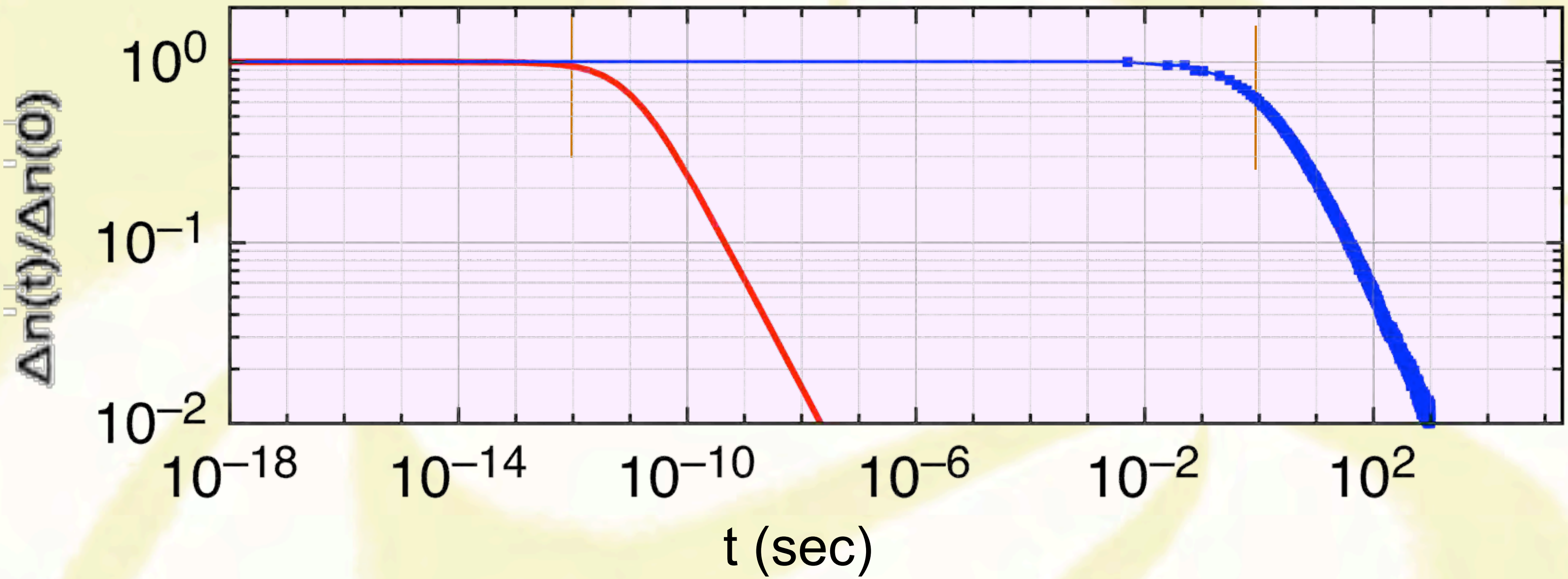
$\tau = a^2/D = a^2\gamma/K$

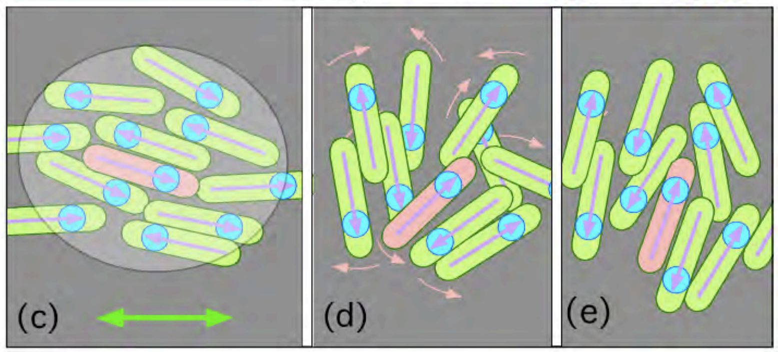
$\tau \sim 10$ psec

comparing SmC and dMR monolayers*



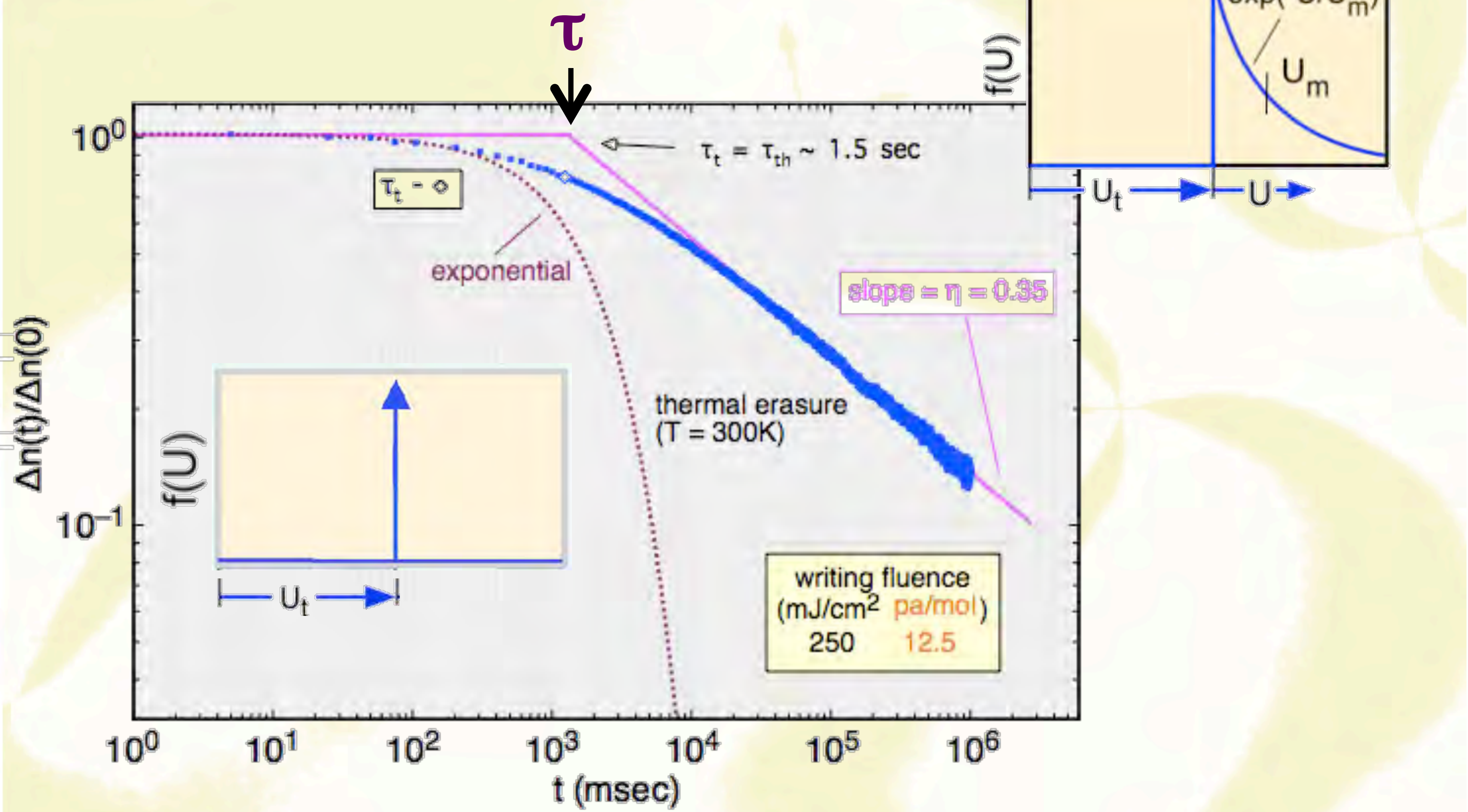
tethered monolayer is a glass





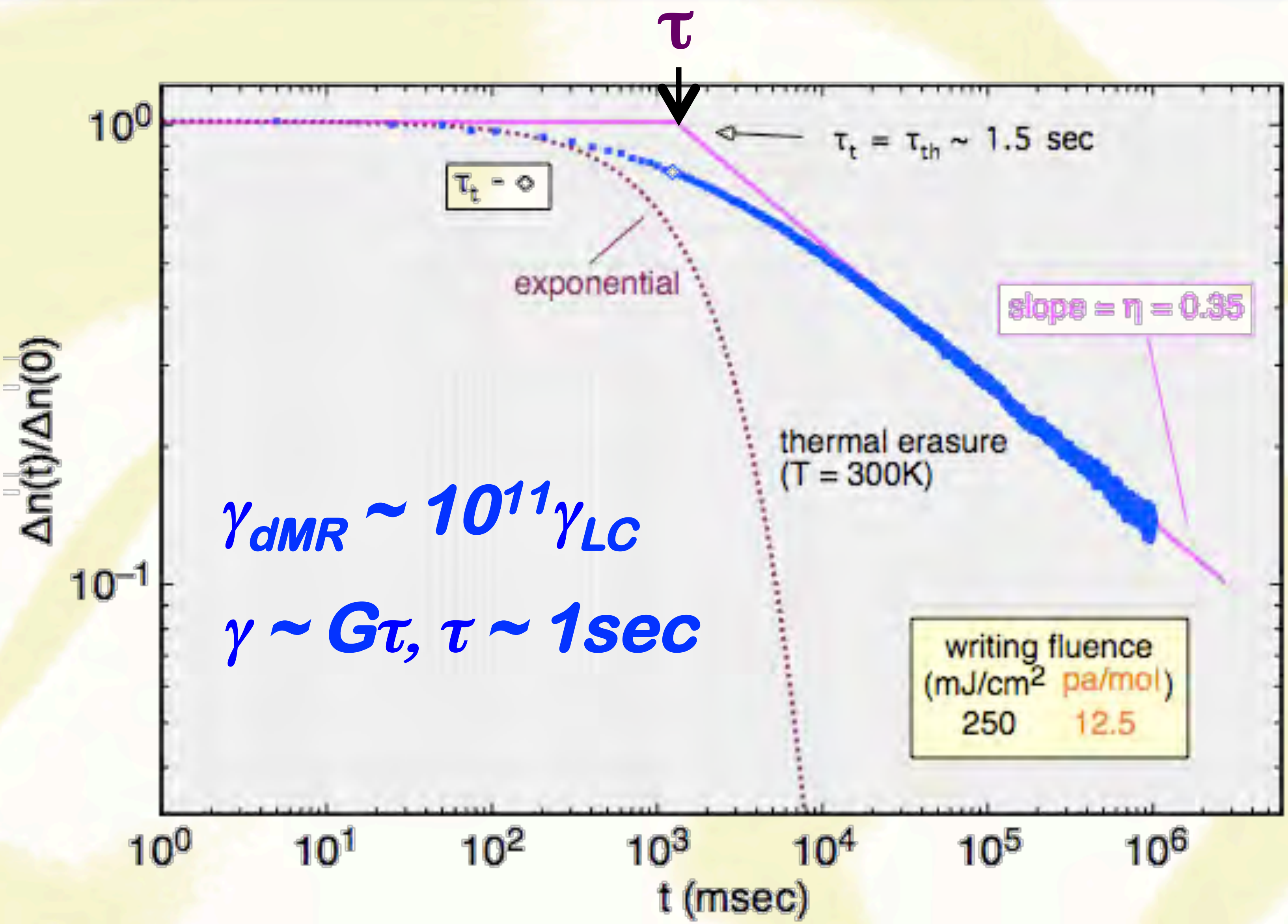
$\gamma_{DMR} \sim 10^{11}\, \gamma_{SmC}$

erasure by $k_B T$ at $T = 300K$



$U_t \sim k_B T \ln(10^{11}) = 7{,}500K$

dMR monolayer is an orientational glass

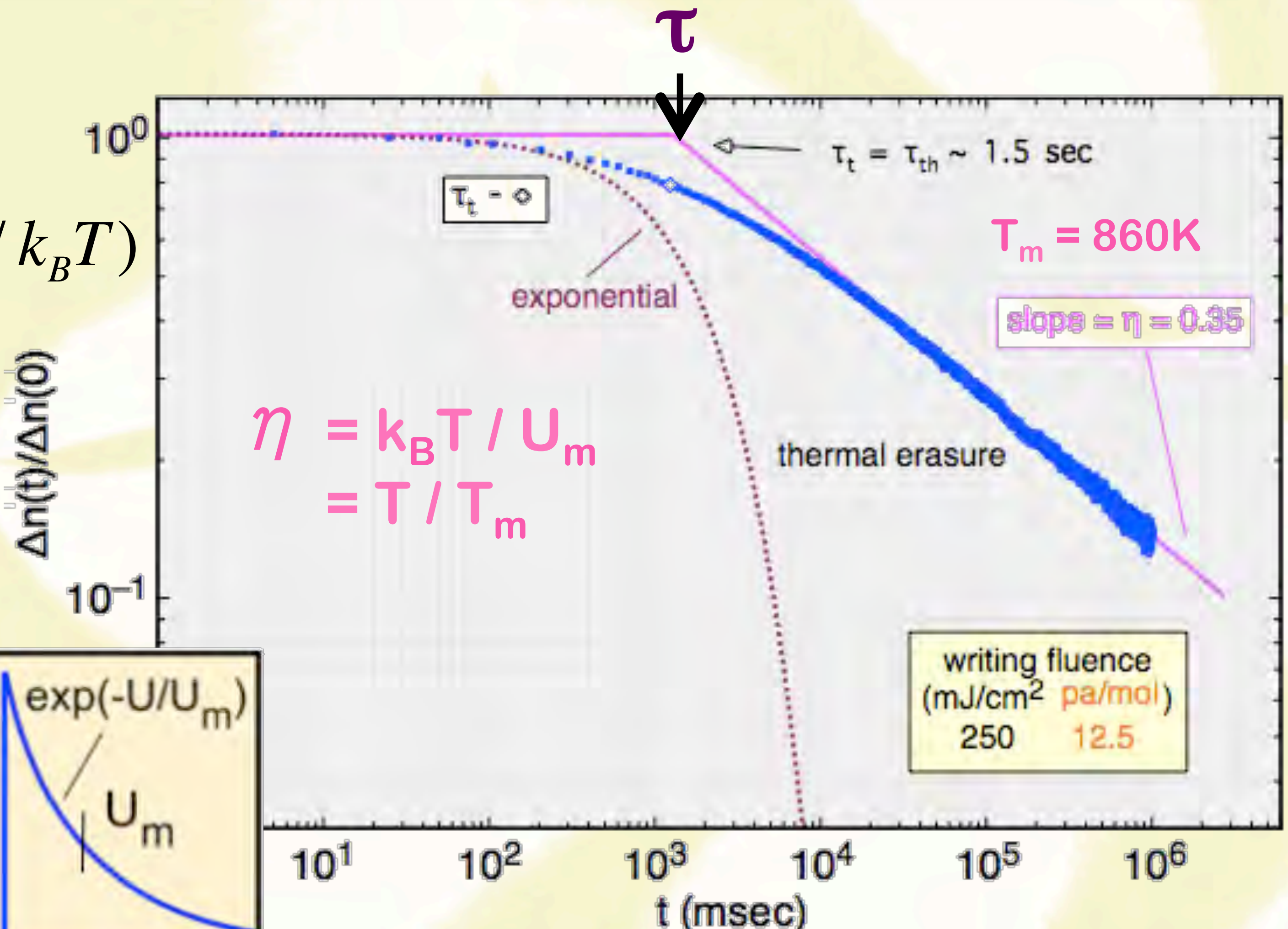


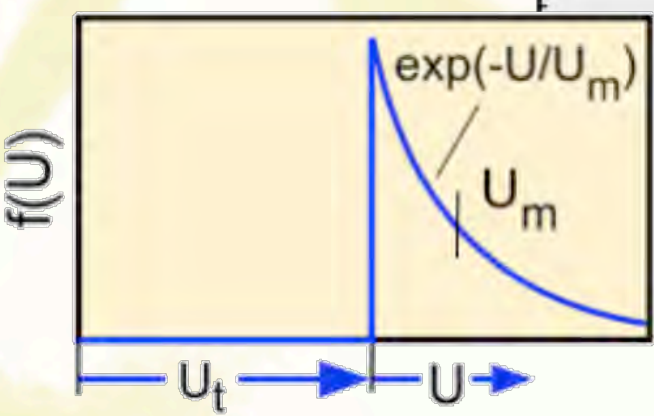
$\gamma_{dMR} \sim 10^{11} \gamma_{LC}$

$\gamma \sim G\tau, \ \tau \sim 1sec$

The barrier gap (activation energy)

