Time-Temperature Superposition in Aging Soft Materials

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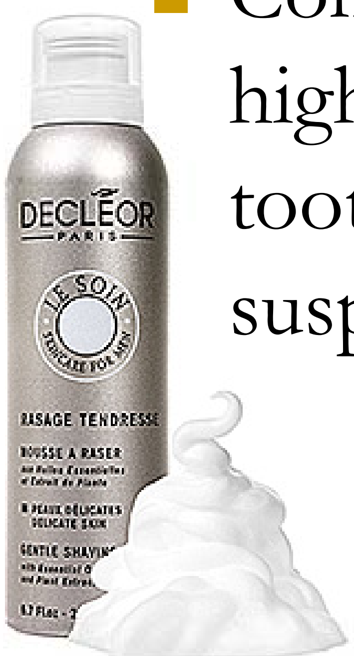
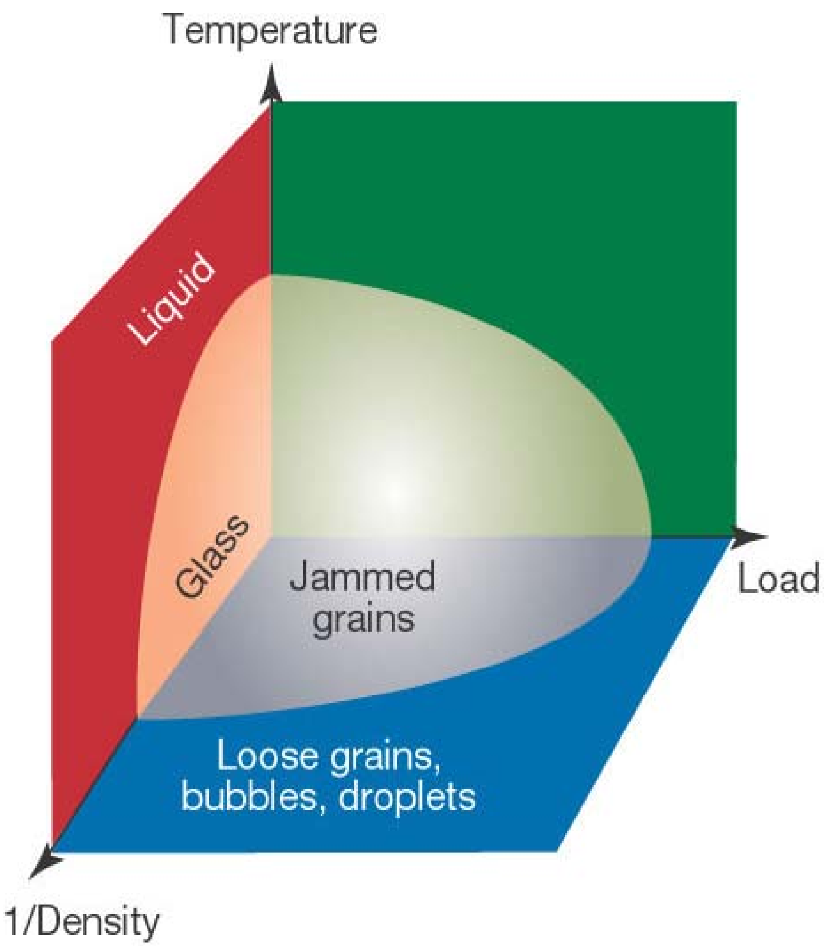
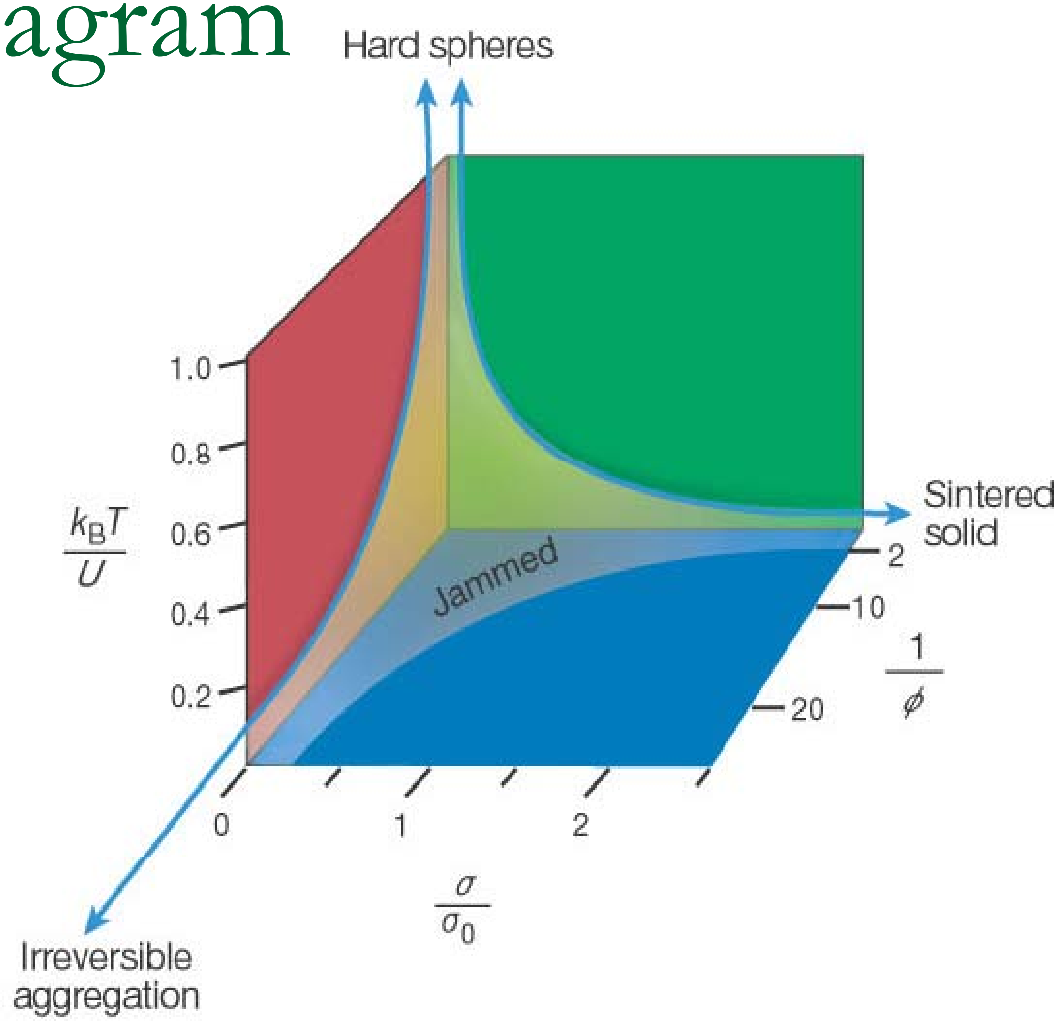
Soft glassy Materials

- Soft glassy Materials fail to reach equilibrium due to structural arrest
- Soft glasses show a strong time dependent viscoelastic (thixotropic) behavior
- Common examples: Polymer nanocomposites, highly filled polymeric systems, paints, toothpaste, hair gel, shaving foam, concentrated suspensions, emulsions, variety of foodstuff, etc.



