Brownian Dynamic simulation in Ageing medium employing Effective Time Transformation

Manish Kumar (15817380)
BS-MS Physics, IIT Kanpur

Supervisor : Prof. Manas Khan
Soft and Active Matter Labs, IIT Kanpur

Contents

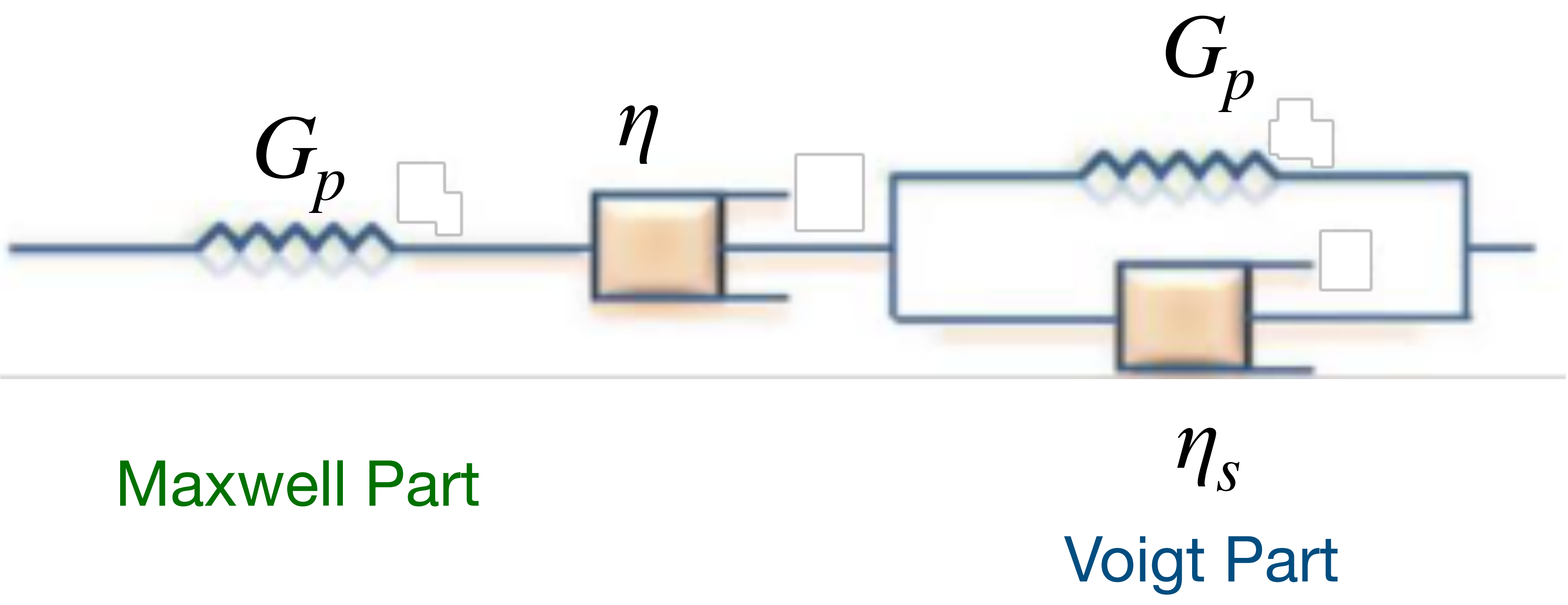
- Maxwell-Voigt Model: Brief Description
- *Effective time Transformation for Ageing Kelvin-Voigt Model (same as we did the last time)*
- *Effective time Transformation for Ageing Maxwell Model (same as we did last time)*
- Struik's approximation for slowing ageing materials
- Ageing in Maxwell-Voigt Model

⭐Brief Summary

- We will start with short description of *Maxwell Voigt Model* of Viscoelasticity.
- We will define Effective Time Transformation for Maxwell part and Voigt part. (This part will lead to the same known result for effective time transformation. This was discussed last time. It will serve the purpose of recap this time.)
- We will discuss about Struik's approximation for slowing ageing materials. (This is briefly mentioned in paper by Dr. Joshi.)
- Then, We will discuss the theory, results and algorithms for ageing in Maxwell-Voigt system under strike's approximation and effective time transformation.
- We are taking slowly ageing system. And we will do simulation for short duration.

Maxwell-Voigt Model : Description

- Short description of Maxwell-Voigt Model:



- Relaxation Time : $\tau = \dfrac{\eta}{G}$
- $k = 6\pi \cdot a \cdot G$

- Maxwell part has low frequency viscosity = η, and the characteristic low-frequency Maxwell relaxation time $\tau = \lambda = \dfrac{\eta}{G_p}$.