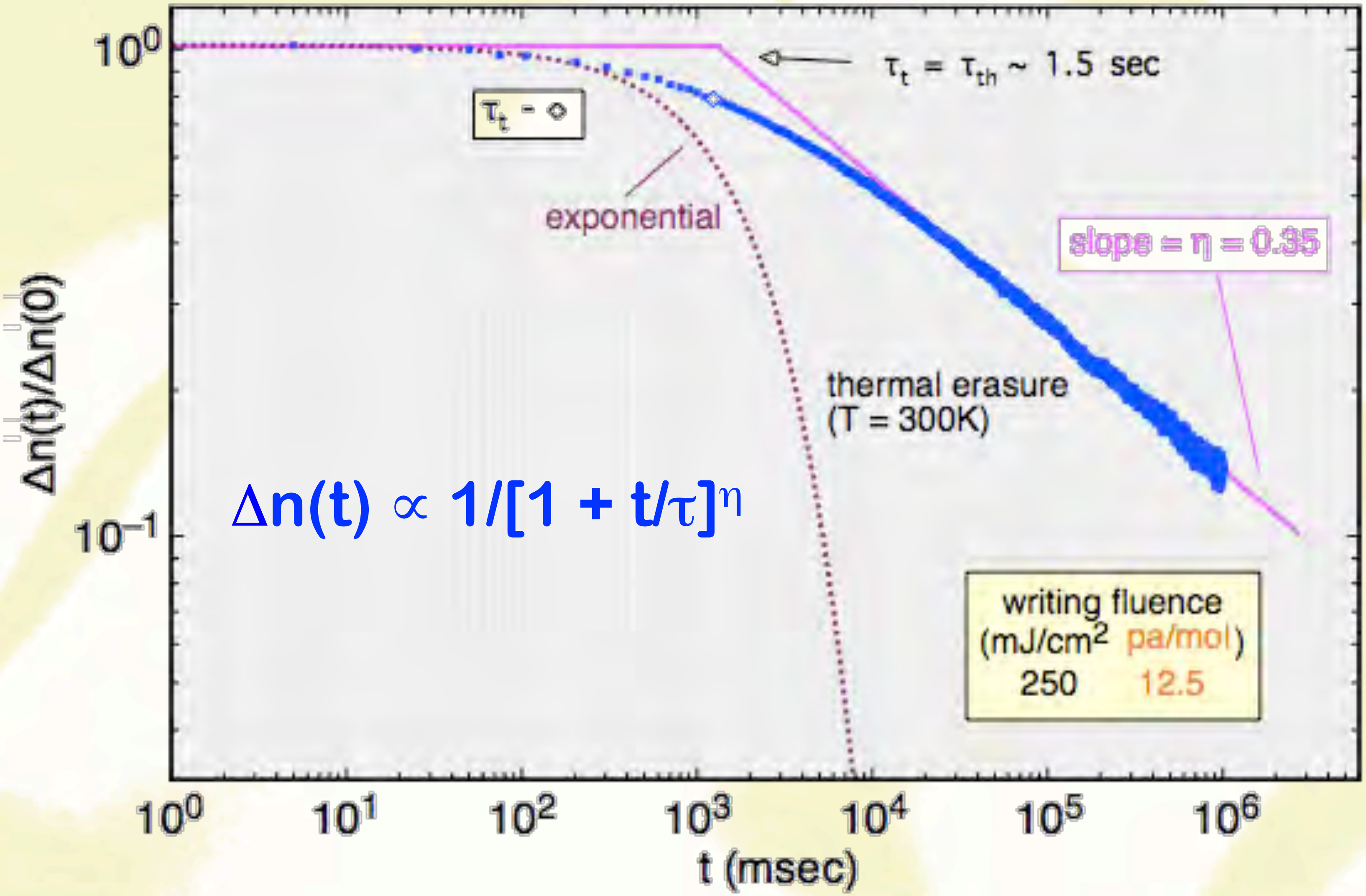
$$\tau(U) = \tau_r \exp(U / k_B T)$$



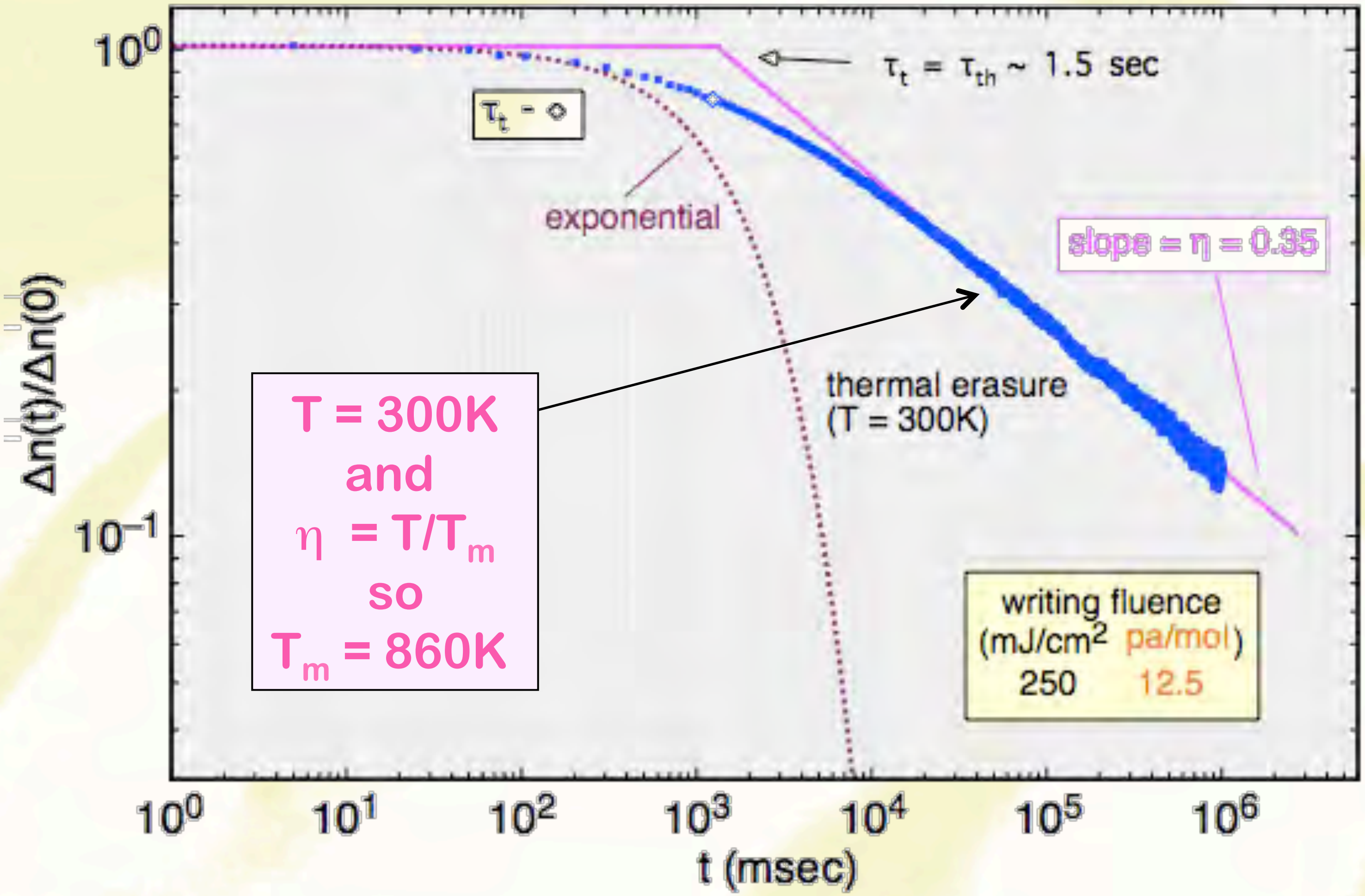


$U_t \sim k_B T \ln(10^{11})$ = 7,500K

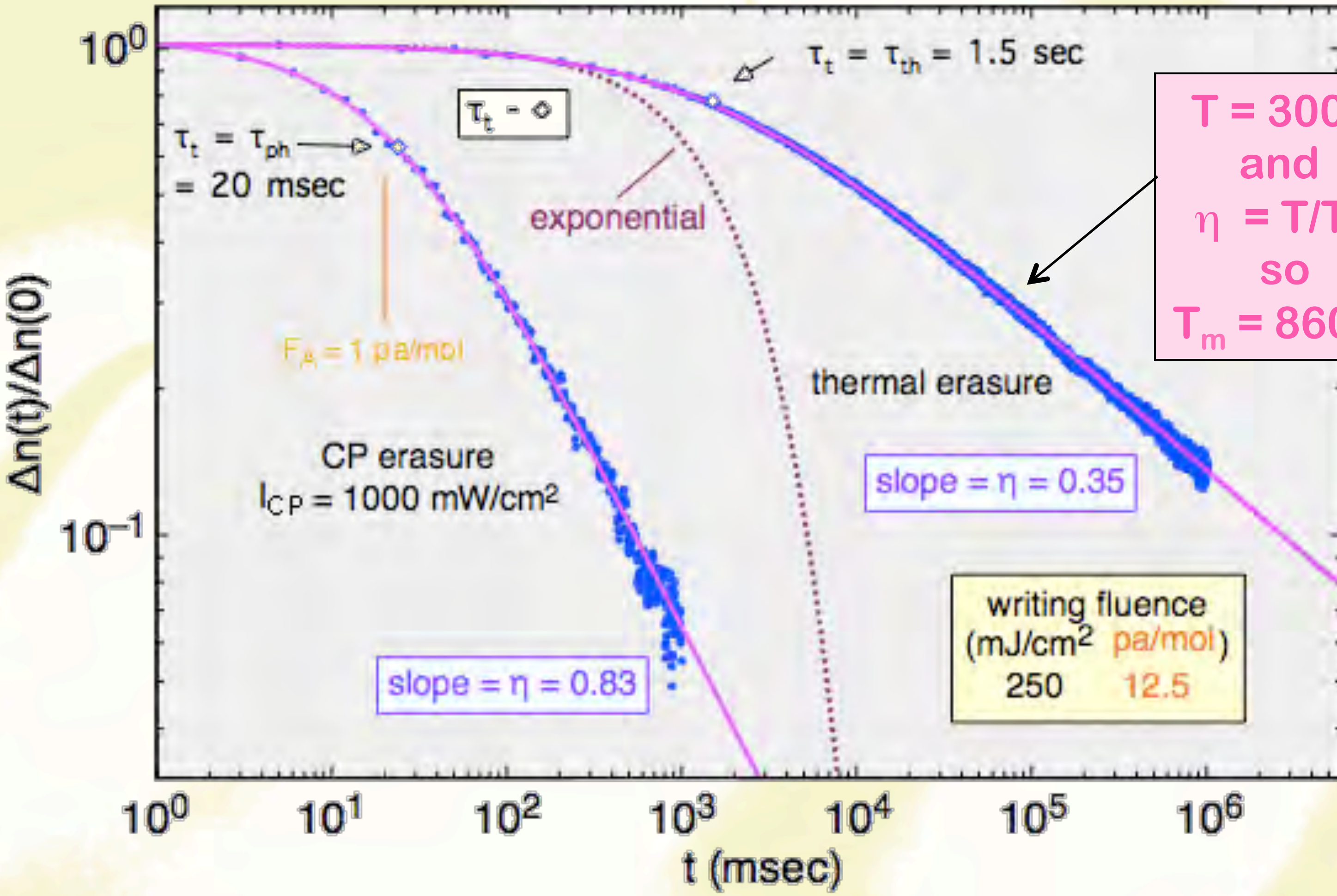
erasure by k_BT at T = 300K



the power law tail

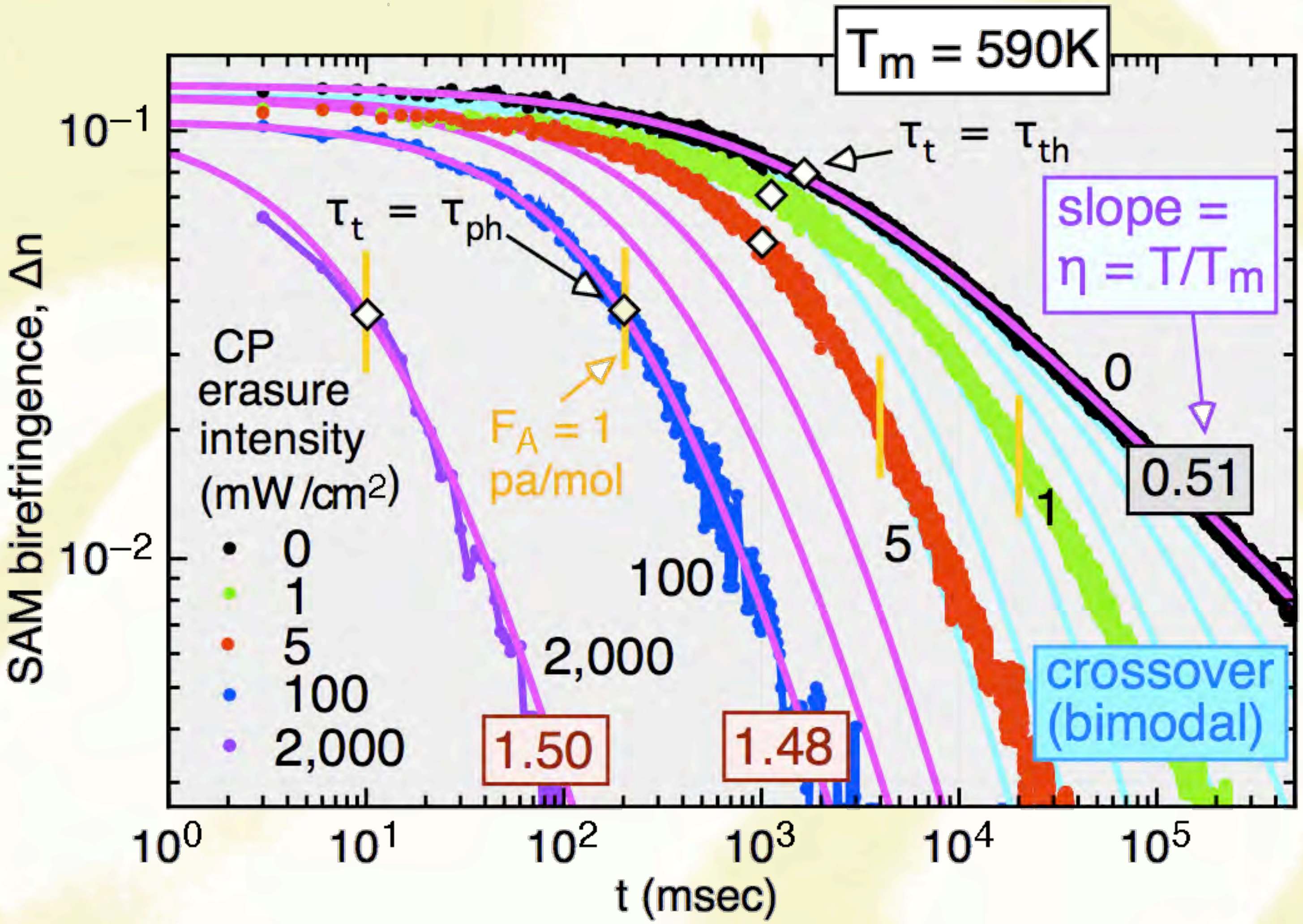


erasure by circularly polarized light

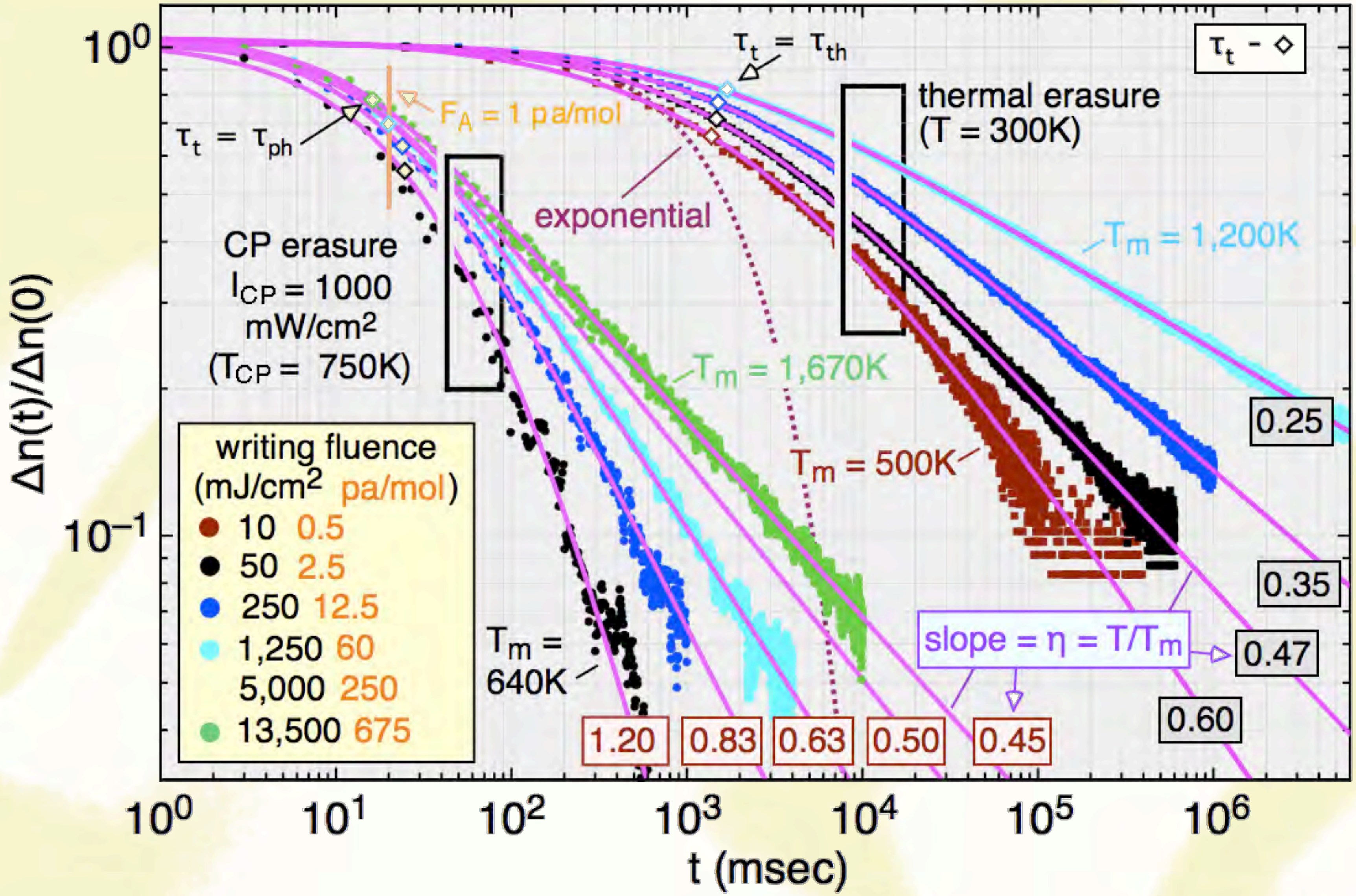


T = 300K