Jamming Phase Diagram

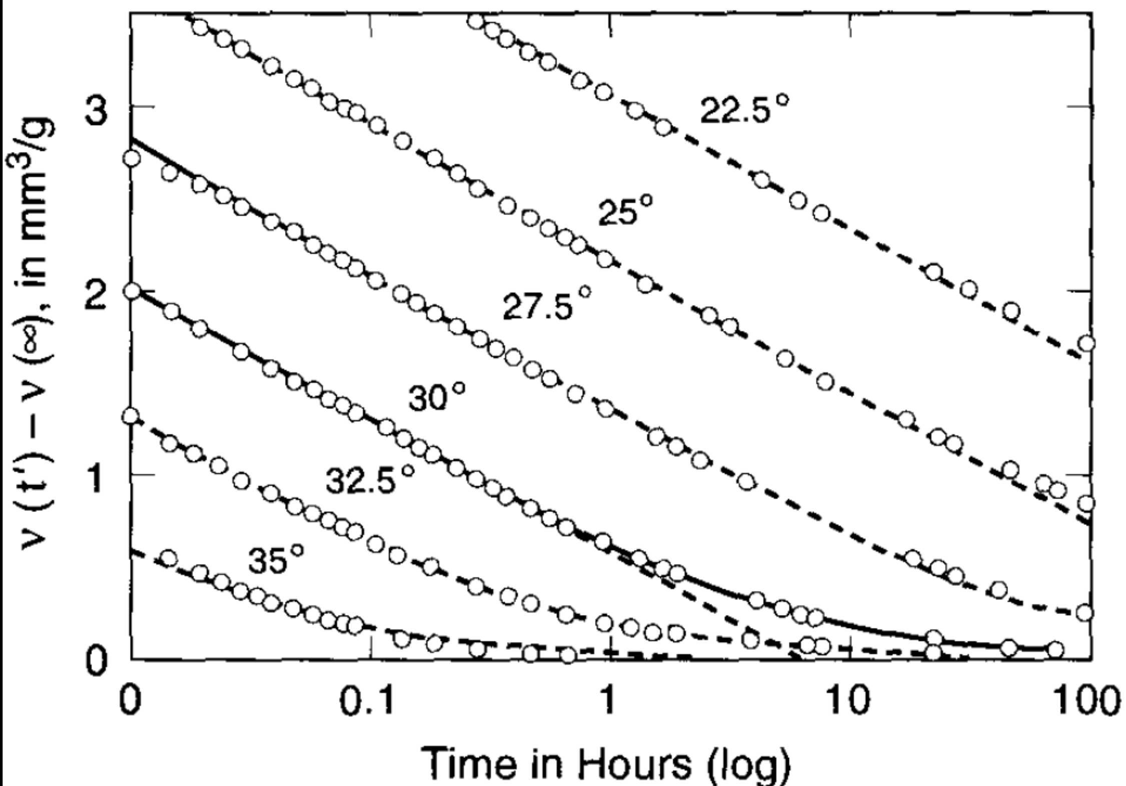


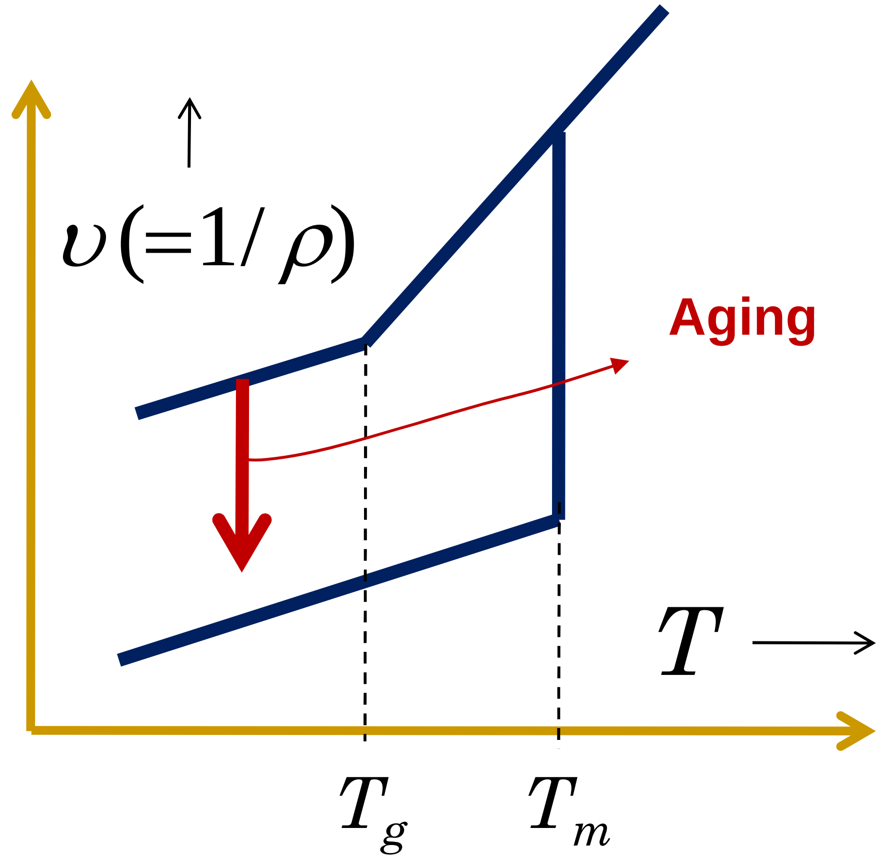


Andria Liu and Sid Nagel, Nature (2000)

David Weitz and coworkers Nature (2001)

Temperature dependent volume recovery in polymeric glass



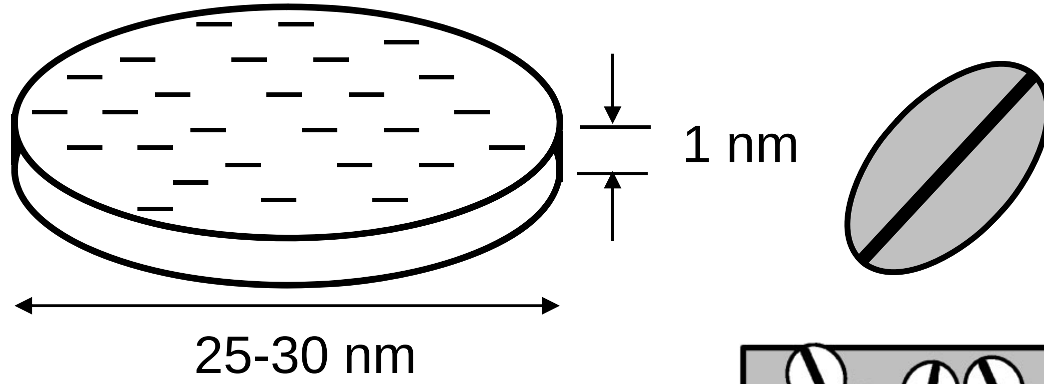


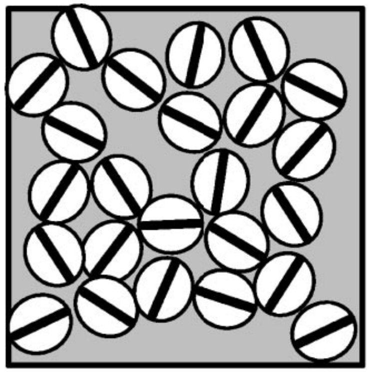
- Poly vinyl acetate
- Volume recovery observed after cooling from well above T_g .

Figure is adapted from Kovacs, J. Polym. Sci. (1958).

Laponite

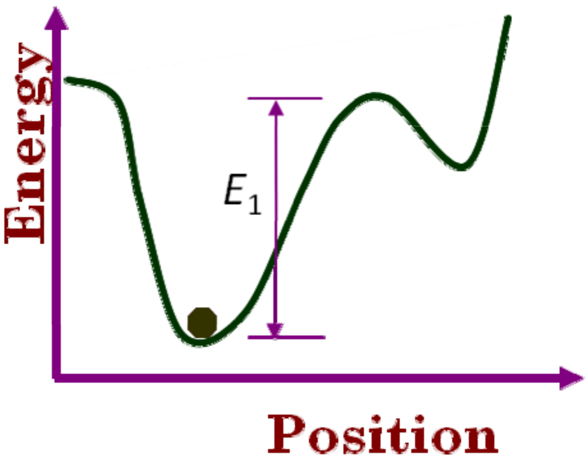
$Na^{+}_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-}_{0.7}$





- Thermal motion is restricted
- Particles undergo microscopic dynamics of structural rearrangement so that its energy decreases
- $\tau \sim t_w$ (under weak deformation or stress field)
- In practice power law dependence is observed:

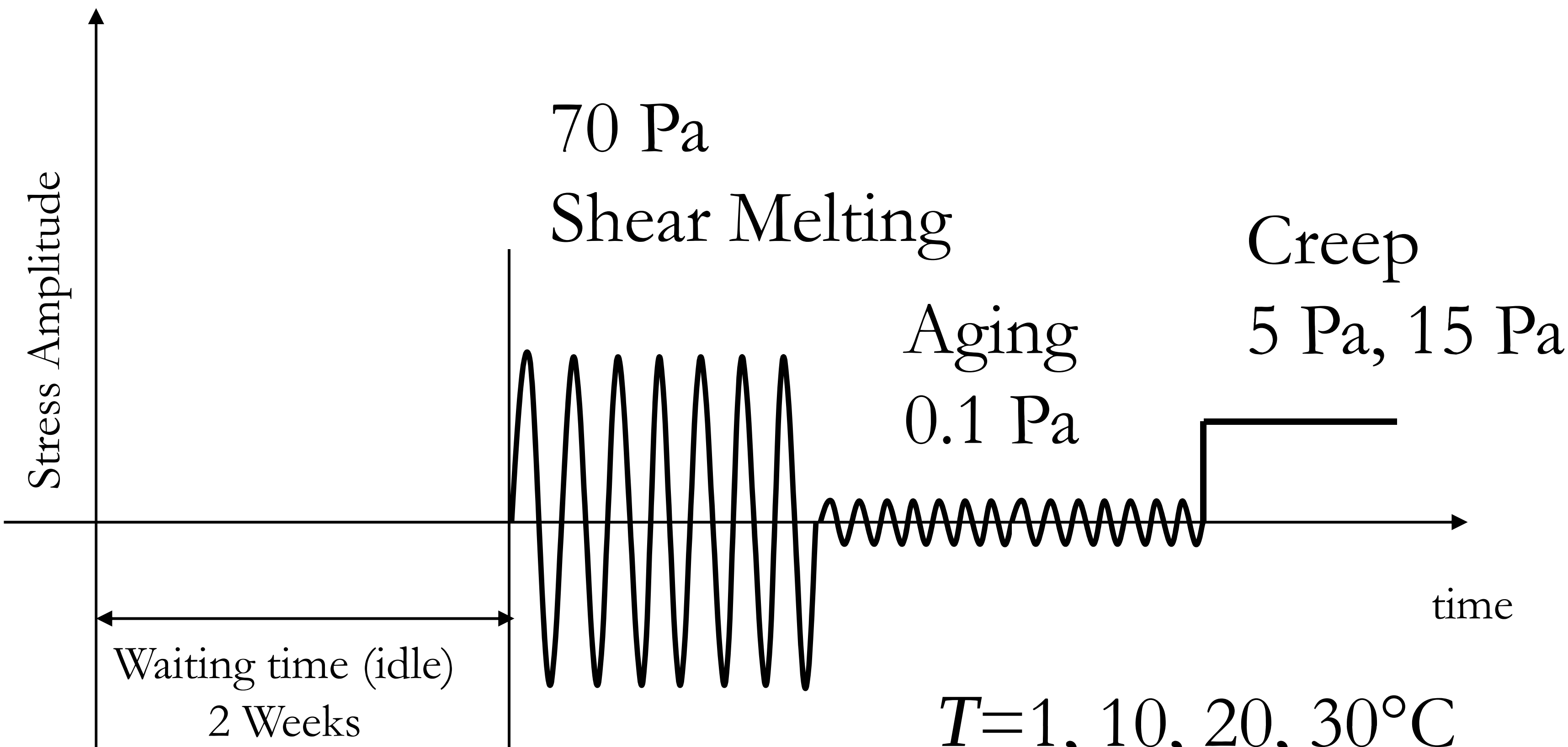
$$\tau = \tau_m^{1-\mu} t_w^{\mu} \qquad \mu = d \ln \tau / d \ln t_w$$