- Voigt part has a matching G_p , and a high-frequency viscosity η_s . The characteristic high-frequency crossover time between elastic and viscous behaviour is $\tau_B = \lambda_B = \dfrac{\eta_s}{G_P}$.

Origin of effective time theory*

-It is defined as :

$$\xi(t) = \tau_0 \int_0^t dt'/\tau(t')$$

-It is first used by was Hopkins(1958)*.

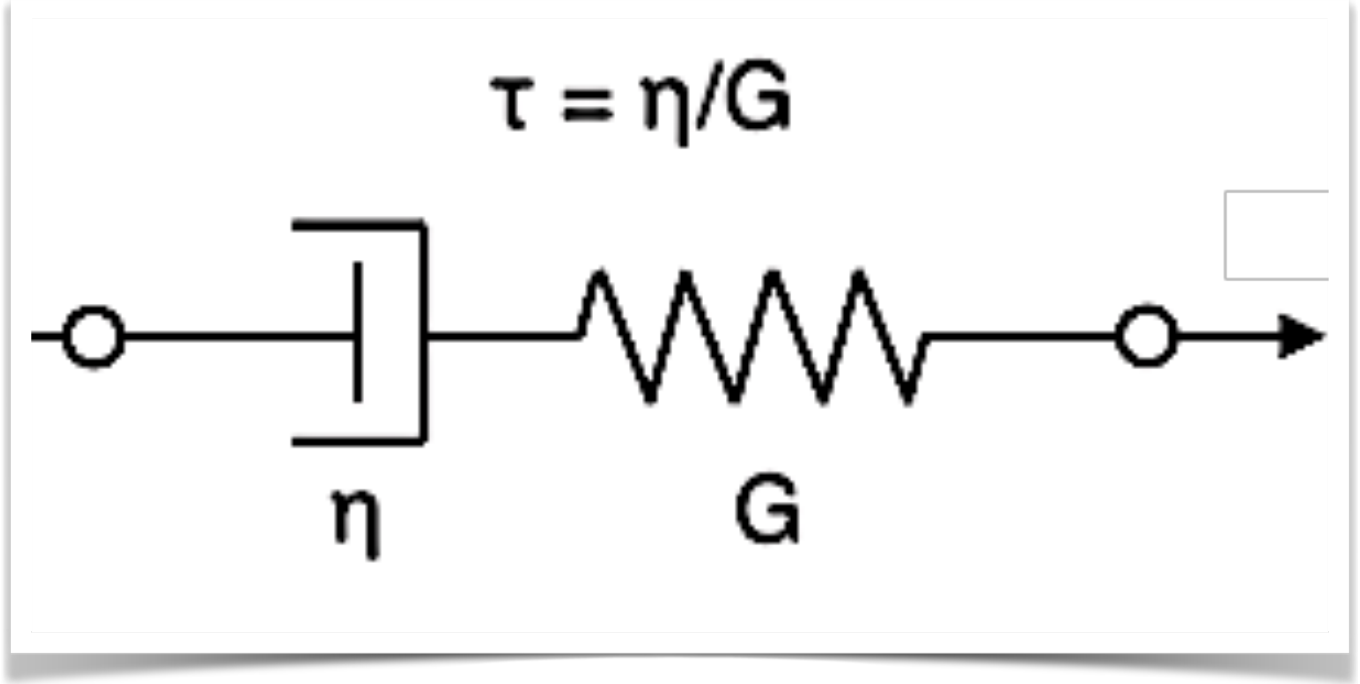
-He used it for analysis of stress relaxation of linear viscoelastic material under varying temperature.

-We use the fact that when temperature of system vary with time (i.e, T=f(t)), then relaxation time of system also become time dependent (i.e, $\tau = \tau_0 a(t)$).

[Google Drive Link to Hopkins(1958) paper]

-Let us take a **Maxwell** unit which is under a force (F), displacement (x), Elastic modulus (G), viscous modulus(η) and relaxation time(τ_0).

$$\frac{dx}{dt} = \frac{1}{G}[\frac{dF}{dt} + \frac{F}{\tau_0}]$$



-suppose relaxation time changes with time then $\tau(t) \equiv \tau_0 a(t)$

$$\frac{dx}{dt} = \frac{1}{G}[\frac{dF}{dt} + \frac{F}{\tau_0 a(t)}] \quad ....(1)$$

