CM4650 Polymer Rheology
Prof. Faith Morrison

Material Behavior Outline

16 March 2015

1. Steady Shear
    a. Linear Polymers
        i. Versus shear rate
        ii. As a function of Molecular weight
        iii. As a function of molecular weight distribution
    b. Linear Polymers with solid filler
        i. Versus shear rate
2. Unsteady Shear (or Elongation) (small strain)
    a. Linear Polymers
        i. Versus frequency
        ii. Cox-Merz rule
    b. Other architectures
3. Effect of temperature
4. Unsteady Shear (large strain)
    a. Start-up
    b. Cessation
    c. Step Strain
5. Steady Elongation
6. Unsteady Elongation (large strain)

Experimental Data
Chapter 6

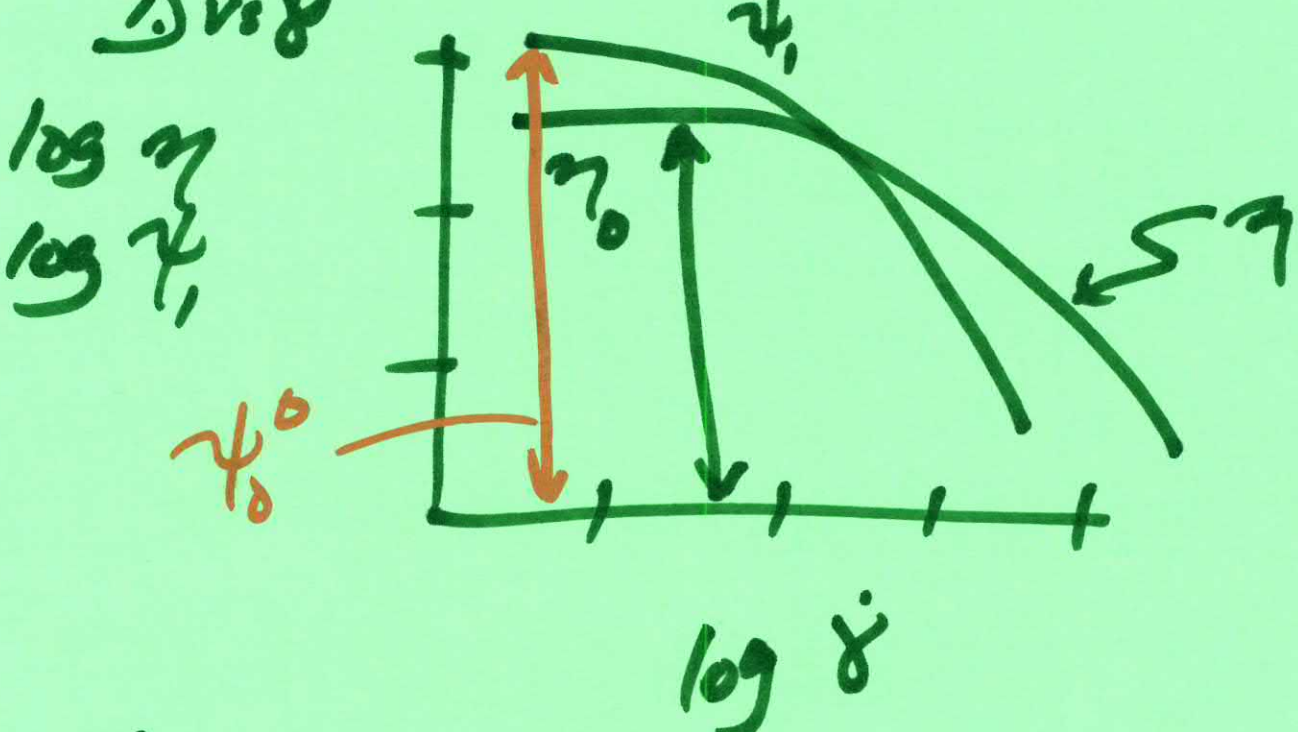
I. Steady Shear

$\dot{\varsigma}(t) = \dot{\gamma}_0$

η, Ψ_1, Ψ_2

A. Linear Polymers

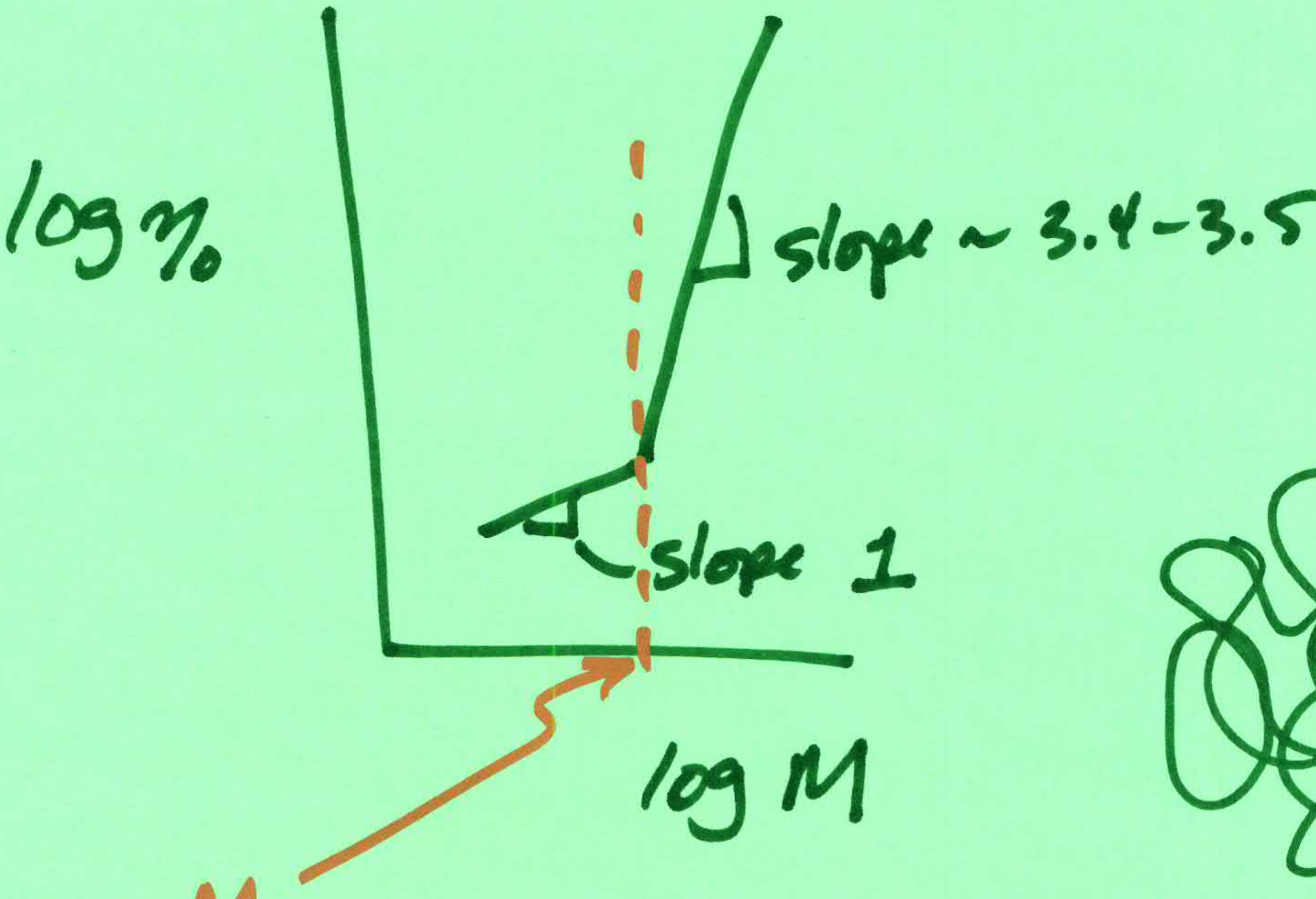
1.) vs $\dot{\gamma}$



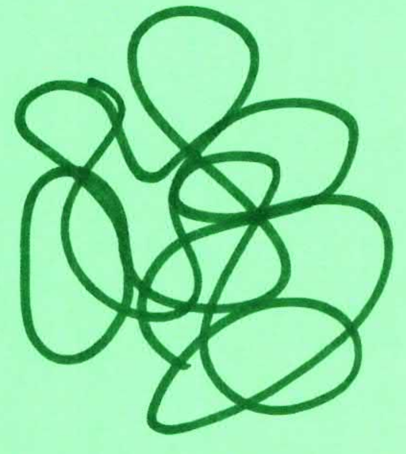
$\lim_{\dot{\gamma} \to 0} \eta = \eta_0$ = zero shear viscosity

Ψ_0 = zero shear 1st normal coef

2) η_0 as a function of M:



M_c
critical MW for entanglement



$M > M_c$
polymers are entangled.

3) $\eta(\dot{\gamma})$ as a function of Molecular Wt Dist (MWD)