Aging under Oscillatory Shear
Experimental Protocol

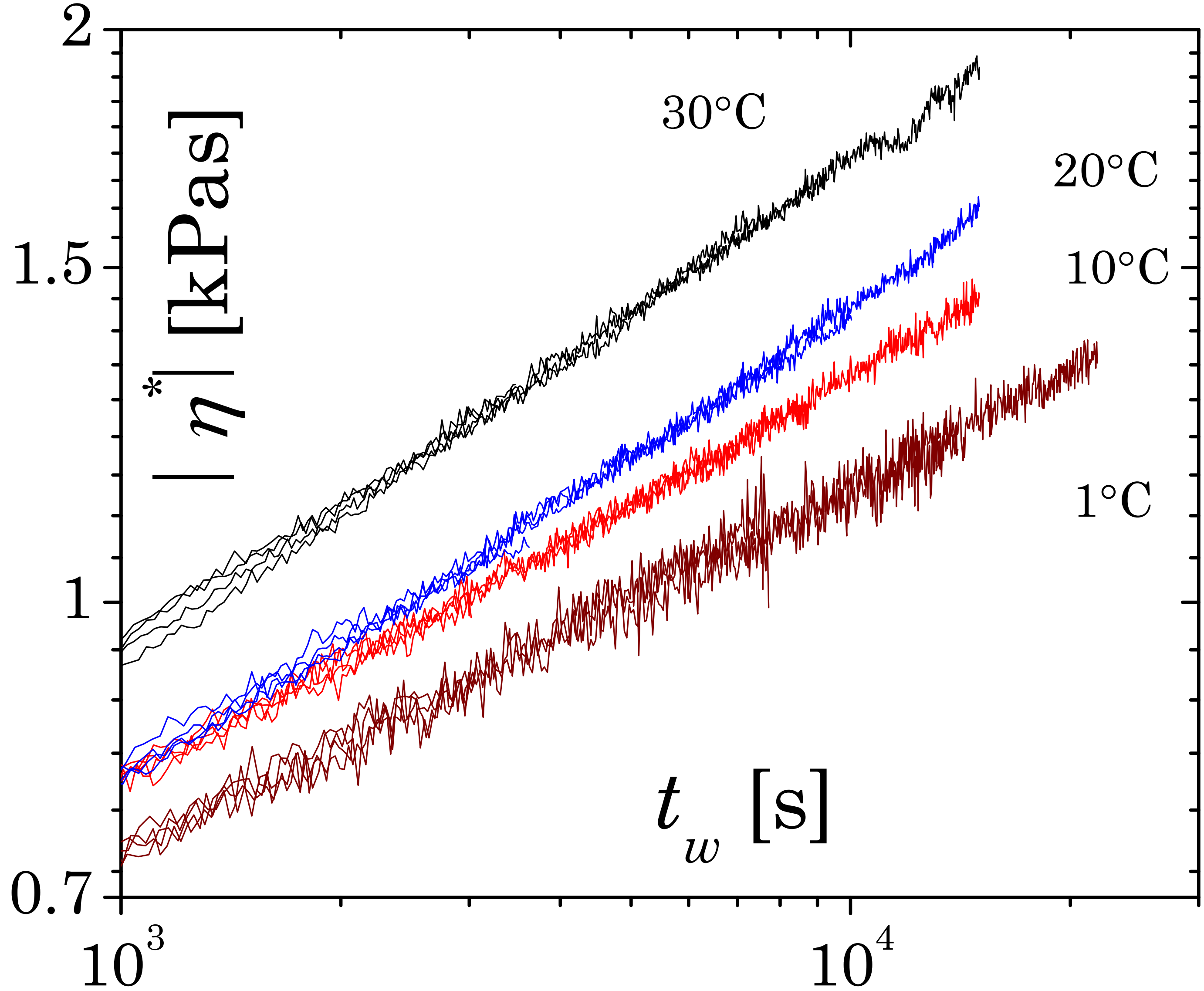
3.2 weight % Laponite

5 weight % Laponite + 0.5 weight % PEO (Mw = 200)



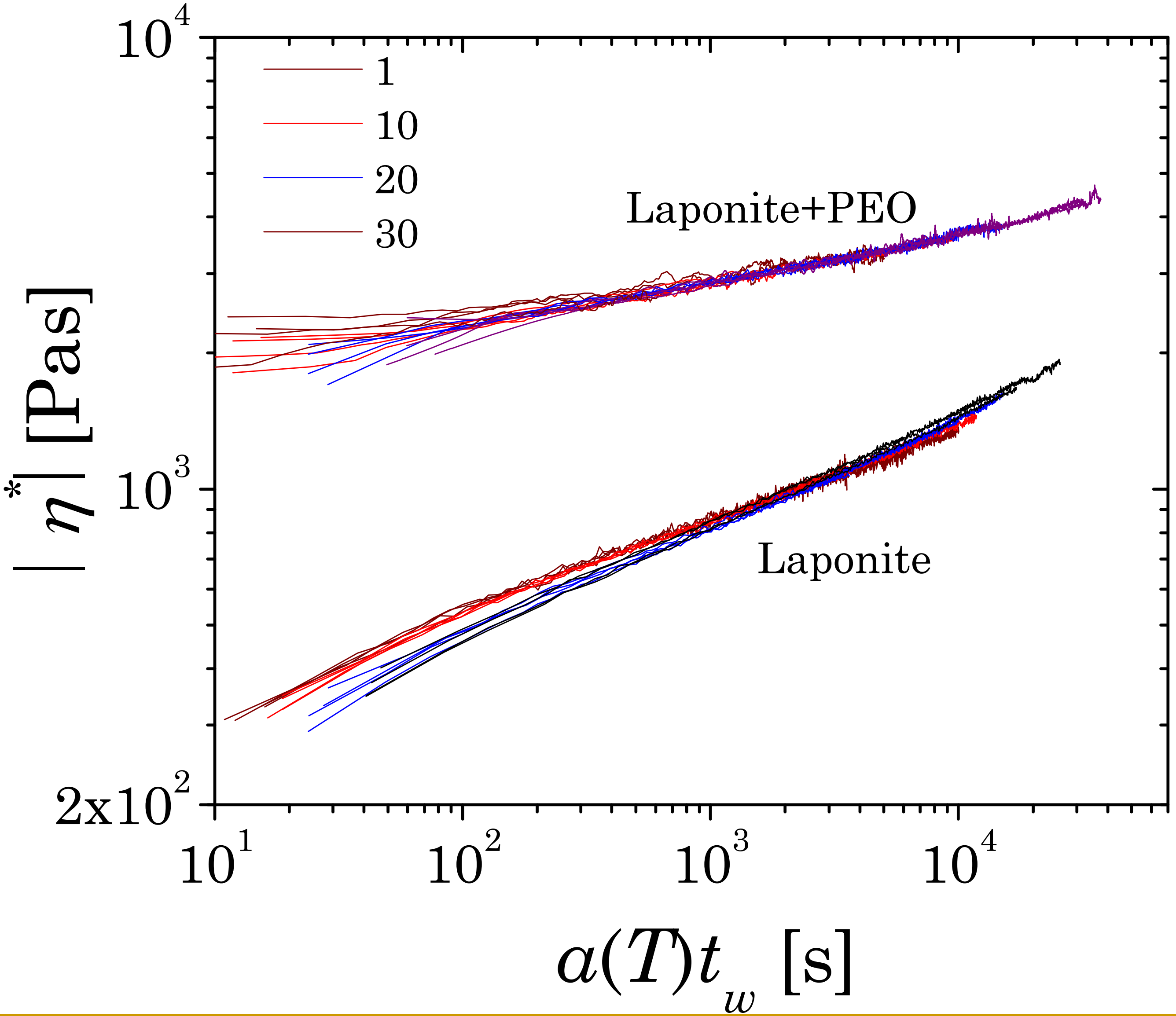
T=1, 10, 20, 30°C

Temperature dependence (3.2 weight % Laponite)