and
$\eta = T/T_m$
so
T_m = 860K

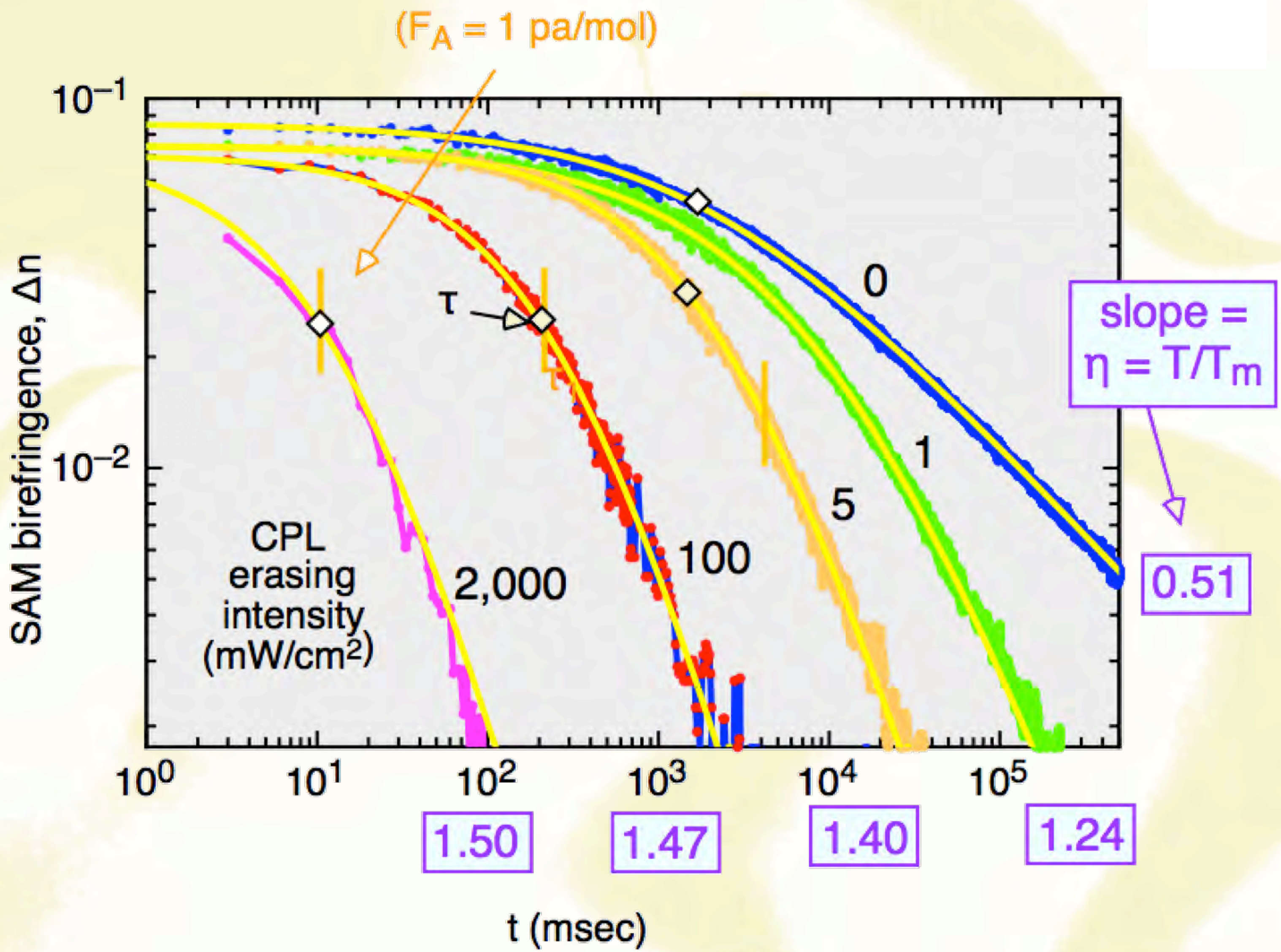
crossover to photo-controlled erasing



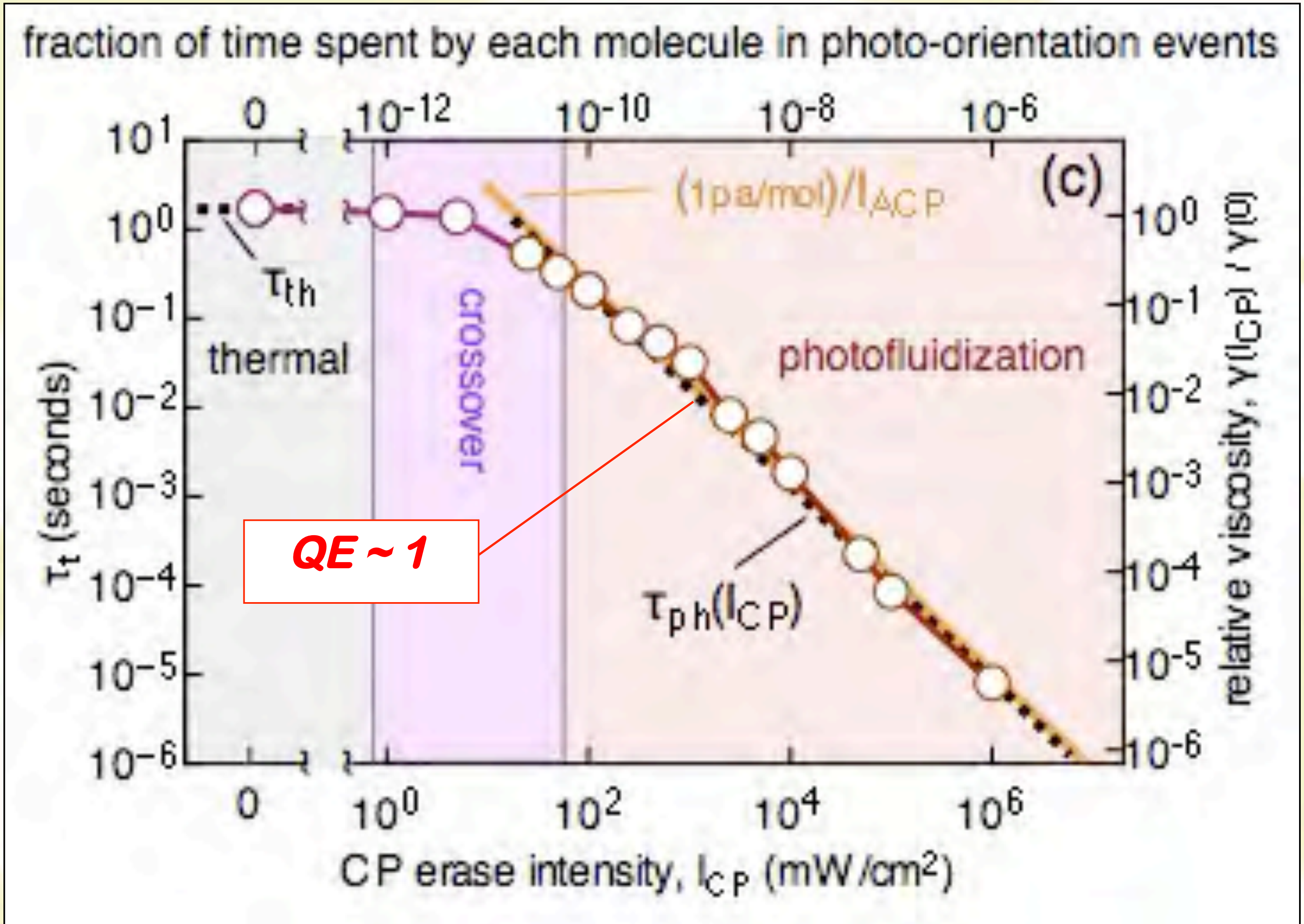
T_m increases with writing fluence



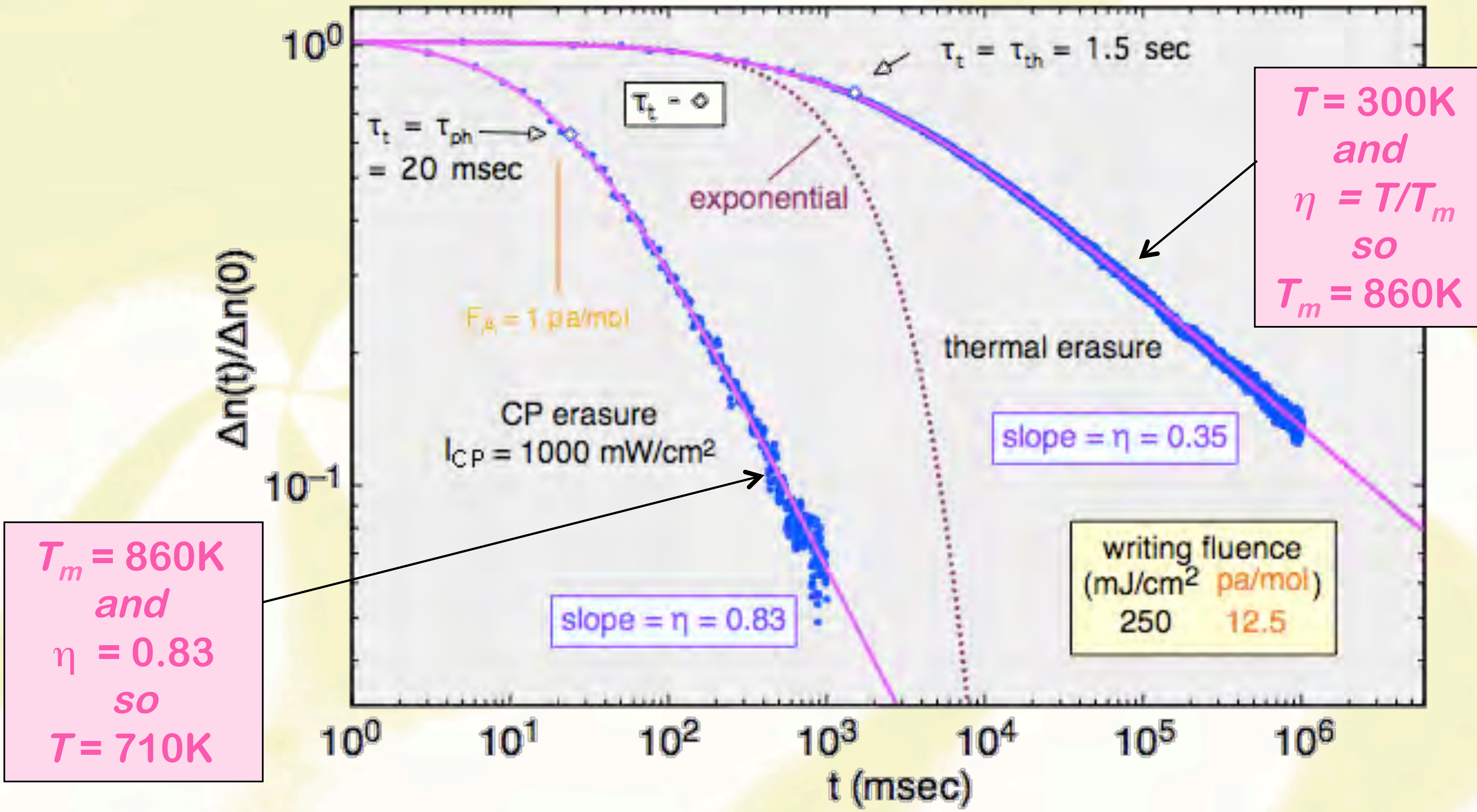
increasing erase intensity



τ occurs at F = 1 photon absorbed/molecule



erasure by circularly polarized light



every absorbed photon induces a local glass transition