B) Linear Polymers + solid filler

1) vs shear rate, $\dot{\gamma}$

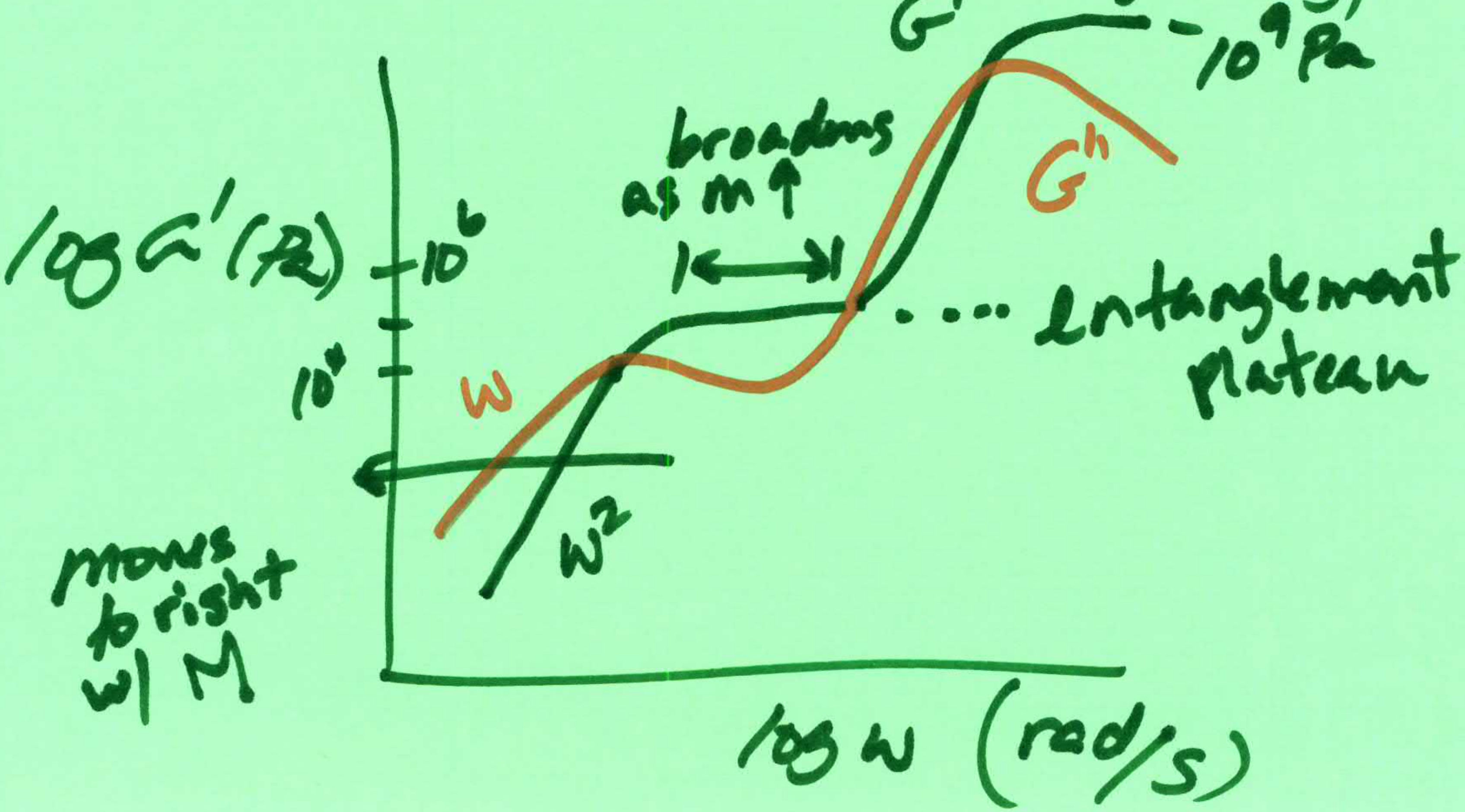
slope of 1 at low $\dot{\gamma}$ $\Rightarrow$ yeild stress

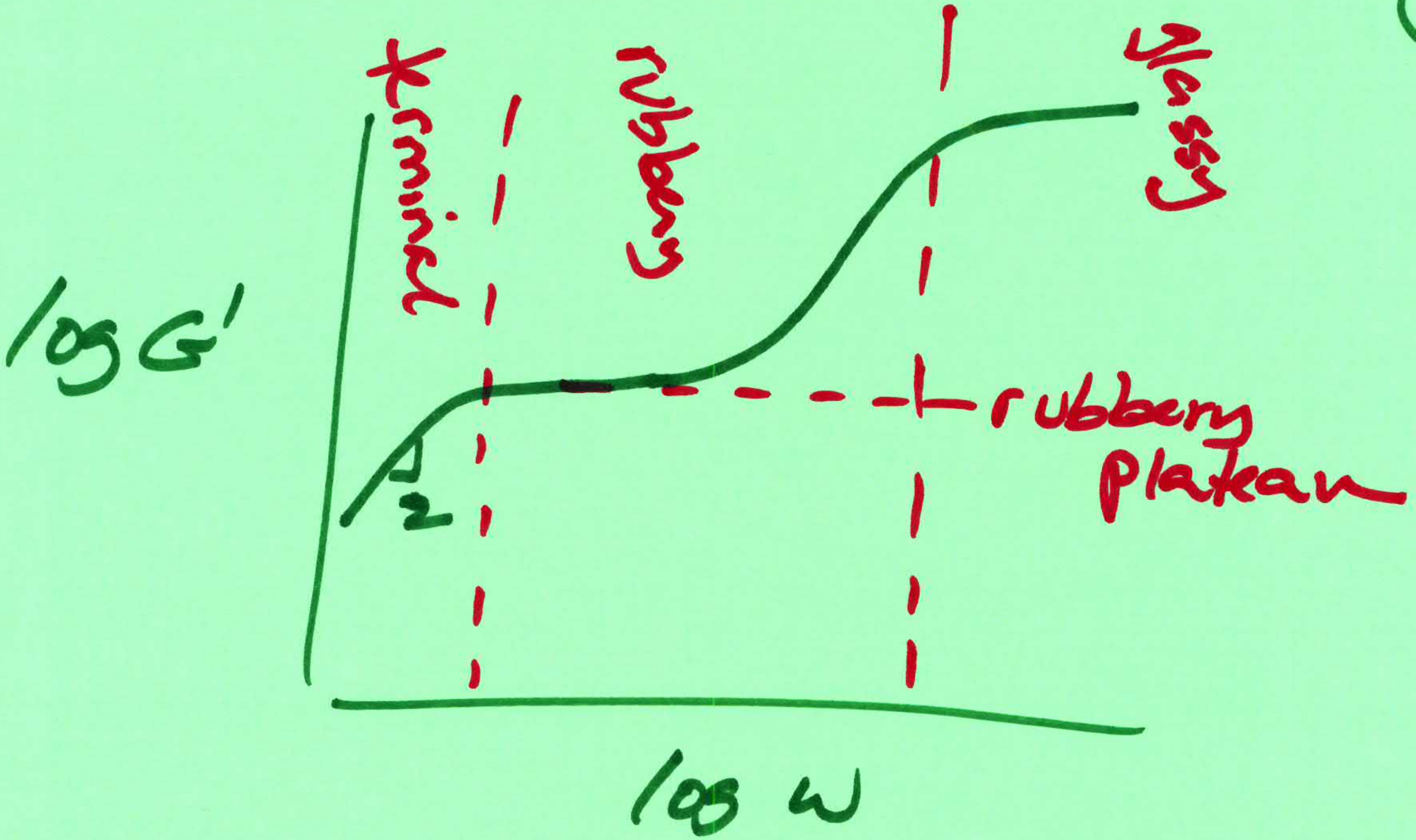
Unsteady Shear (or Elongation)
(small strain)