$G' \approx \omega|\eta^*|$

Aging experiments



$$G' \approx \omega |\eta^*|$$

Aging Dynamics

- Cage diffusion timescale can be defined as:

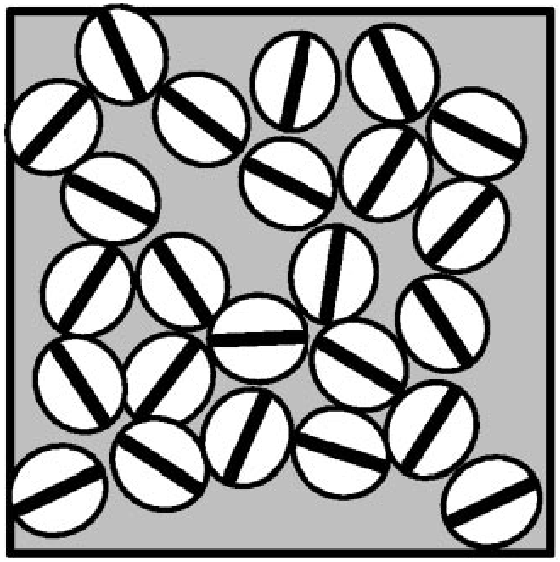
$$\tau = \tau_m \exp\left(E/kT\right)$$

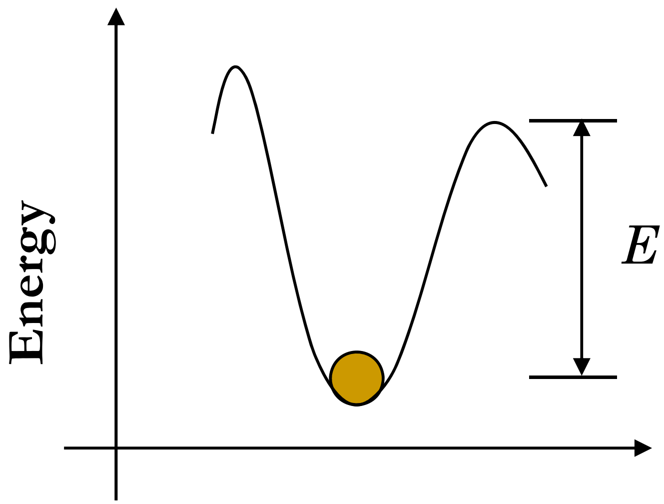
- Arrested particle undergoes microscopic dynamics within the cage and prefers those states that lower its energy

$$\tau_m = \tau_{m0} \exp\left(U/kT\right)$$

- Therefore barrier height (*E*) is a function of

$$E = E\left(t_w/\tau_m\right)$$





Aging Dynamics (Cont.)

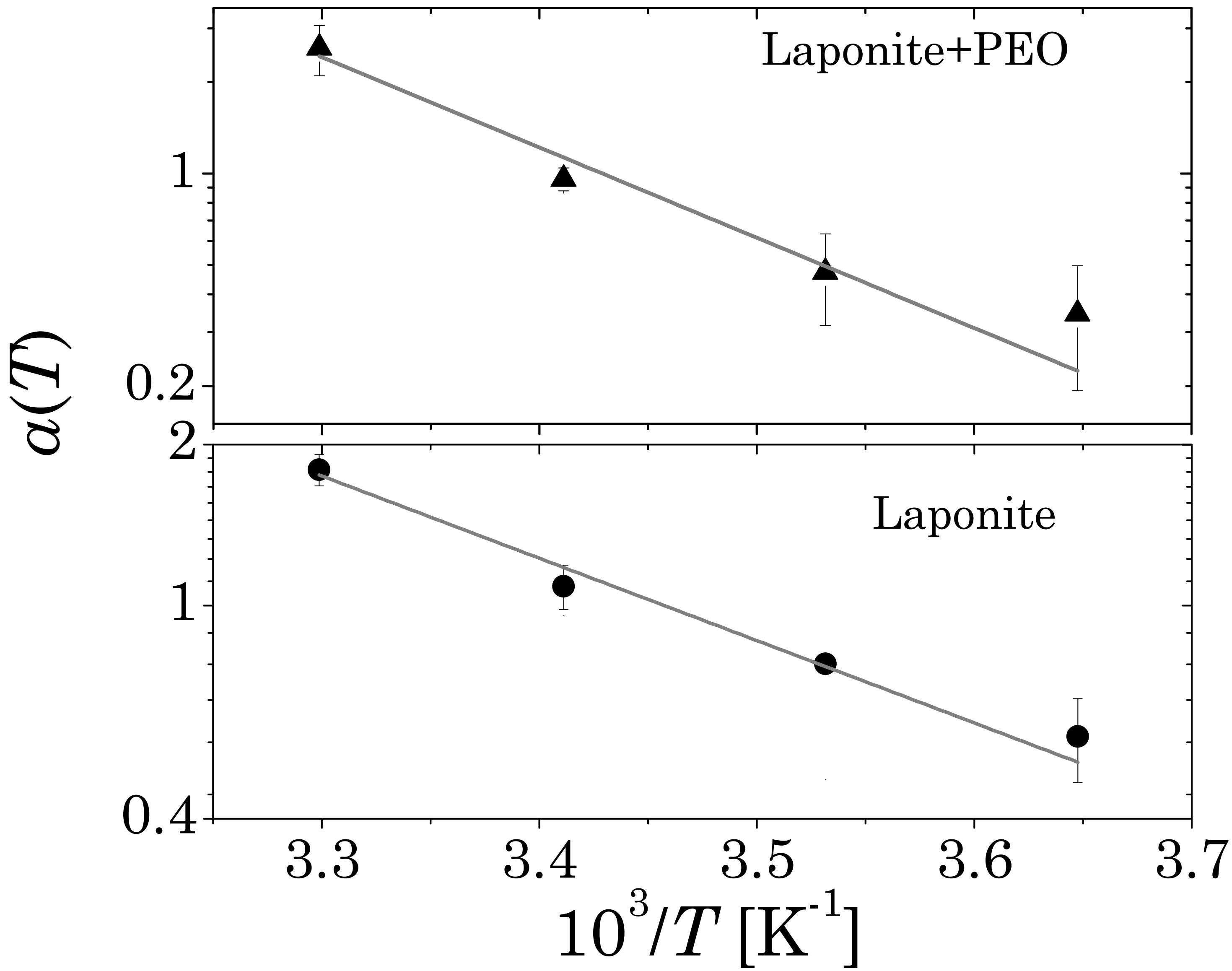
- If b is Characteristic length-scale, $G' = E\left(t_w/\tau_m\right)/b^3$
- Assumption: b does not change with waiting time t_w
- Temperature dependence of Modulus is given by:

$$G' = G'\left(t_w/\tau_m\right)$$

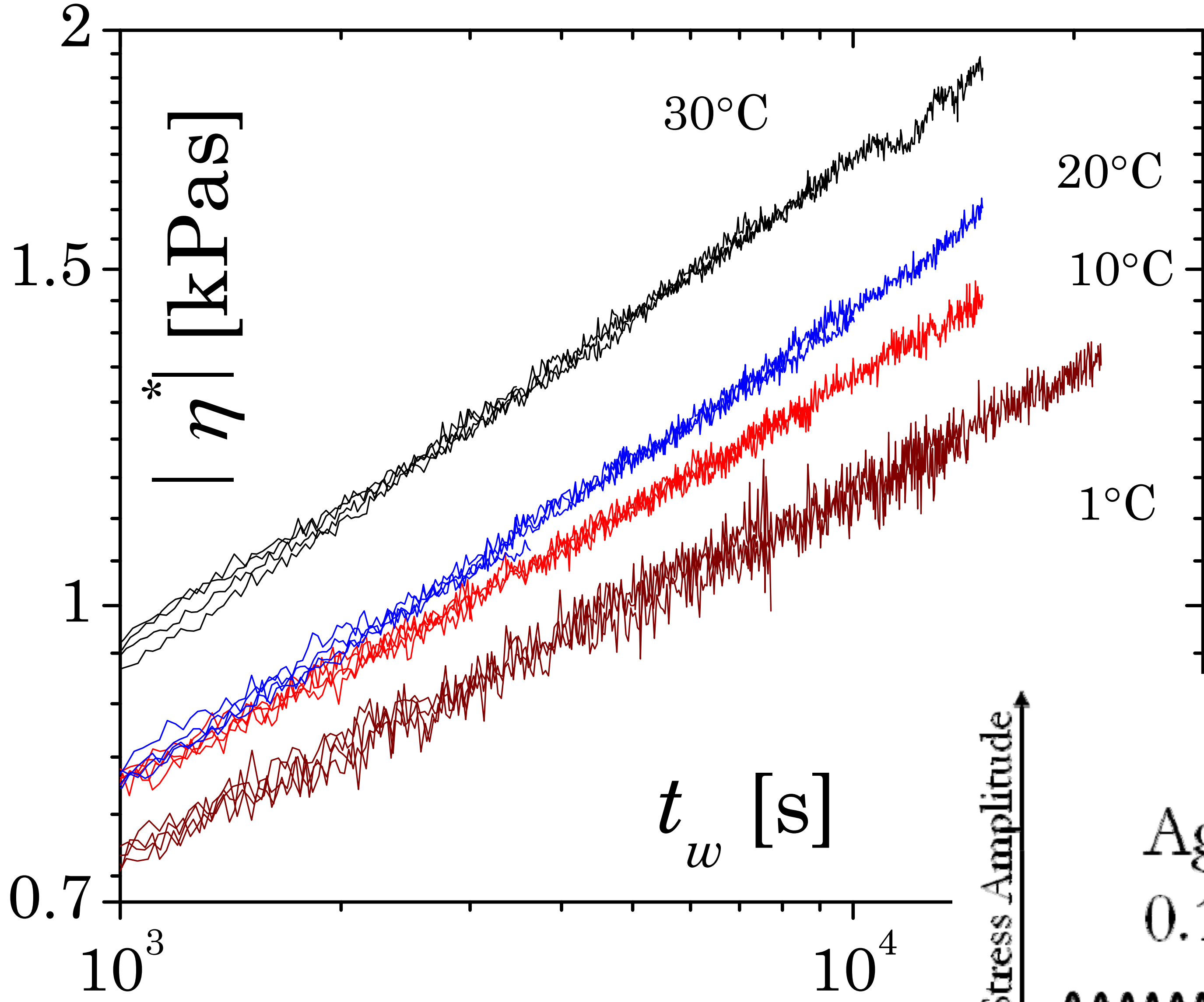
- Therefore, shifting parameter $a(T)$ is given by:

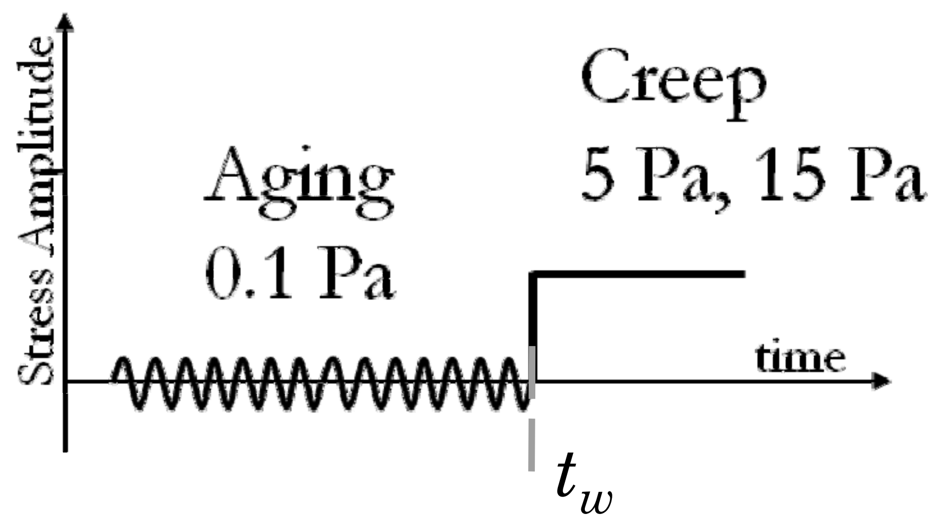
$$a(T) = 1/\tau_m = \tau_{m0}^{-1}\exp\left(-U/kT\right) \longrightarrow \ln\left[a(T)\right] \sim -U/kT$$

Shift Parameters

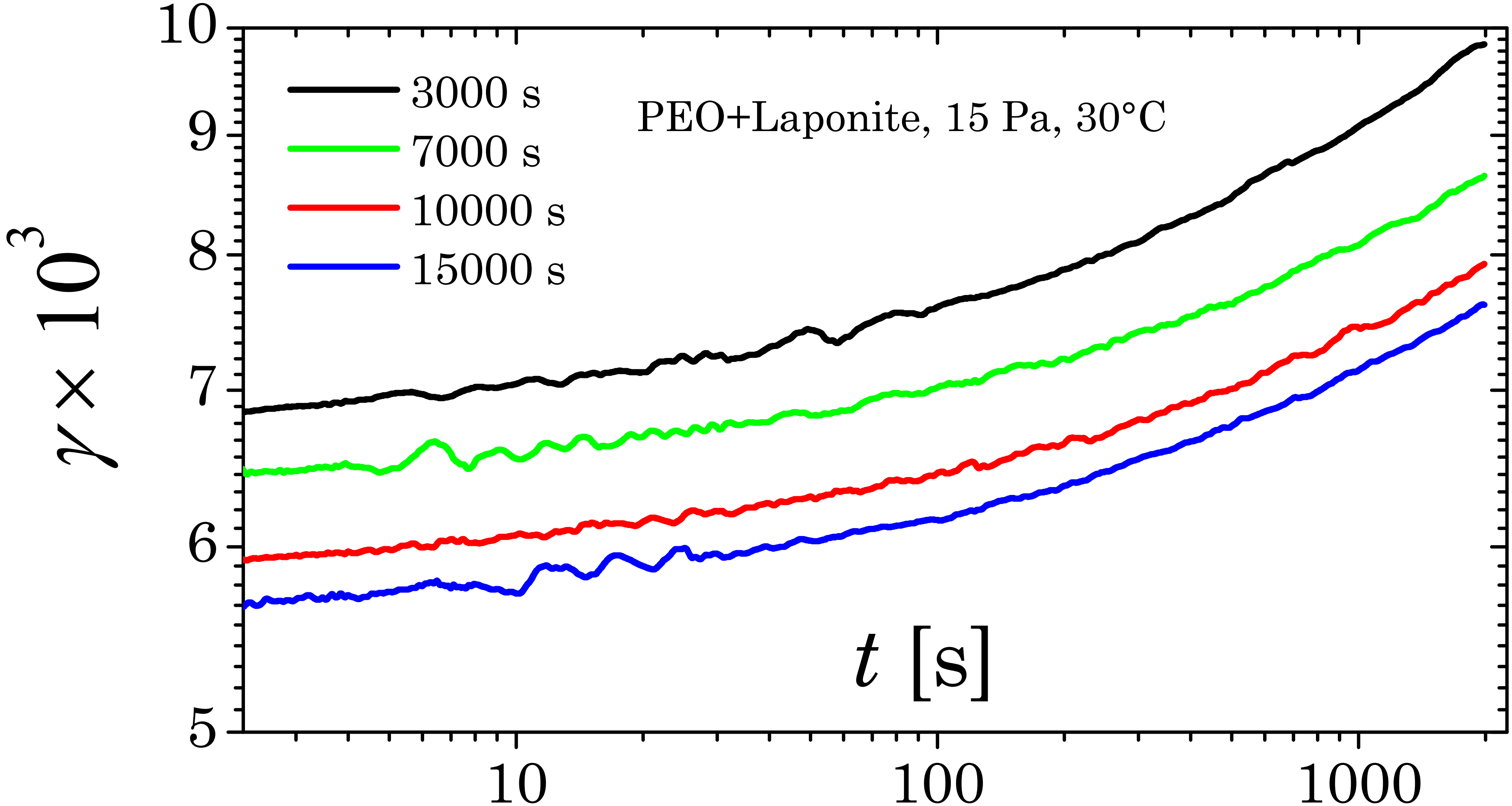


Aging time dependence (3.2 weight % Laponite)





Creep Behavior



Maxwell Model Prediction

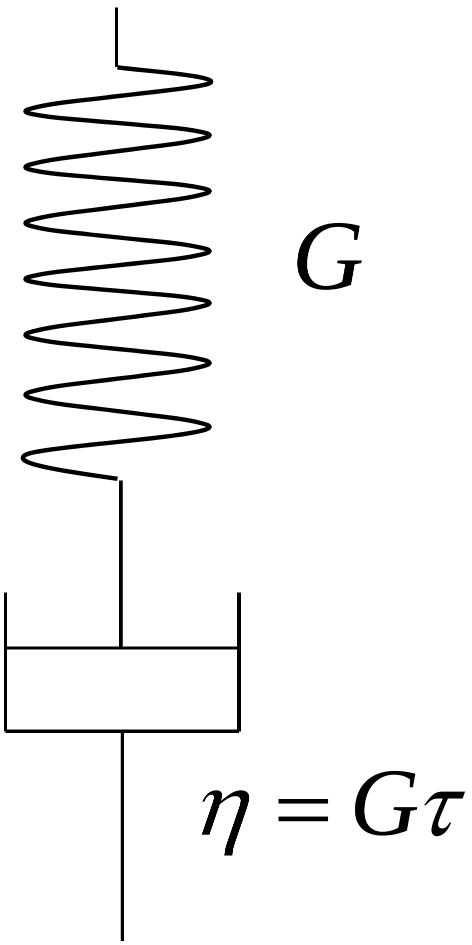
$$\gamma\left(t_w + t\right) = \frac{\sigma}{G} + \int_0^t \frac{\sigma}{\eta} dt$$