U_t = 7,500

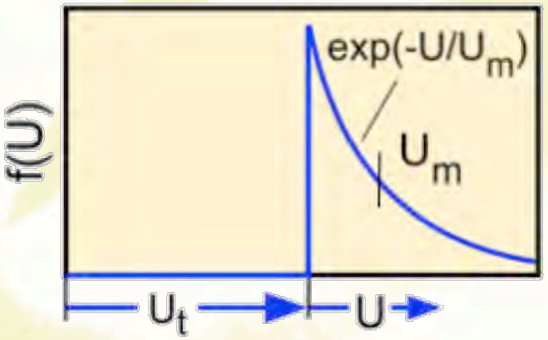
T = 800K

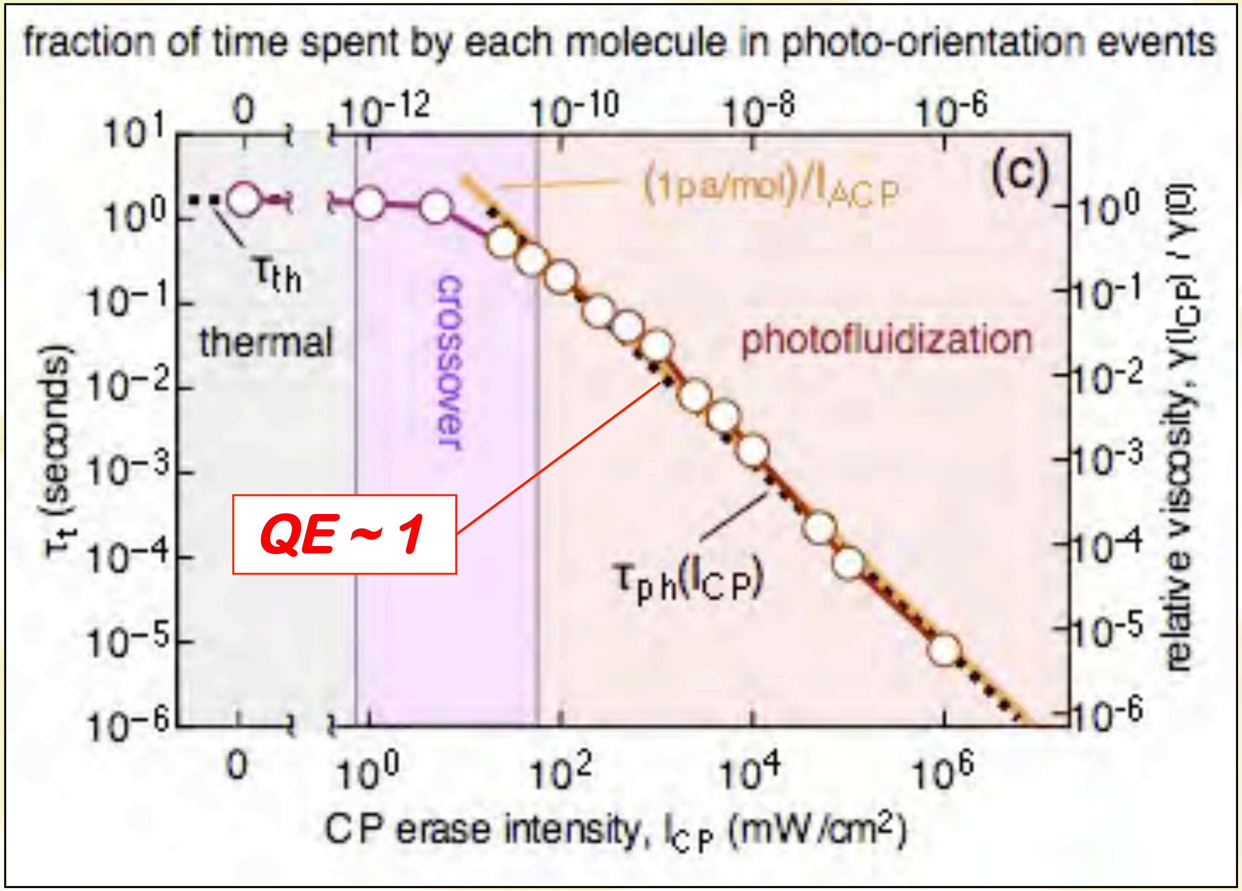
gives

QE ~ exp(-7,500/800)

but we find

QE ~ 1!



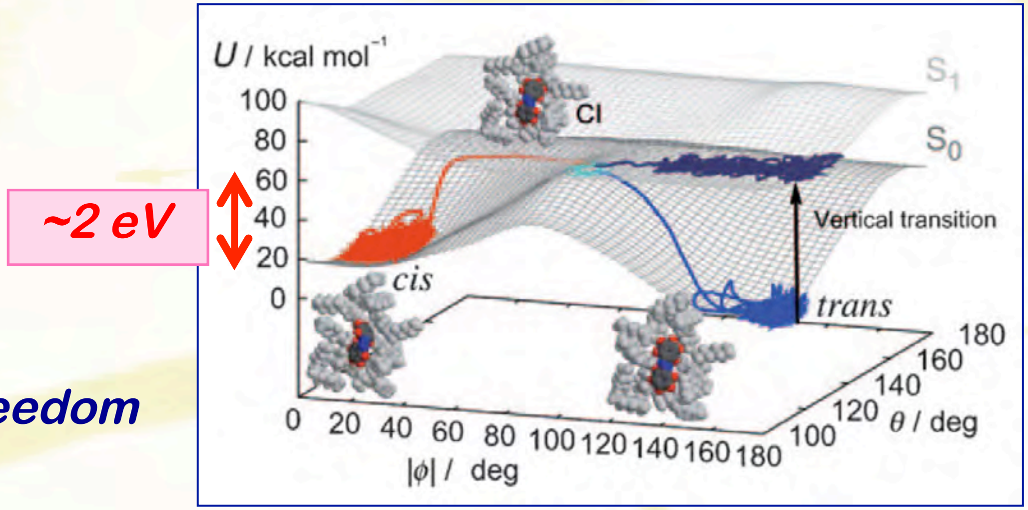


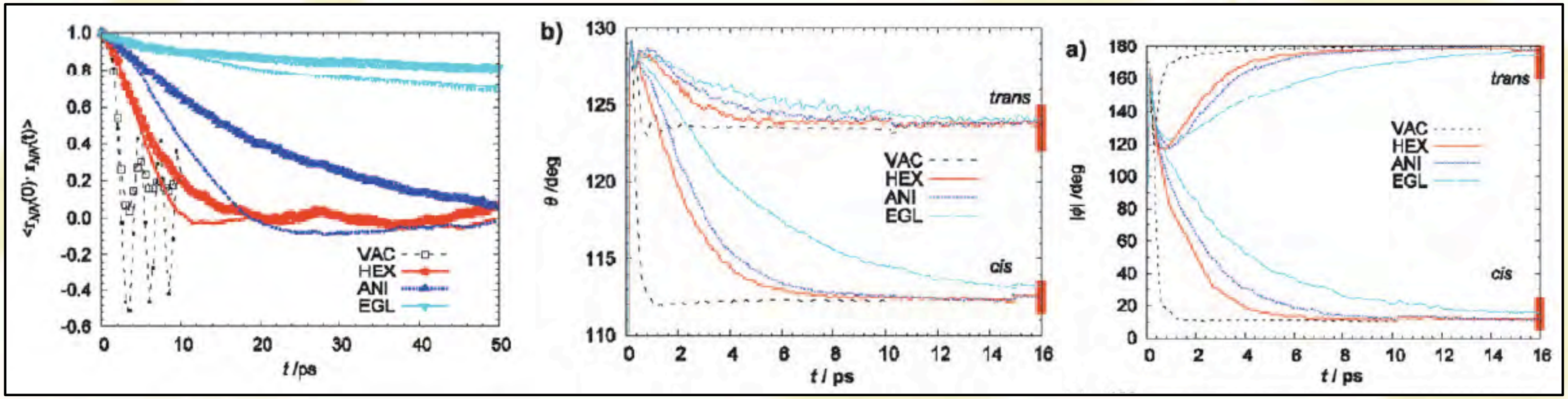
This means that each 800K photo event melts (fluidizes) the local 7,500K barrier, i.e. produces a local glass transition