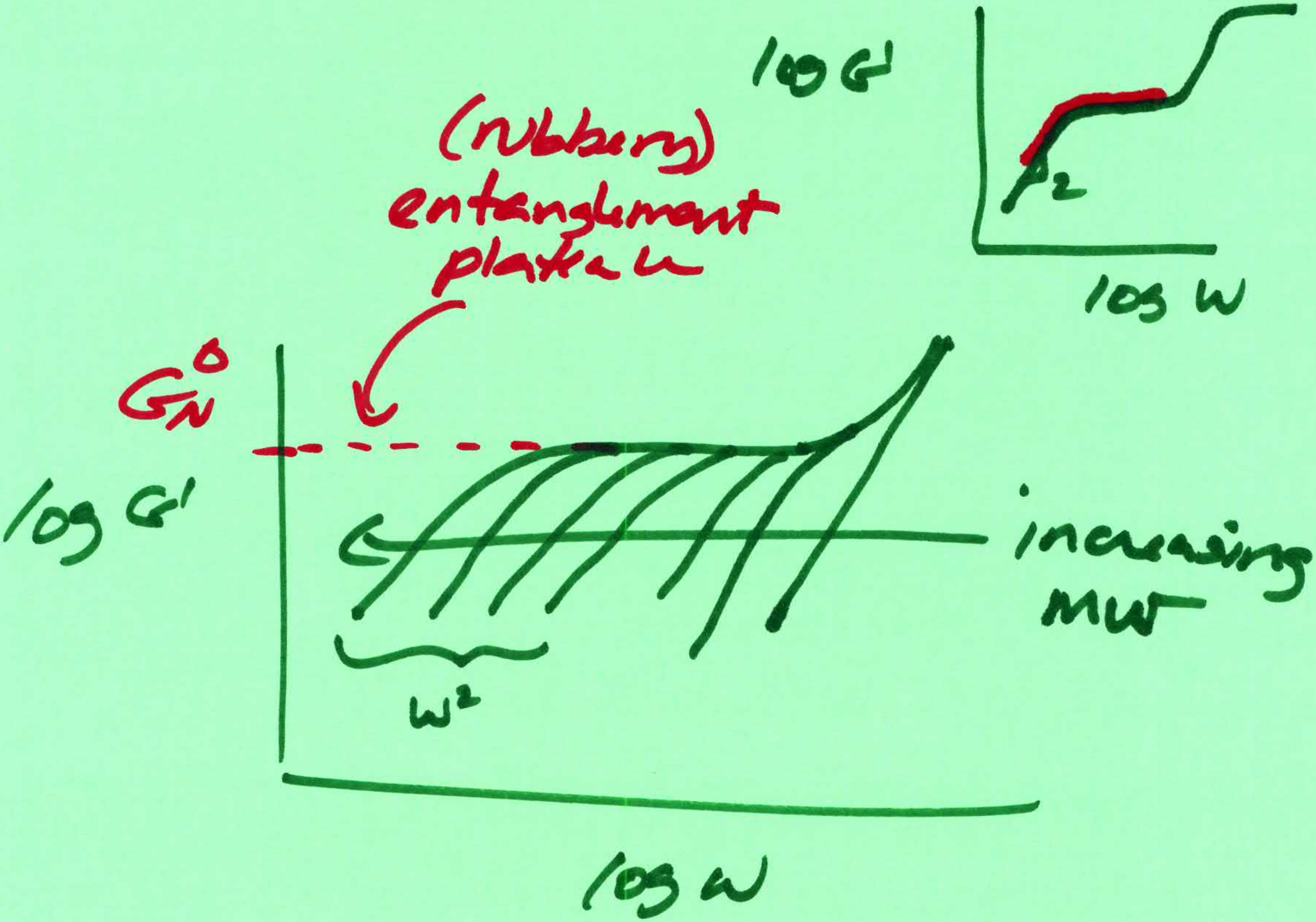
II <u>S</u>AOS

A. Linear Polymers

1. versus ω (frequency)