$$\tau = \eta / G = \tau_m^{1-\mu} t_w^{\mu}$$

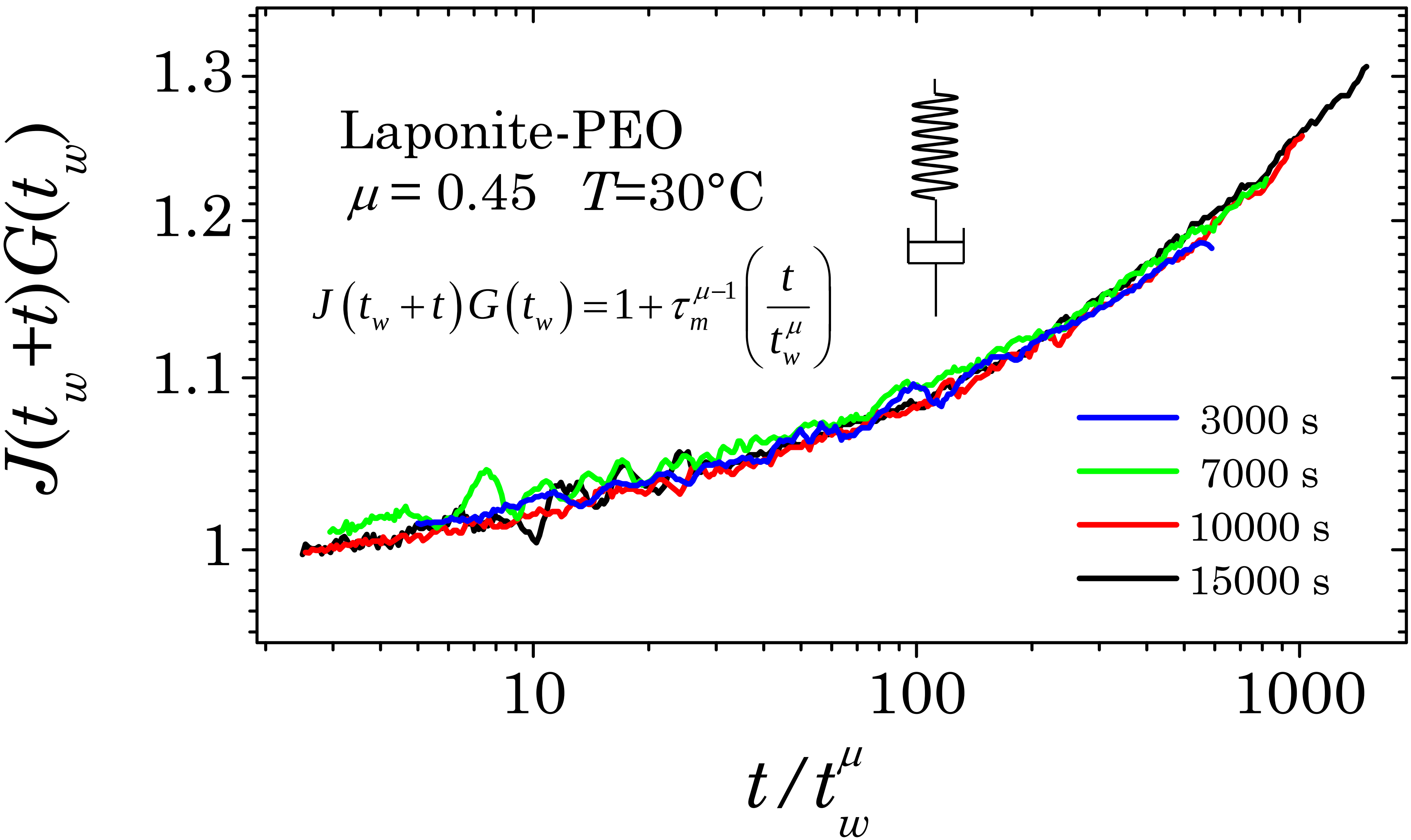
$$\gamma\left(t_w + t\right) = \frac{\sigma}{G} + \sigma\tau_m^{\mu-1} \int_0^t \frac{1}{G\left(t_w + t\right)^{\mu}} dt$$

In the limit of $t << t_w$

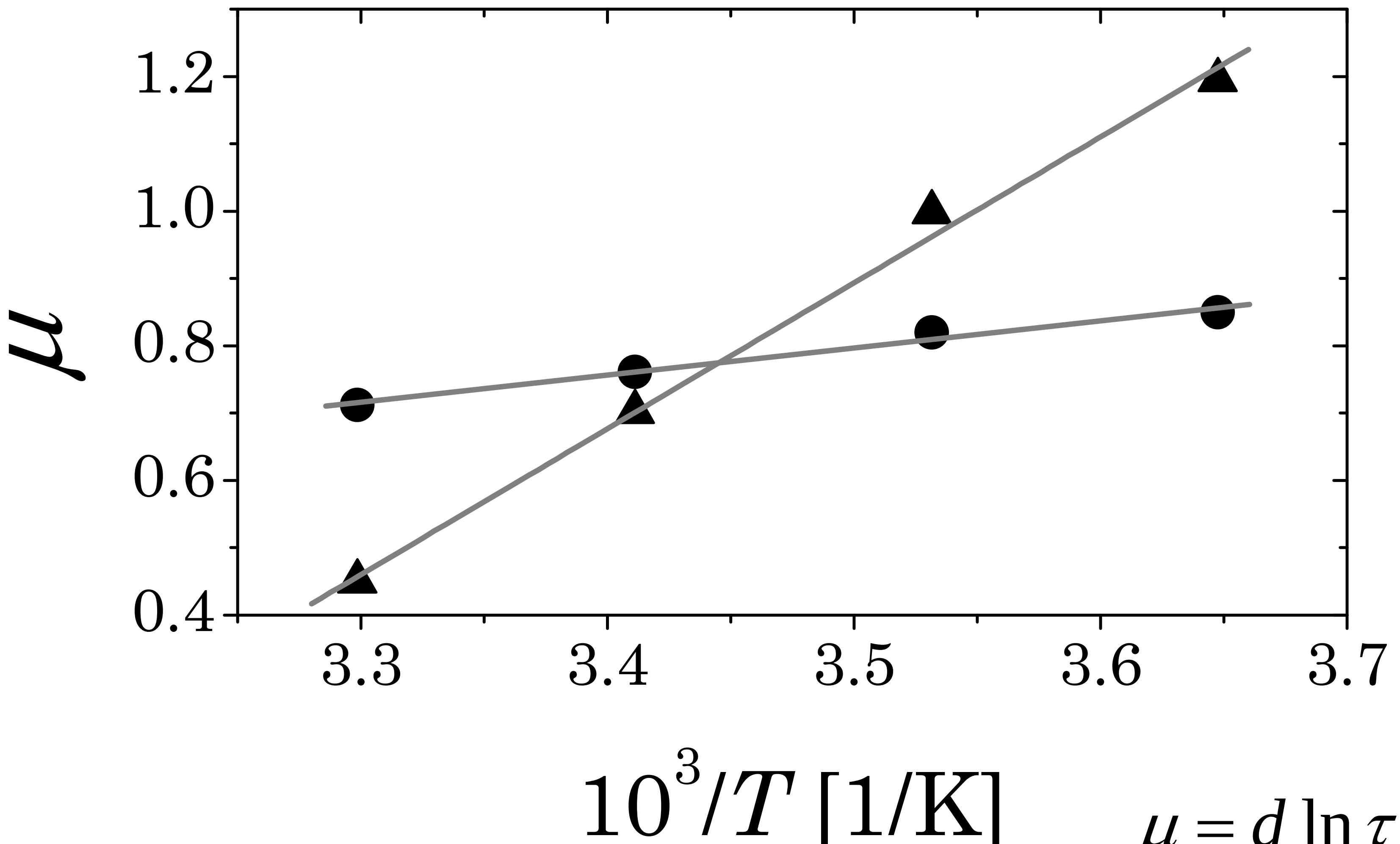
$$J\left(t_w + t\right) G\left(t_w\right) = 1 + \tau_m^{\mu-1}\left(\frac{t}{t_w^{\mu}}\right)$$



Creep time – Aging time Superposition



Variation in μ with Temperature



$$\mu = d \ln \tau / d \ln t_w$$

Relaxation time and Shift rate μ

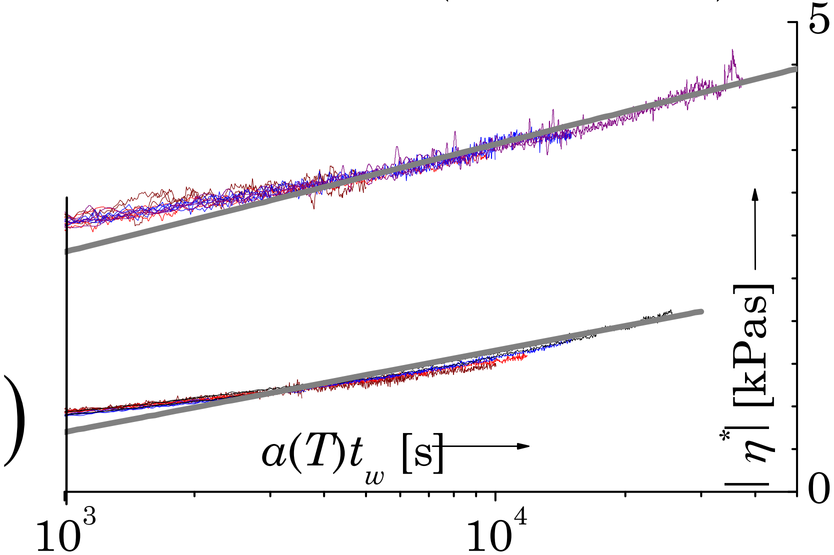
- Two expressions for the Relaxation time dependence on age expressed as:

$$\tau = \tau_m^{1-\mu} t_w^{\mu} \quad \& \quad \tau = \tau_m \exp\left(E/kT\right) = \tau_m \exp\left(G' b^3/kT\right)$$

are equivalent by considering

$$G' = G_0 \ln\left(t_w/\tau_m\right)$$

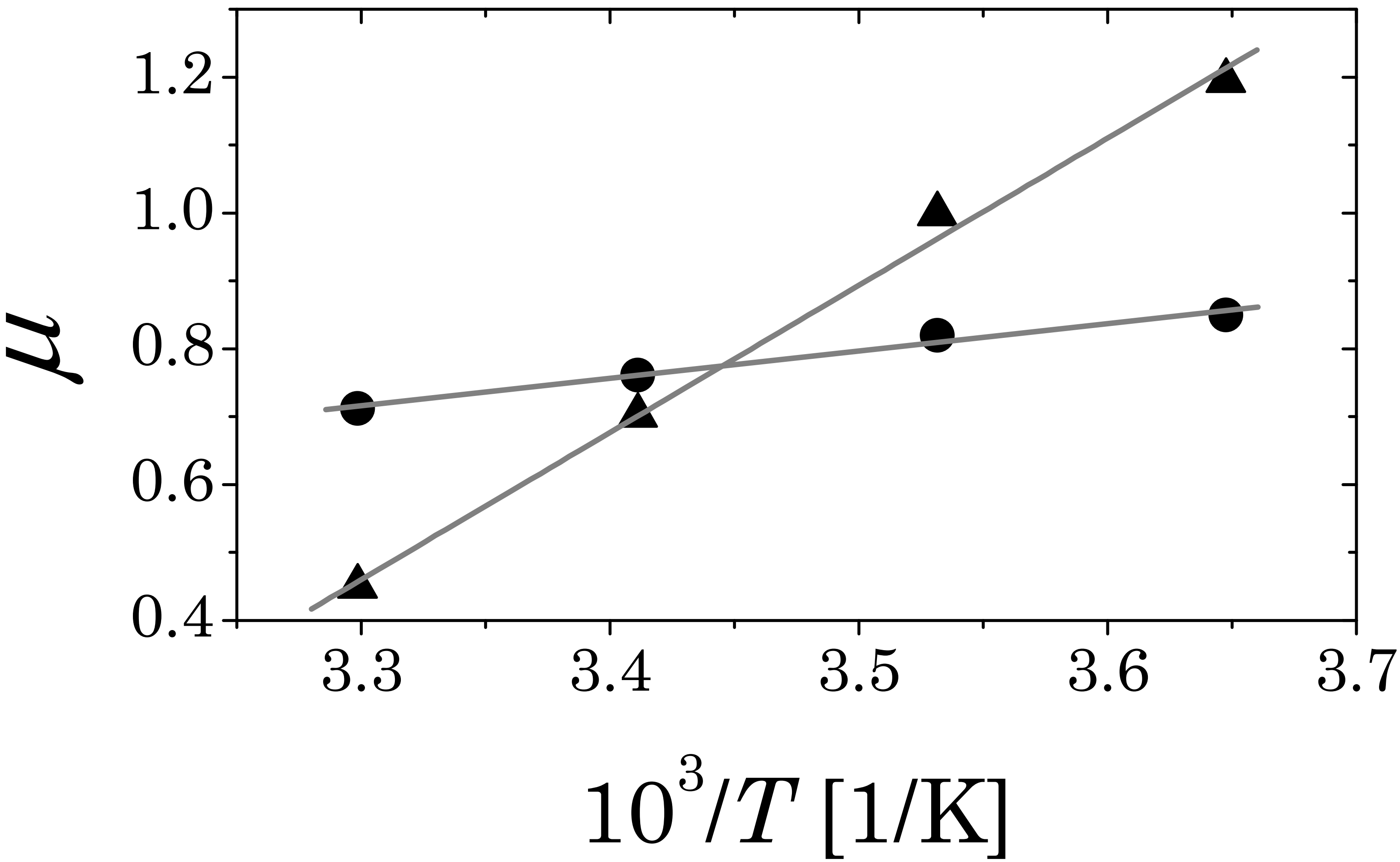
$$\ln\tau = \ln\tau_m + \left(G_0 b^3/kT\right)\ln\left(t_w/\tau_m\right)$$