the photo-absorption event

- *$h\nu$ = 2.4 eV*
- *$T = h\nu/k_B$ = 29,000K*
- *each molecule:*

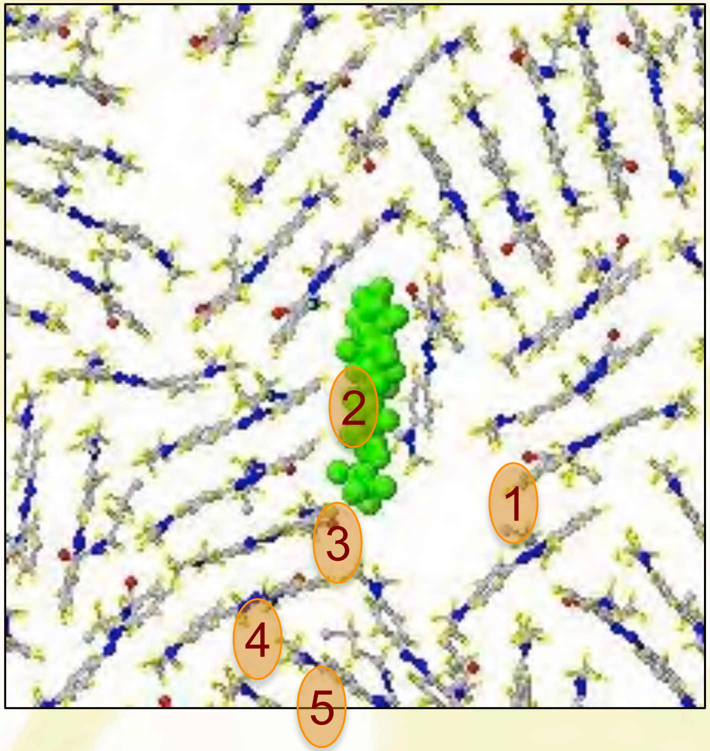
  ~100 motional degrees of freedom

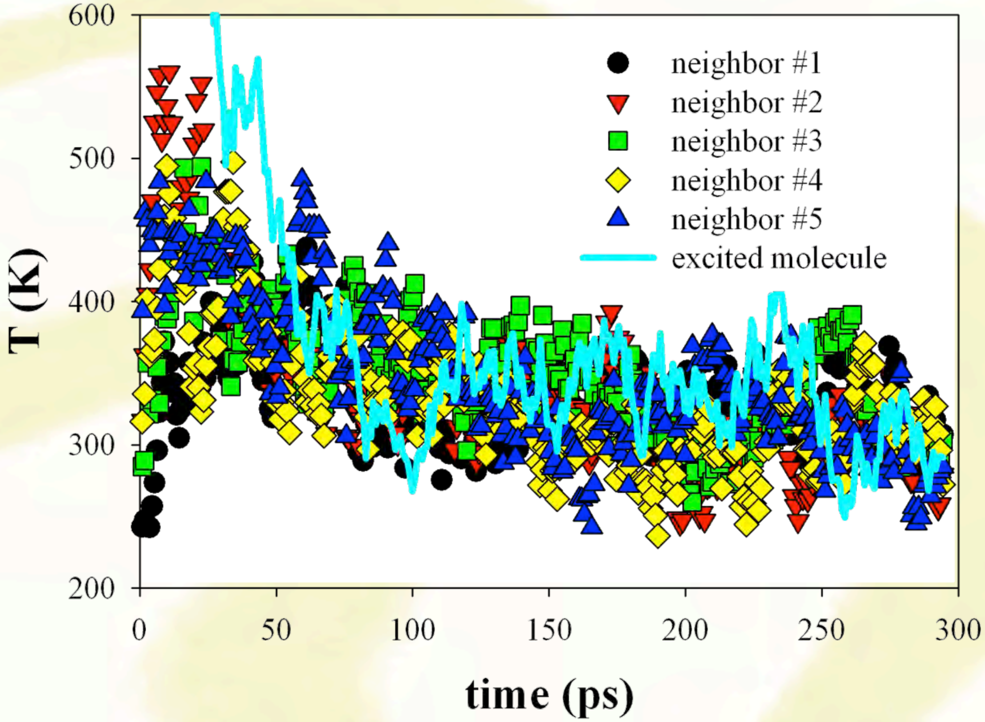




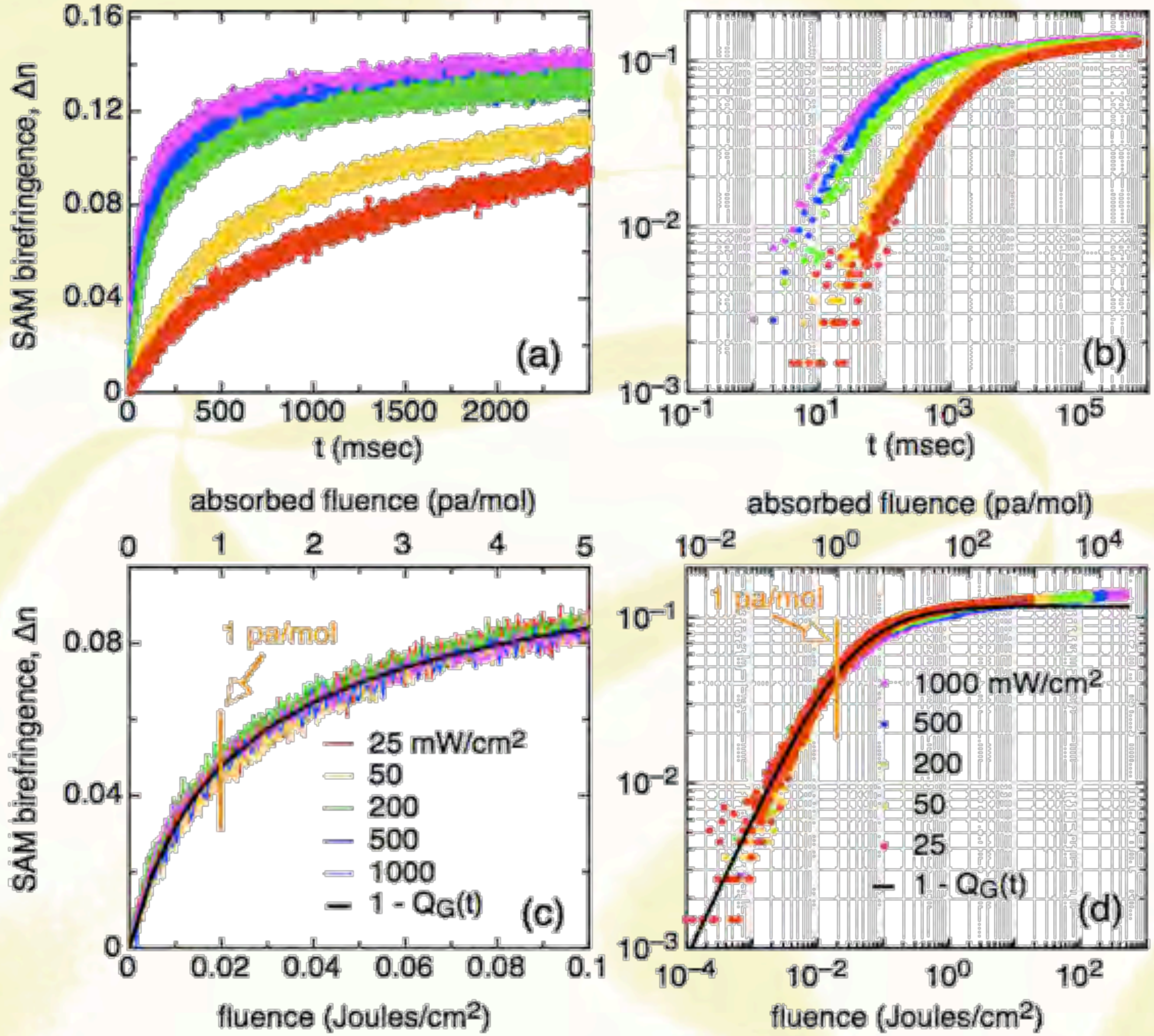
Tiberio, Muccioli, Berardi, & Zannoni, ChemPhysChem (2010)