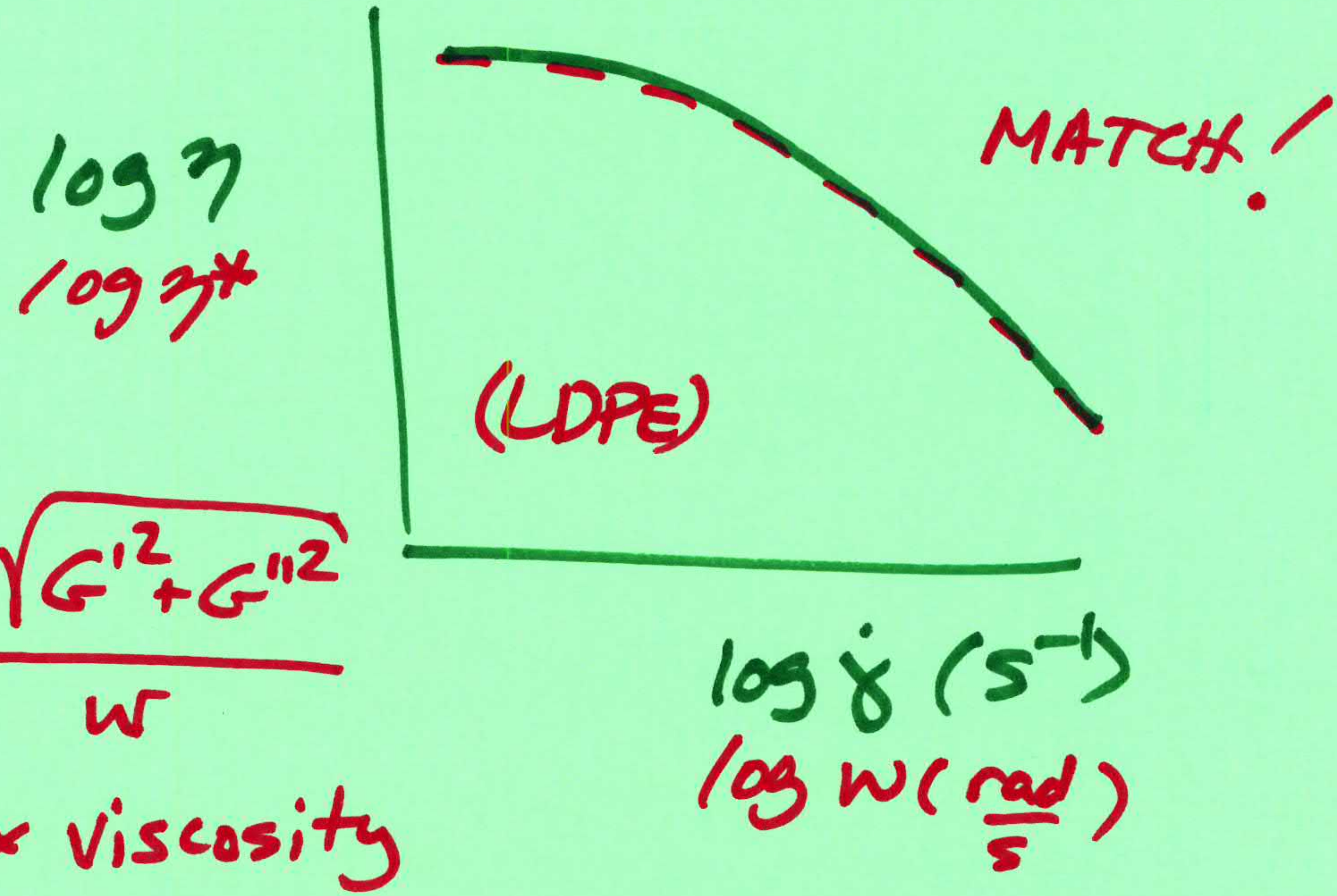



terminal
rubbery
glassy
log G'
rubbery plateau
1
2
log ω


log G'
log W
ω^2
(rubbery)
entanglement
plateau
G_N^0
log G'
ω^2
increasing
MW
log ω

Cox-Merz Rule

(It only works when it works. mat'l w/ complex structures do not follow Cox-Merz)



$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$

complex viscosity

III Effect of Temperature on $\eta(\dot{\gamma})$ and SAOS

- time/temperature superposition allows "master curves" to be produced (with shift factors, a_T)
- works for $\eta(a_T\dot{\gamma})$
  $G'(a_T\omega)$, $G''(a_T\omega)$