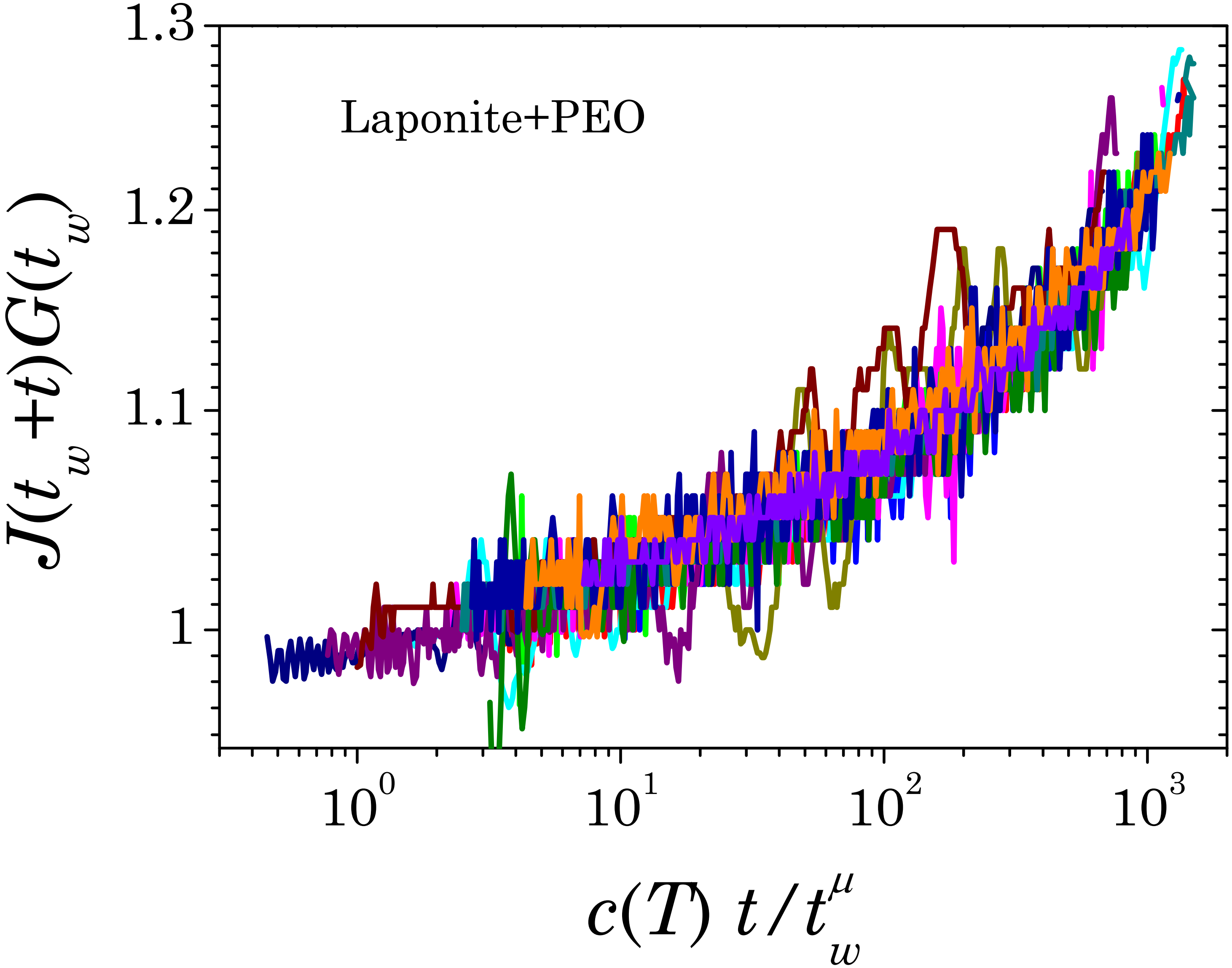
- Shift rate μ is given by

$$\mu = d\ln\tau / d\ln t_w \qquad \mu = G_0 b^3/kT$$

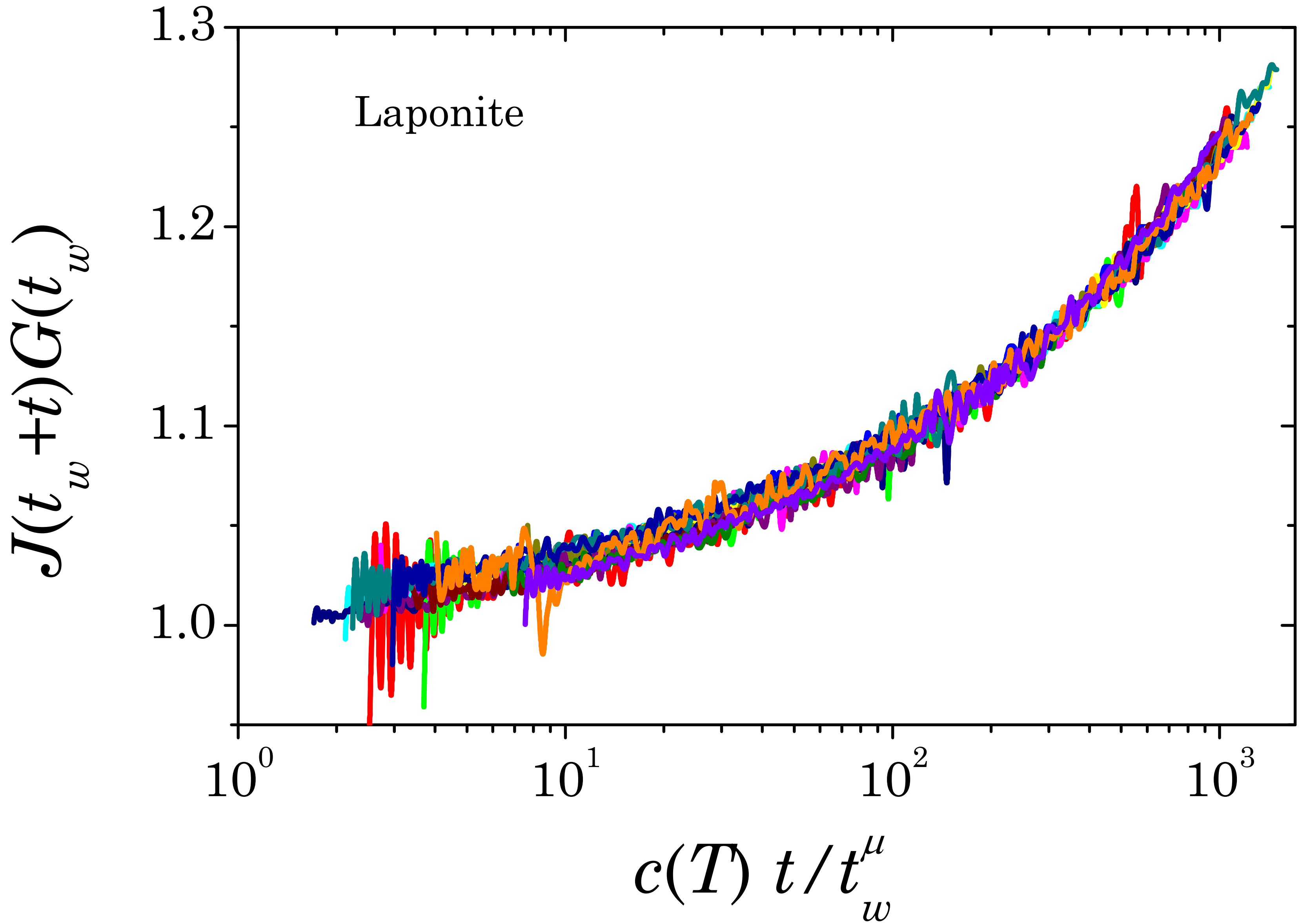
Variation in μ with Temperature



Time-Aging Time-Temperature Superposition



Time-Aging Time-Temperature Superposition



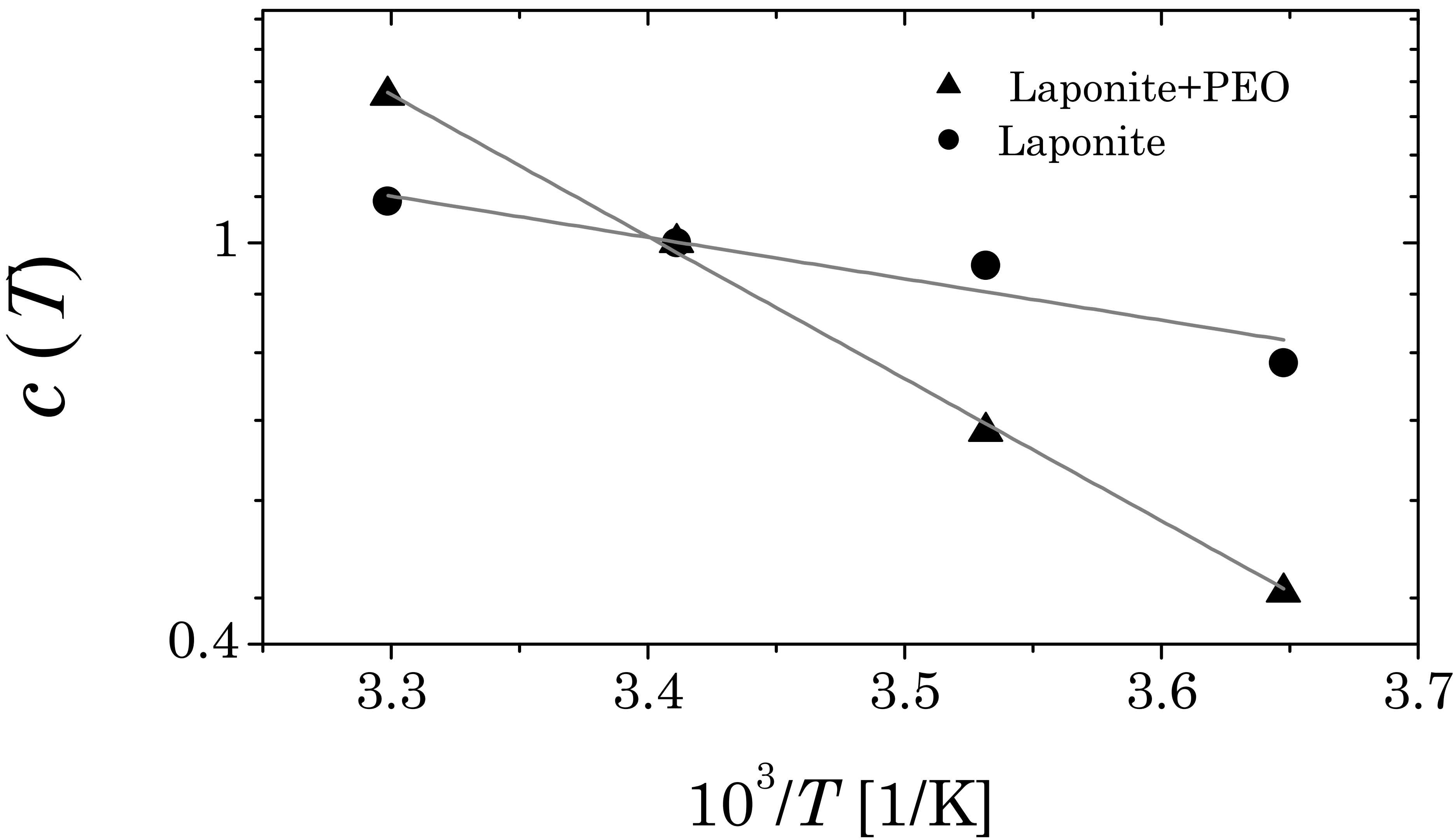
Time superposition

- Effect of aging time on relaxation time:
- Therefore normalized time ($\sim t/\tau$) showed creep time-aging time superposition.
- By same analogy:

$$c(T)\frac{t}{t_w^{\mu}} = \frac{t}{\tau} = \frac{t}{\tau_m (t_w/\tau_m)^{\mu}}$$

$$\ln c(T) \sim (\mu - 1)\left(\ln \tau_{m0} + \bar{U}/k_B T\right) \sim \frac{\left(b^3 G_0 \ln \tau_{m0} - \bar{U}\right)}{k_B T} + \frac{b^3 G_0 \bar{U}}{(k_B T)^2} - \ln \tau_{m0}$$

Sift factor for Time-Temperature Superposition



Conclusions

- Evolution of structure (or aging) depends on waiting time (age) normalized by microscopic timescale
- Therefore, faster microscopic motions at higher temperatures shift the aging process to lower age
- Although aging gets shifted to lower age, rate of structural evolution (μ) decreases with increase in temperature
- Irrespective of waiting time and temperature, process (creep) time normalized by dominating relaxation mode intrinsically affects the rheological behavior
- This procedure can be used to predict the long time viscoelastic behavior of pasty materials from short time experiments

Acknowledgement

Financial support by **Department of Science and Technology**, Government of India.

Effect of temperature on aging and time–temperature superposition in nonergodic laponite suspensions

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Received 27th July 2009, Accepted 21st September 2009
First published as an Advance Article on the web 16th October 2009
DOI: 10.1039/b915105b

We have studied the effect of temperature on the aging dynamics of laponite suspensions by carrying out the rheological oscillatory and creep experiments. We observed that at higher temperatures the mechanism responsible for aging became faster thereby shifting the evolution of elastic modulus to lower ages. Significantly, in the creep experiments, all the aging time and the temperature dependent strain data superposed to form a master curve. The possibility of such a superposition suggests that the rheological behavior depends on the temperature and the aging time only through the relaxation processes and both the variables do not affect the distribution but only the average value of the relaxation times. In addition, this procedure allows us to predict long time rheological behavior by carrying out short time tests at high temperatures and small ages.