the photo-absorption event

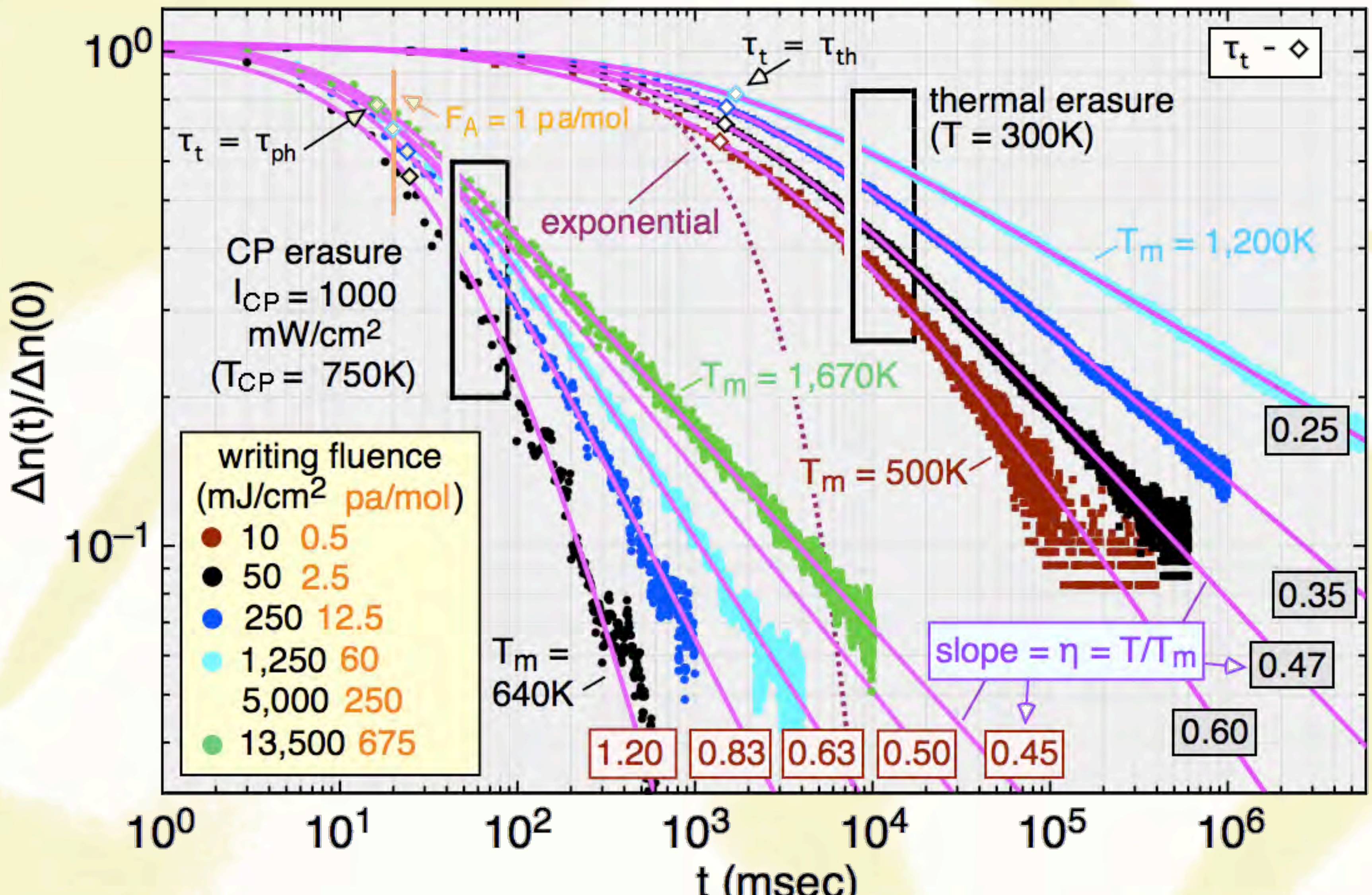




writing dynamics



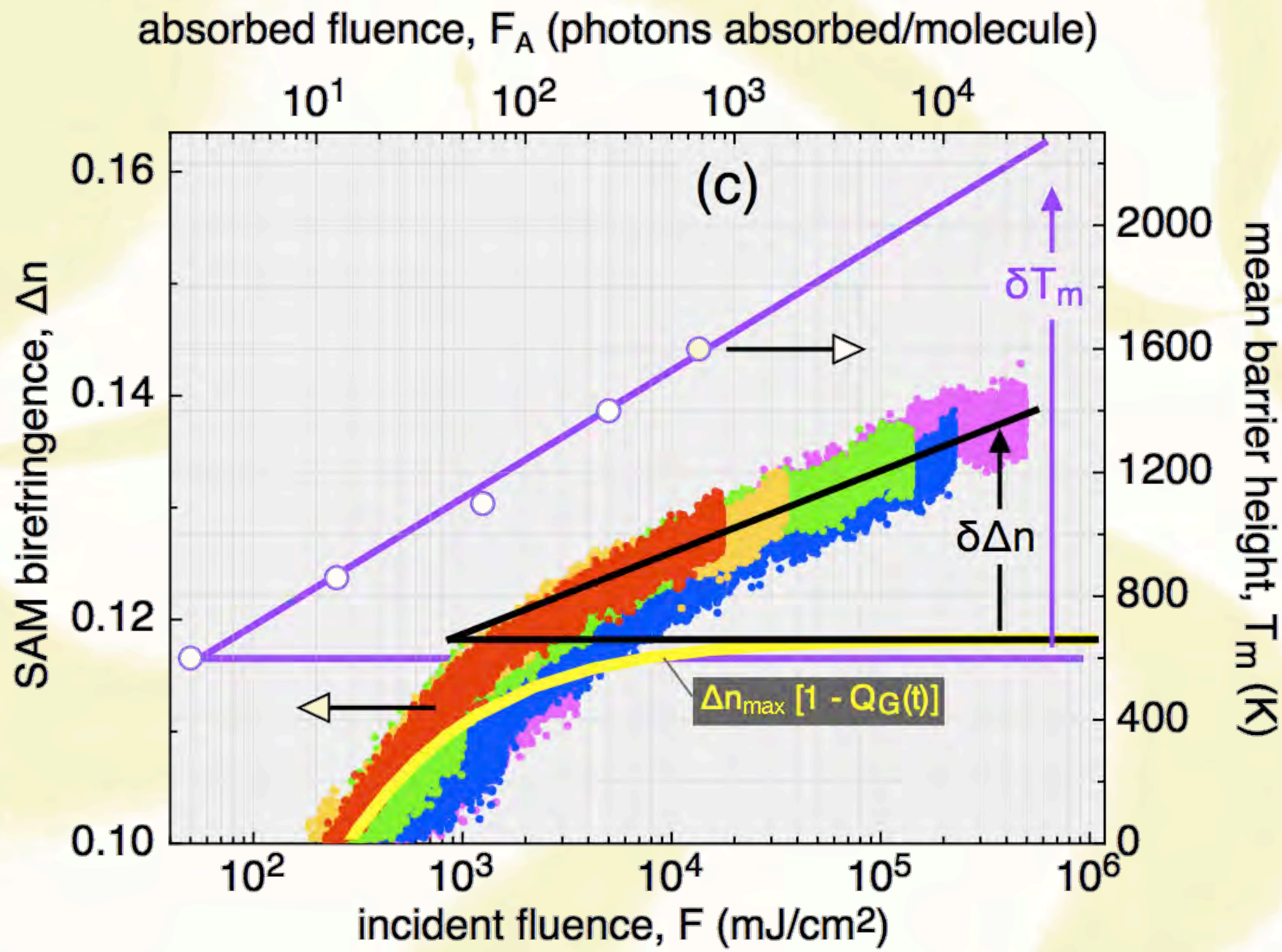
T_m increases with writing fluence



orientational work hardening at large fluence

$\delta\Delta n \sim log(t)$

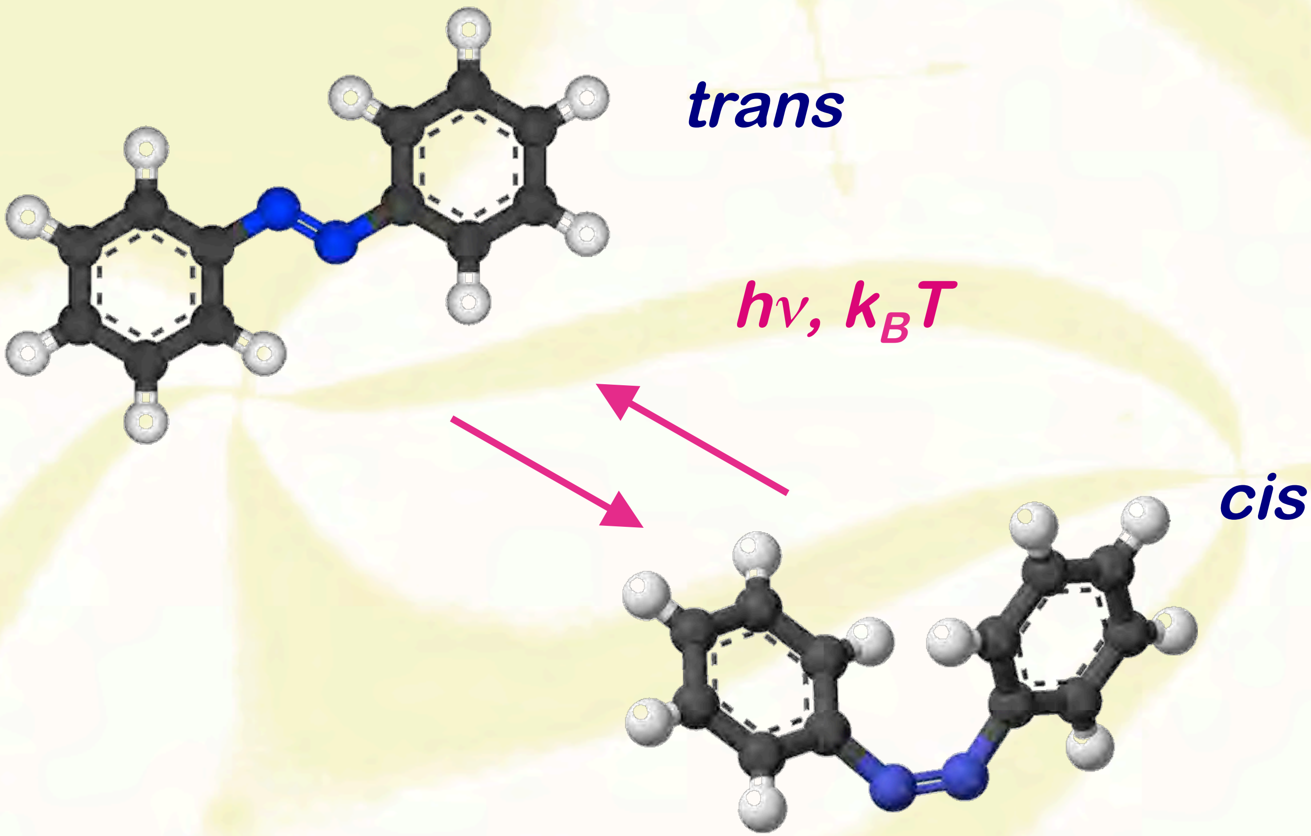
$\delta T_m \sim log(t)$



$$1 \approx P(t) = t\nu_w \exp(-\delta T_m(t)/T)$$

Nabarro Mat. Sci. and Eng. A (2001)

azobenzene



summary

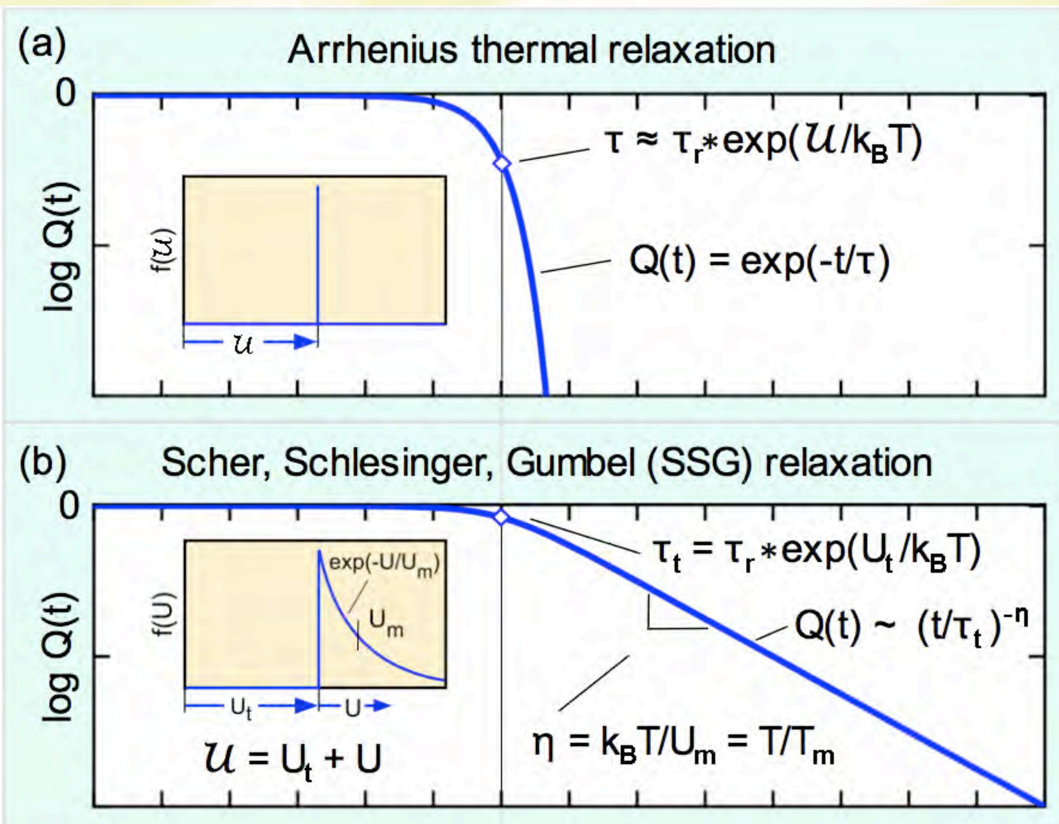
- *photo-indiced relaxation is essentially isothermal*
- *thermal and photo-induced relaxation events occur by random sequences of discrete local relaxation events.*
- *isomerizing molecules attack their confining barriers with an effective T ~ 800K*
- *the T ~ 800K attacks produce local glass transitions, such that every photon generates a barrier escape event*

the end

barrier height distributions

$$\tau(U) = \tau_r \exp(U / k_B T)$$

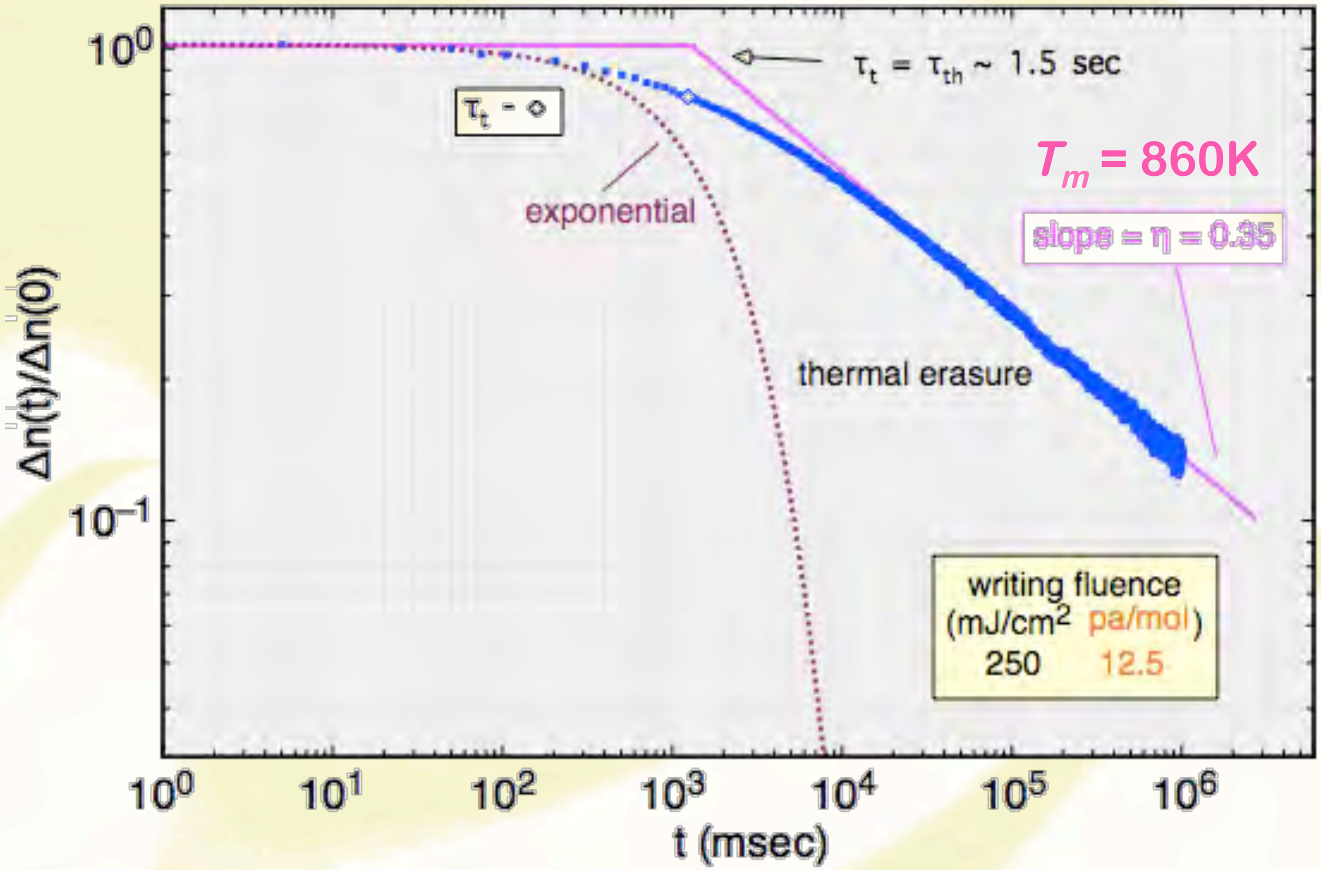
$$Q(t) = A \int_0^\infty e^{-(t/\tau)} H(\tau) d\tau = \int_0^\infty e^{-(t/\tau(U))} f(U) dU$$