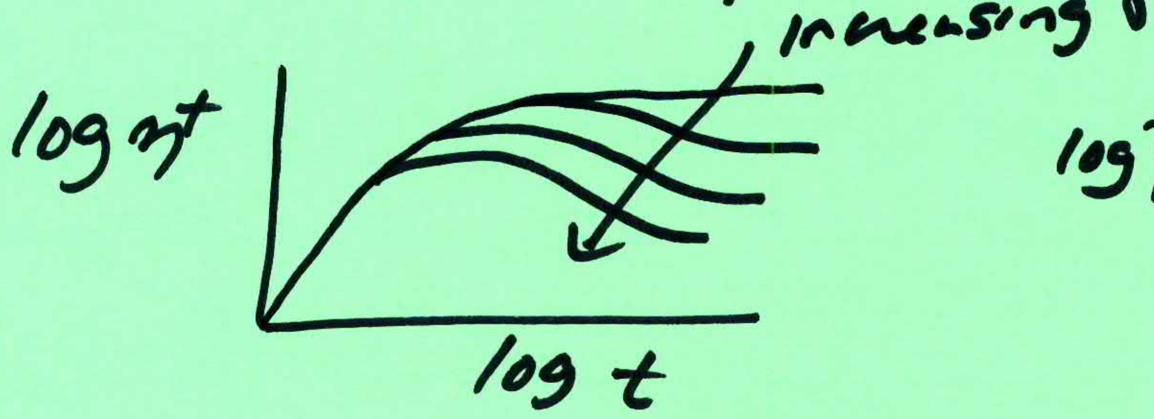
- $\log a_T \propto \frac{1}{T(k)}$ (at high T)

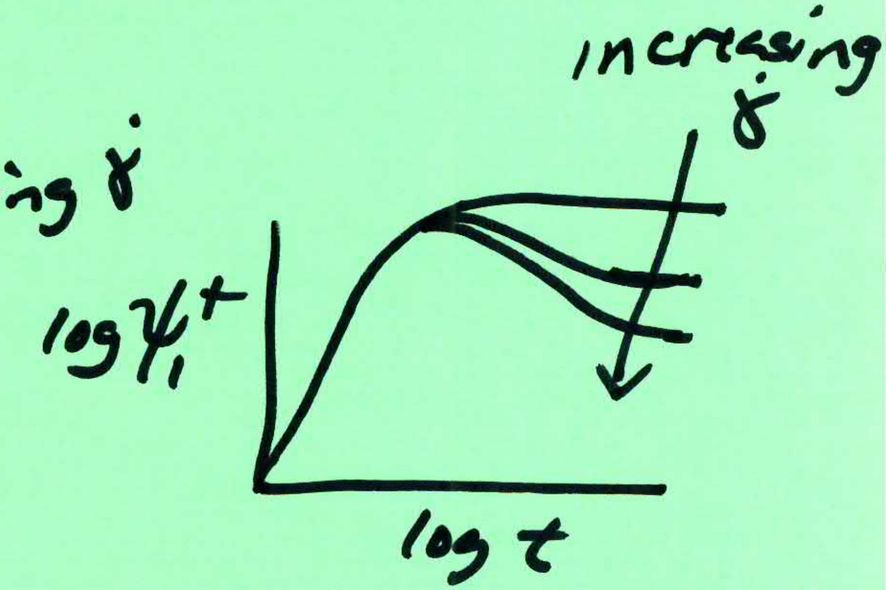
  Arrhenius eqn

- empirical method to compactly represent data

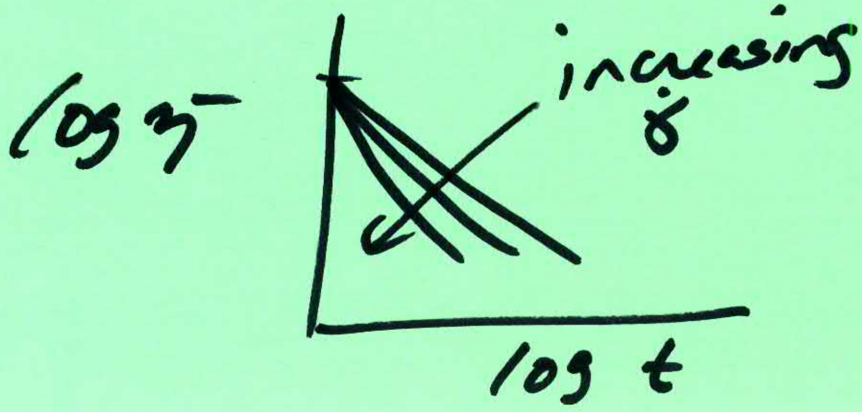
IV Unsteady Shear
(large strain)

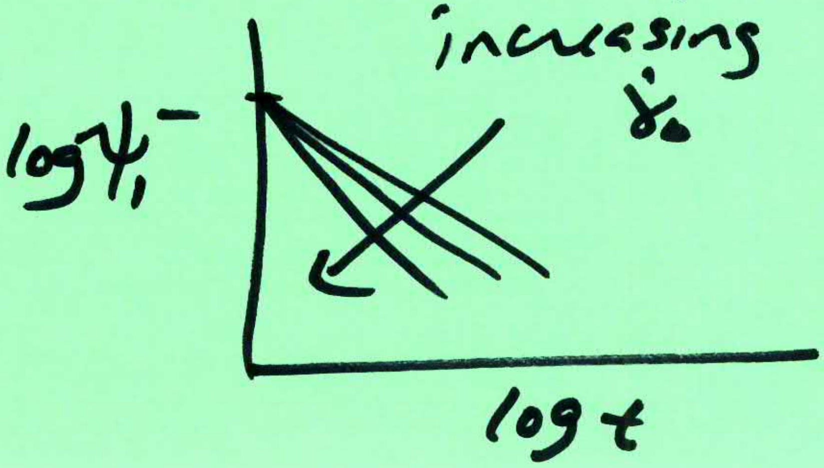
1. Start-up



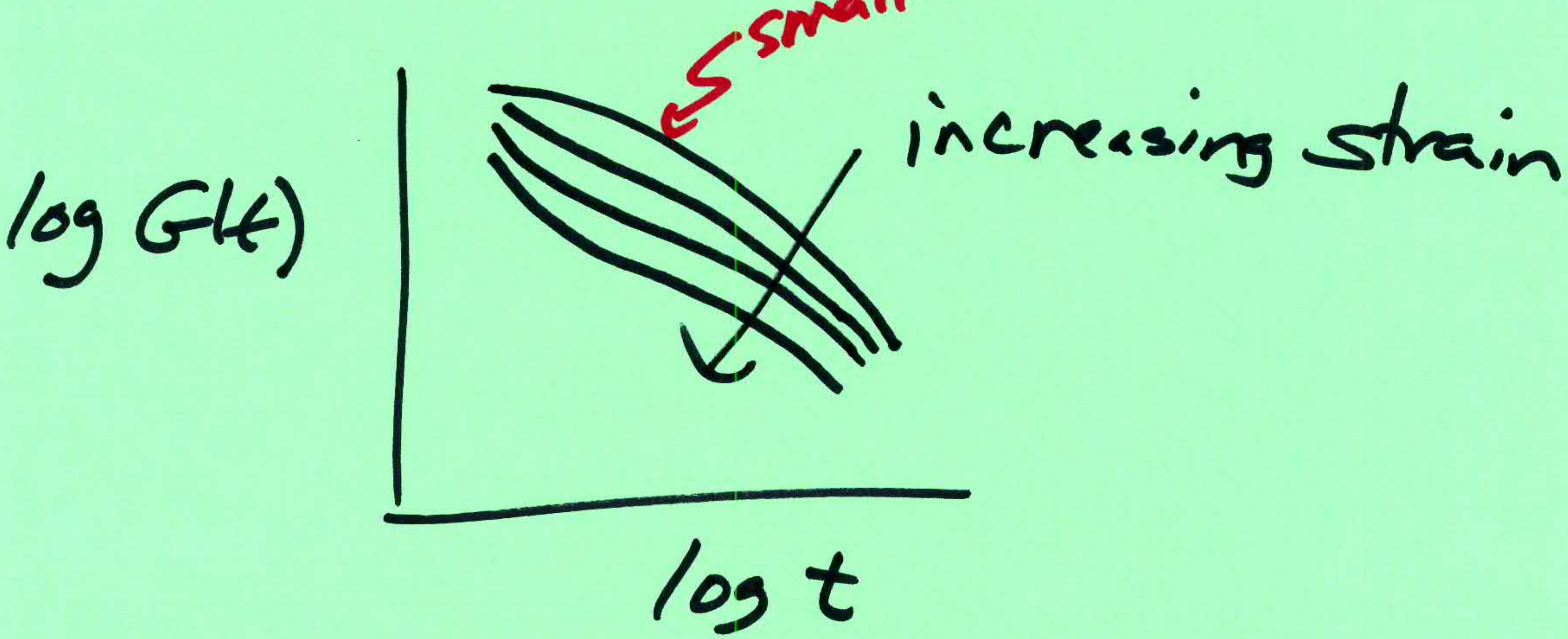


2. Cessation

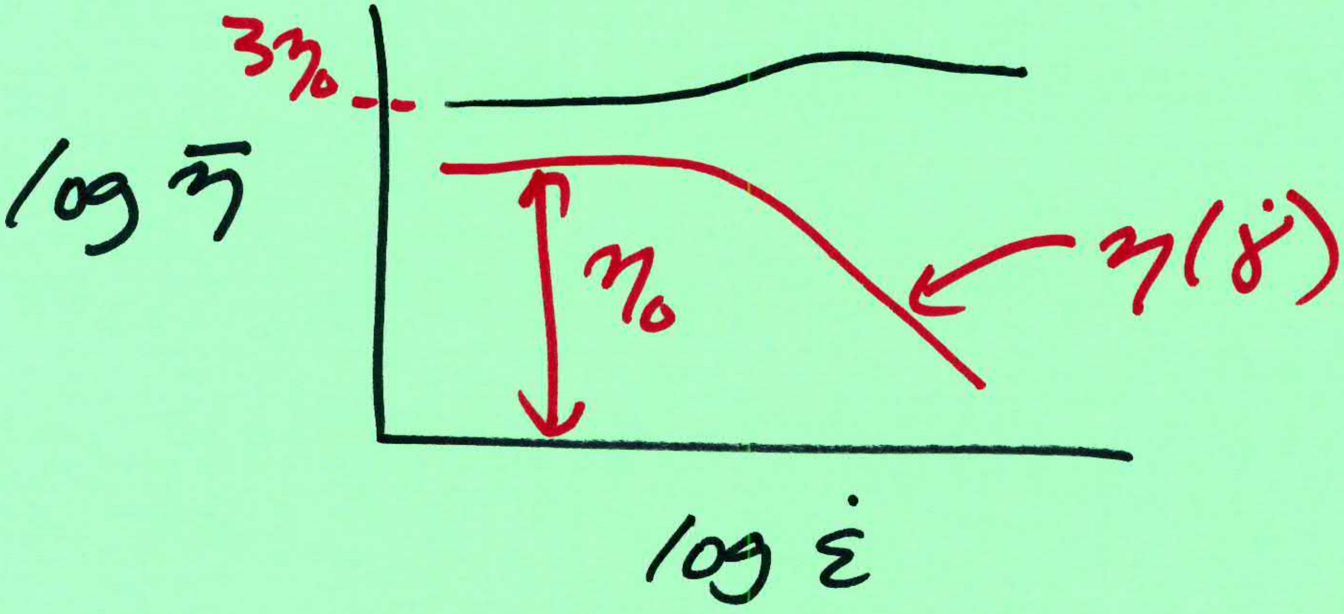




3. Step Strain



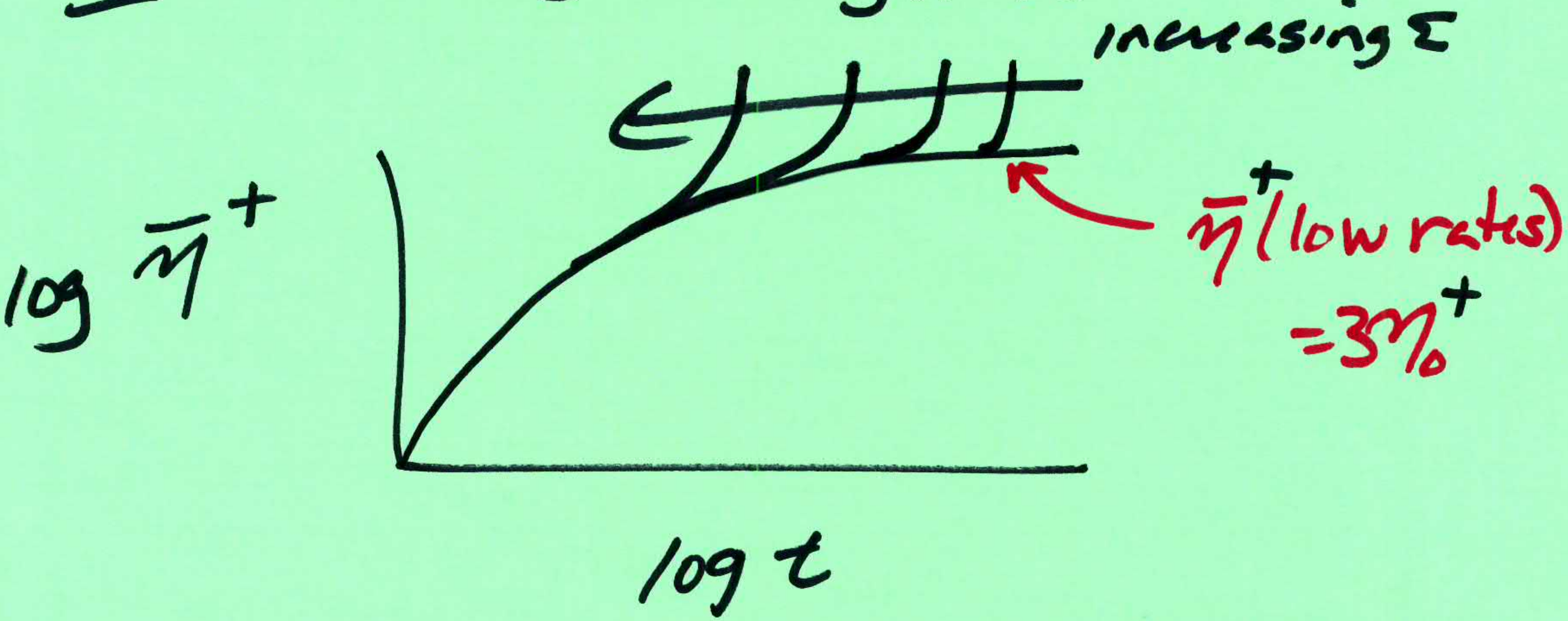
V Steady Elongation



Trouton Ratio: $Tr \equiv \dfrac{\bar{\eta}(\dot{\varepsilon})}{\eta(\dot{\gamma})}$

$$\lim_{\substack{\dot{\varepsilon} \to 0 \\ \dot{\gamma} \to 0}} Tr = 3$$

VI Unsteady Elongation



Has a low rate "envelope" that is 3x the shear start-up result.