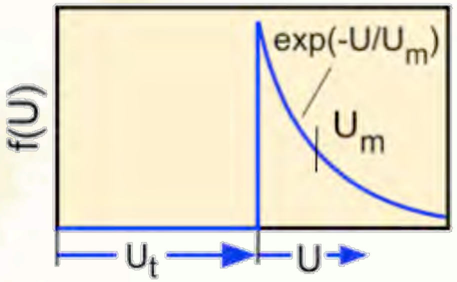


$$\tau = \tau_r \exp(U(t) / k_B T)$$

$$U() = k_B T \log(/\tau_r)$$

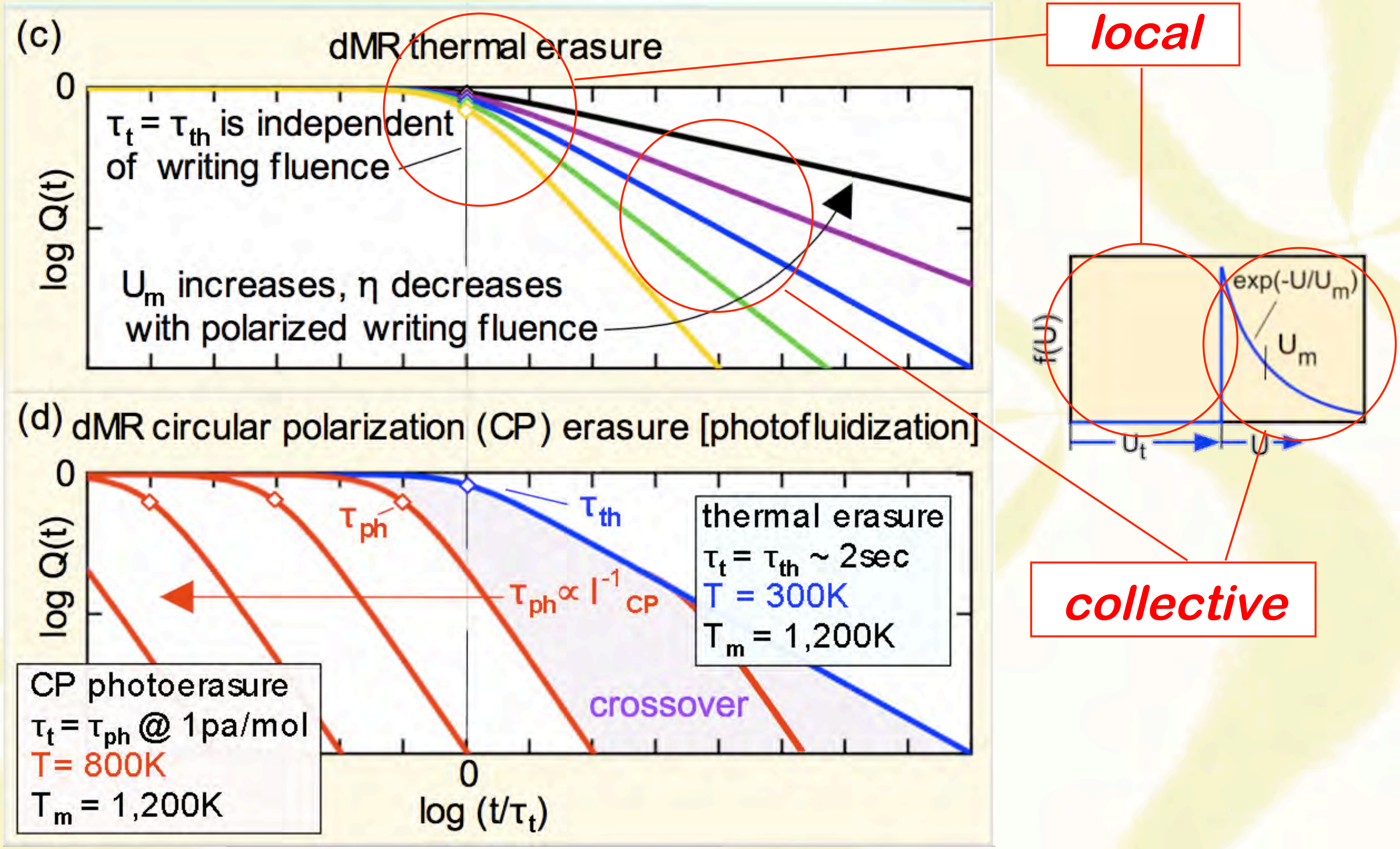
it's an orientational glass





$U_t \sim k_B T \ln(10^{11}) = 7{,}500K$

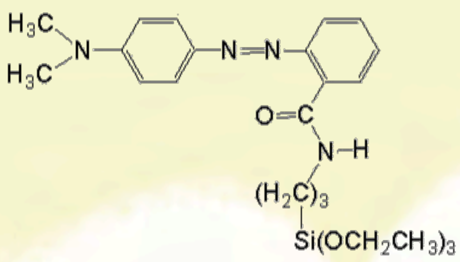
dependence on writing and erasing



azo-based tethered molecular monolayer

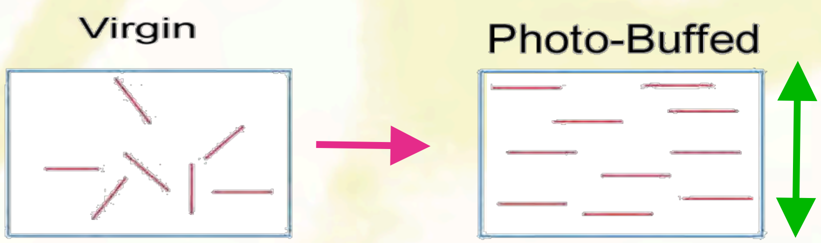
- ***precursor***

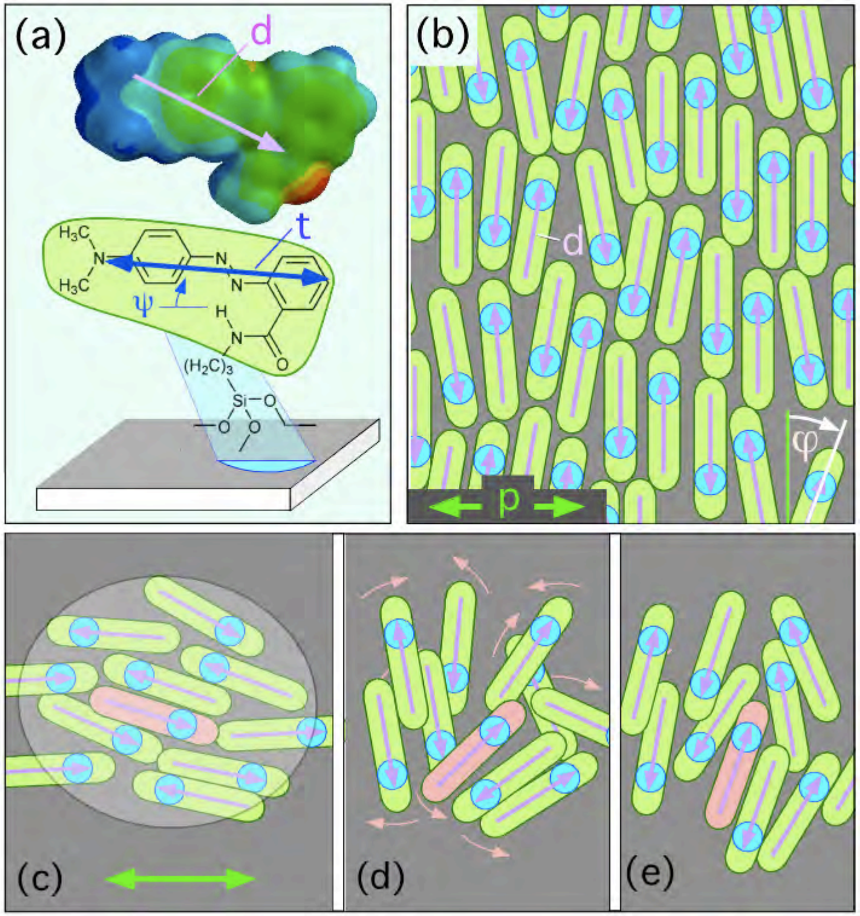
  (a derivative of methyl red - dMR)



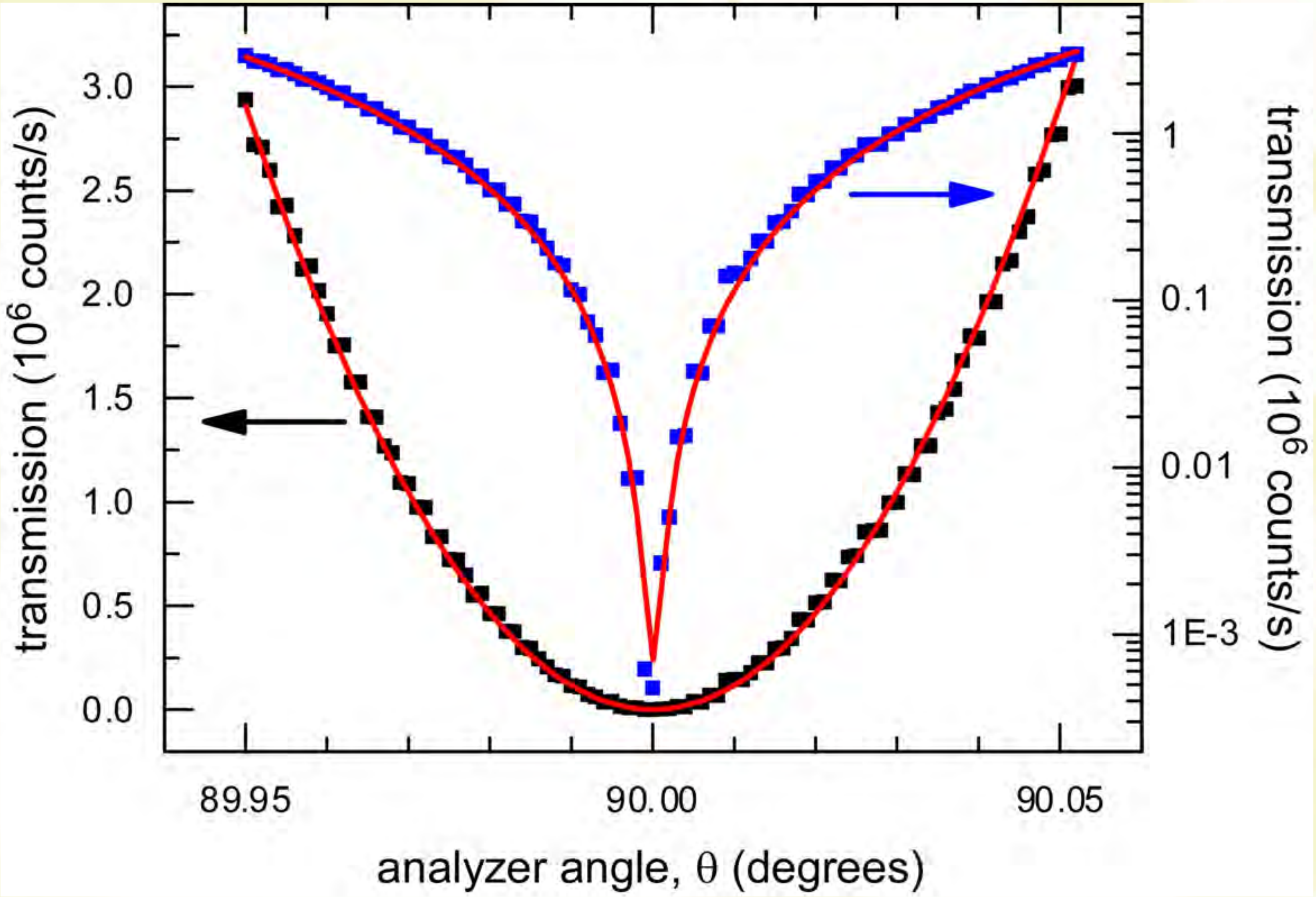
- ***covalently bonded to glass surface***
- ***photo-orients in-plane***

Weigert mechanism:





- ***photo-orientable 2D XY system***



transmission (10^6 counts/s)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1
0.1
0.01
1E-3
89.95
90.00
90.05
analyzer angle, θ (degrees)

a different model

Michael F. Shlesinger Ann. Rev. Phys. Chem. 1988. 39: 269–90

- orientational diffusion with a divergent distribution of waiting times:

$$Q(t) = \int \exp(-t/\tau)\, H(\tau)\, d\tau$$

- $\tau = \tau_o \exp(\Delta/kT)$, the rate is determined by activated hopping with barrier Δ
- $f(\Delta) = (kT_o)^{-1} \exp(-\Delta/kT_o)$, the barrier is distributed with a mean width kT_o
- With these assumptions Schlesinger shows

$$H(\tau) \propto (\tau_o/\tau)^{\beta}$$

with

$$\beta - 1 = T/T_o$$

barrier model results

- *integration gives*

$$Q_e(t) = [1 + (t/\tau_o)]^{(1-\beta)}, \text{ with } \beta > 1$$

- *power-law writing and erasing:*
  - β *controls erasing:* $\Delta n(t) \sim Q_e(t) = (t/\tau_o)^{(1-\beta)} = (t/\tau_o)^{-T/To}$ *at large t*
  - *writing:* $\Delta n_w \propto (1 - Q_e(t)) \propto (t/\tau_o)$ *at small t*

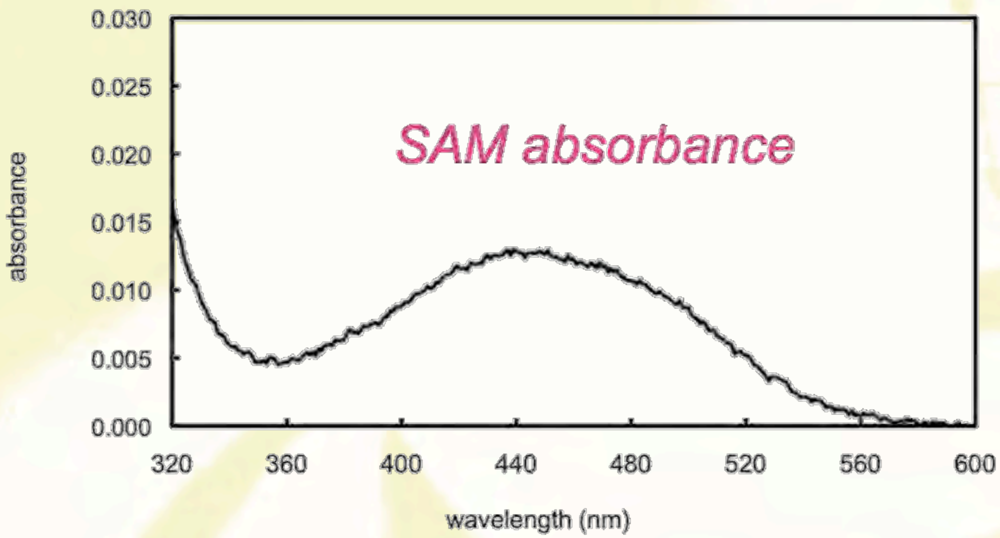
- β *depends on net energy that generated the written state through mean barrier height* T_o

$$\beta - 1 = T/T_o$$

- T_o *increases as log(dose)*

$$T_o \propto \delta(t)$$

coverage measured by absorbance



$$\frac{1}{N_s} = \frac{3}{2A}\frac{\sigma_{iso}}{\ln 10}\left\langle \sin^2\theta \right\rangle$$

A : absorbance

θ : tilt angle

N_s : number of molecule/area

$$\sigma_{iso} = 1.1\times 10^{-16}\ \mathrm{cm}^2$$

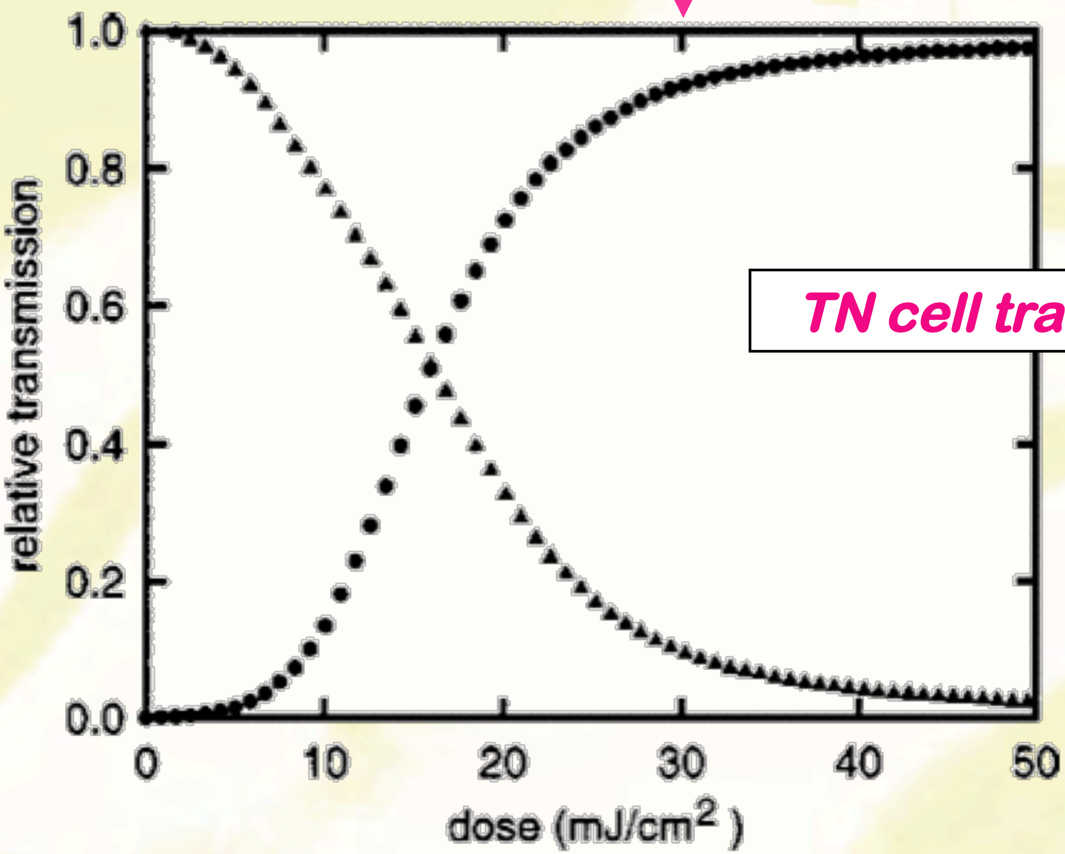
(d-MR in chloroform at 40 nm)

$$\frac{1}{N_s} \approx 1.0\ \mathrm{nm}^2$$ ➡ **monolayer (~ 70% coverage)***

** AFM shows uniform layer morphology*

aligns nematics

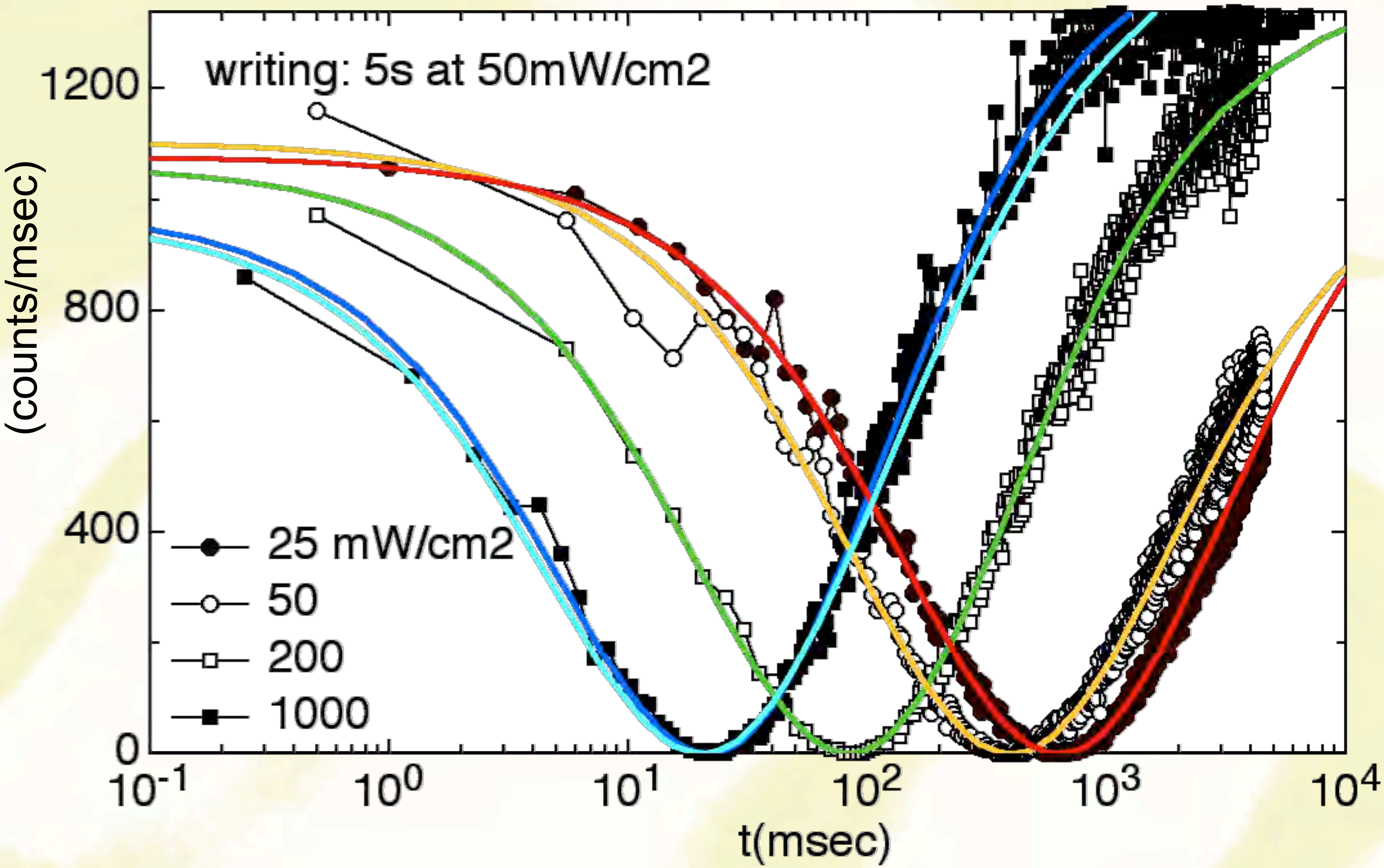
~2 absorbed 450 nm photons/molecule



TN cell transmission

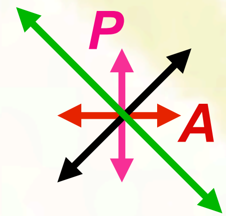
Yi & Furtak, APL 2004

reorienting the writing polarization (+45° to -45°)



model (motivated by data)

- $Q(t)$ = in-plane nematic-like order parameter $\propto \Delta n$
- transmission (thin layer) = $T \propto \Delta n^2 \propto Q^2$

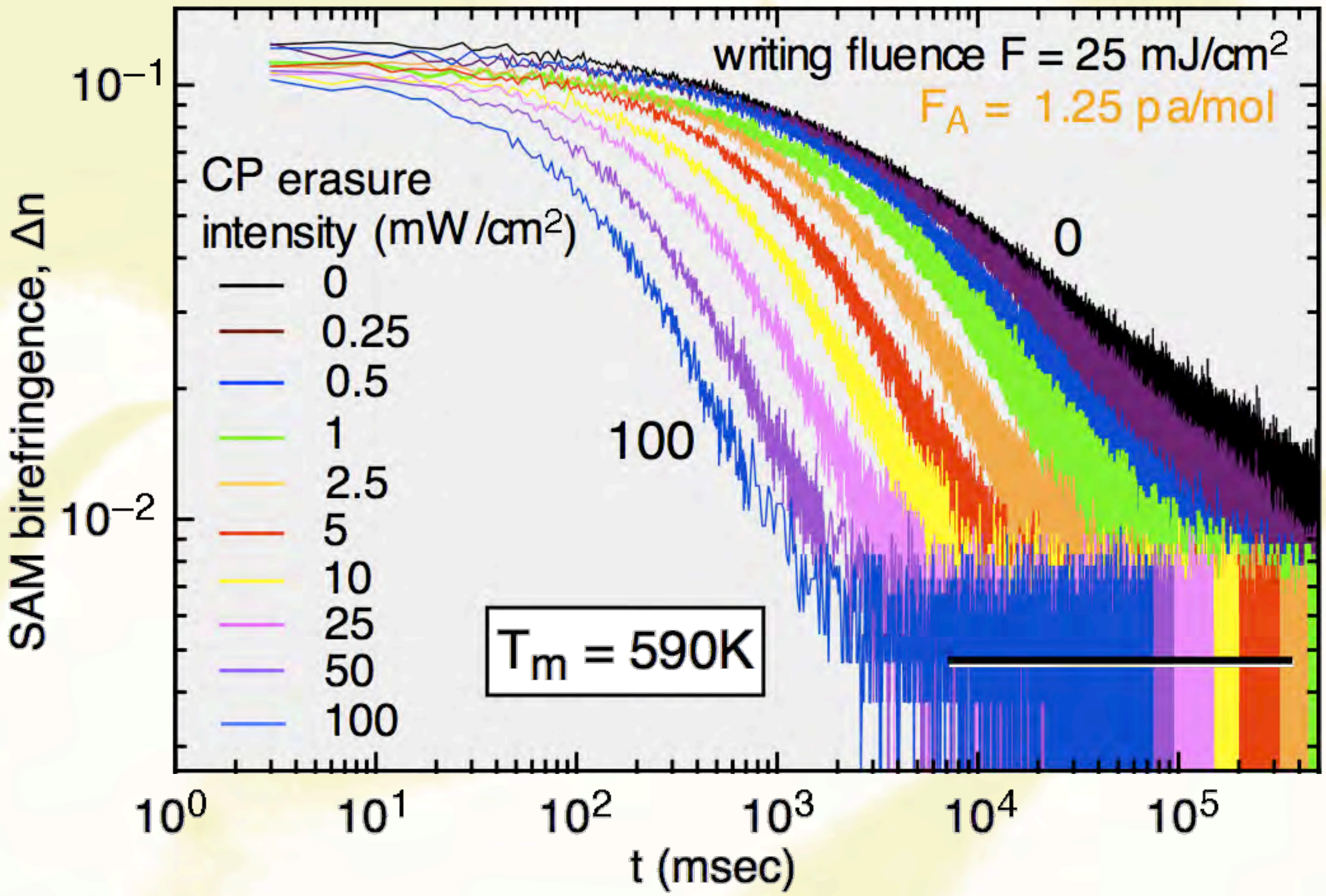


- model: orientational diffusion with a divergent distribution of waiting times:

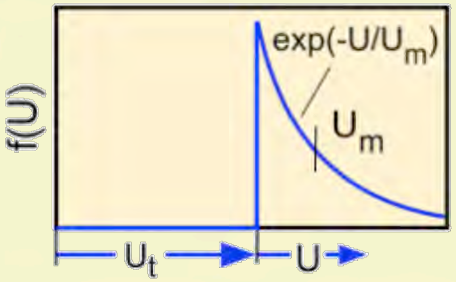
relaxation: $Q_e(t) = \int H(\tau) * \exp -(t/\tau)^{\alpha}\, d\tau$

where data indicates: $H(\tau) \sim (\tau_o/\tau)^{\beta} * \exp -(\tau_o/\tau)^{\alpha}$

erasing the birefringence with circular polarized light

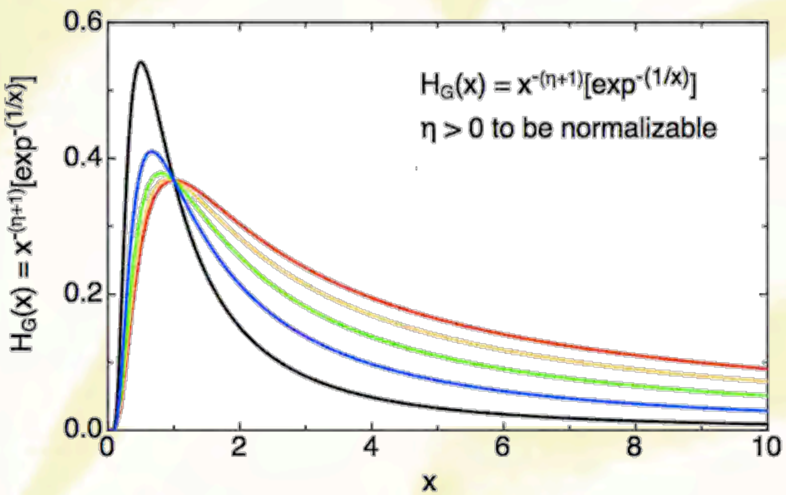


statistics of extreme values of random functions



Scher Shlesinger distribution

Schlesinger, Ann. Rev. Phys. Chem. (1988)



Gumbel distribution

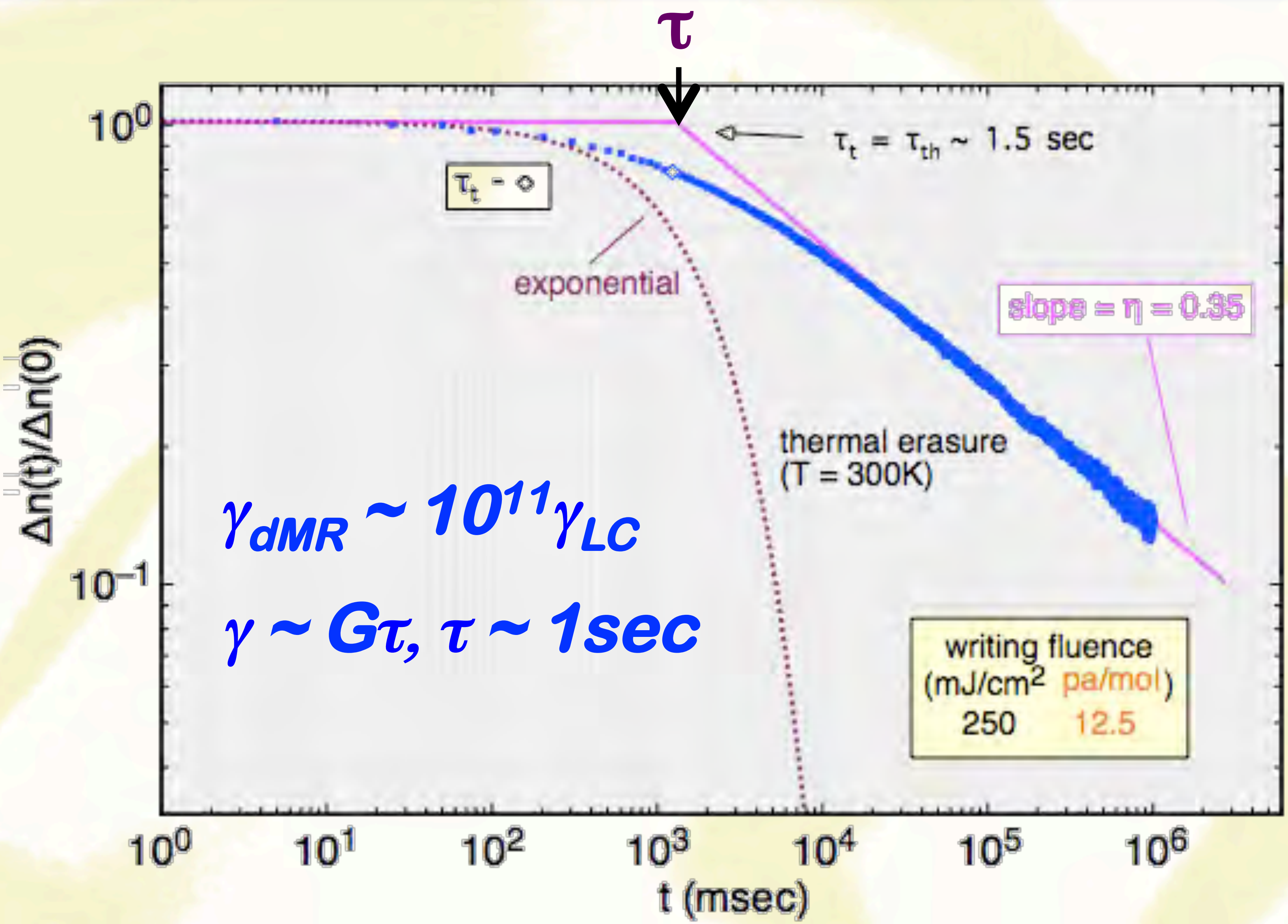
Schleshinger, Ann. Rev. Phys. Chem. (1988)

$$f_G(U) = \{\beta/[U_m\Gamma(1/\beta)]\}\{exp\text{-}[U/U_m + exp\text{-}(\beta U/U_m)]\}$$

$$H_G(\tau) = [\alpha/\Gamma(h/\beta)\tau_t]\ [exp\text{-}(\tau_t/\tau)^{\alpha}]\ [\tau/\tau_t]^{-(\eta+1)}$$

$$\Delta n(t) \propto Q_G(t) = 1/[1 + (t/\tau_t)^{\alpha}]^{\eta/\alpha}$$

dMR monolayer is an orientational glass



$$\gamma_{dMR} \sim 10^{11} \gamma_{LC}$$

$$\gamma \sim G\tau, \tau \sim 1sec$$