-dividing denominator of above equation with a(t), we get:

$$\frac{dx}{dt/a(t)} = \frac{1}{G}[\frac{dF}{dt/a(t)} + \frac{F}{\tau_0}]$$

-now we take :

$$dt/a(t) = d\xi(t)$$

Hence,

$$\xi(t) = \int_0^t d\xi(t) = \int_0^t \frac{dt'}{a(t')}$$

-now we can write equation (1) as

$$\frac{dx}{d\xi} = \frac{1}{G}[\frac{dF}{d\xi} + \frac{F}{\tau_0}] \quad ......(2)$$

-equation (2) is free from time dependence of relaxation time.
-equation (1) and (2) is identical with $t \rightarrow \xi(t)$

Since,

$$\tau(t') = \tau_0 \cdot a(t')$$

$$\xi(t) - \xi(t_w) = \tau_o \int_{t_w}^{t} \frac{dt'}{\tau(t')}$$

Such transformation implies that the relaxation that occurs over time 't' with time dependent relaxation time τ(t′) in the real time domain is equivalent to what occurs in the effective time domain over time ξ with constant relaxation time τ_o.

Defining Effective Time Transformation for Kelvin Voigt Material

- Let us take a **Kelvin Voigt** Material which is under a force (F), displacement (x), Elastic modulus (G), viscous modulus(η) and relaxation time (τ).

$$\frac{dx}{dt} = \frac{F}{\eta} - G\frac{x}{\eta}$$; [which is equivalent to the form $\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} - G\frac{\epsilon}{\eta}$.]

Where 'ϵ' is strain and 'σ' stress.

- Multiply Both Side by '$\frac{\eta}{G}$' :

$$\frac{\eta}{G}\frac{dx}{dt} = \frac{F}{G} - x$$

- $taking,\ \tau = \frac{\eta}{G} \quad \Rightarrow \quad \tau\frac{dx}{dt} = \frac{F}{G} - x$ ...... Equation(i)

- Let us take an ageing material. Then, $\tau \equiv \tau(t) = \tau_0 \cdot a(t)$,

then Equation(i) becomes, $\tau(t) \cdot \frac{dx}{dt} = \frac{F}{G} - x \ \Rightarrow \tau_0 \cdot a(t) \cdot \frac{dx}{dt} = \frac{F}{G} - x$

- $$\tau_0 \cdot a(t) \cdot \frac{dx}{dt} = \frac{F}{G} - x \quad \Rightarrow \quad \tau_0 \cdot \frac{dx}{\frac{dt}{a(t)}} = \frac{F}{G} - x$$ ..... Equation(ii)
- Defining , $\frac{dt}{a(t)} = d\xi(t)$ (*This definition will resolve the problem.*)
- makes, Equation(ii). as $\tau_0 \cdot \frac{dx}{d\xi(t)} = \frac{F}{G} - x$ .... Equation(iii)
- Equation(i) and Equation(iii) is similar in form. The difference is that *'dt' is replaced by* $d\xi(t)$.
- $\frac{dt}{a(t)} = d\xi(t)$ can be written as $\frac{dt}{a(t)} = \tau_0 \cdot \frac{dt}{\tau(t)}$
- Hence,
- $$\int_{t_w}^{t} d\xi(t) = \tau_0 \cdot \int_{t_w}^{t} \frac{dt'}{\tau(t')} = \xi(t) - \xi(t_w)$$ [Transformation Defined] ... Equation(iv)
- This identical to what we get for Maxwell Material.

Struik's Approximation

- Below is a excerpt from from the paper by Shahin and Joshi '***PRL 106, 038302 (2011)***'*
- It talks about superposition for slowing ageing medium.

In a limit $t - t_w \ll t_w$, where evolution of relaxation time over duration of creep time $t - t_w$ can be neglected, $\tau(t) \approx \tau(t_w)$, we get $\xi(t) - \xi(t_w) = \tau_0(t - t_w)/\tau(t_w)$. Struik [4] was the first to propose a time-aging time superposition procedure wherein he considered a rheological response at different aging times t_w only in a limit of $t - t_w \ll t_w$. The corresponding shifting on the time axis to get a superposition yielded a dependence of relaxation time on aging time: $\tau(t_w)$.

Taken from Paragraph-2 in page -2

- We can derive the above expression as follow:
- Since author defined ,

$$\xi(t) - \xi(t_w) = \tau_0 \int_{t_w}^{t} \frac{dt'}{\tau(t')}$$

* Link to Shahin and Joshi Paper

Struik's Approximation (Continue…)

- Taking $\tau(t) \approx \tau(t_w)$, under the condition of slow ageing I.e., $t - t_w \ll t_w$.

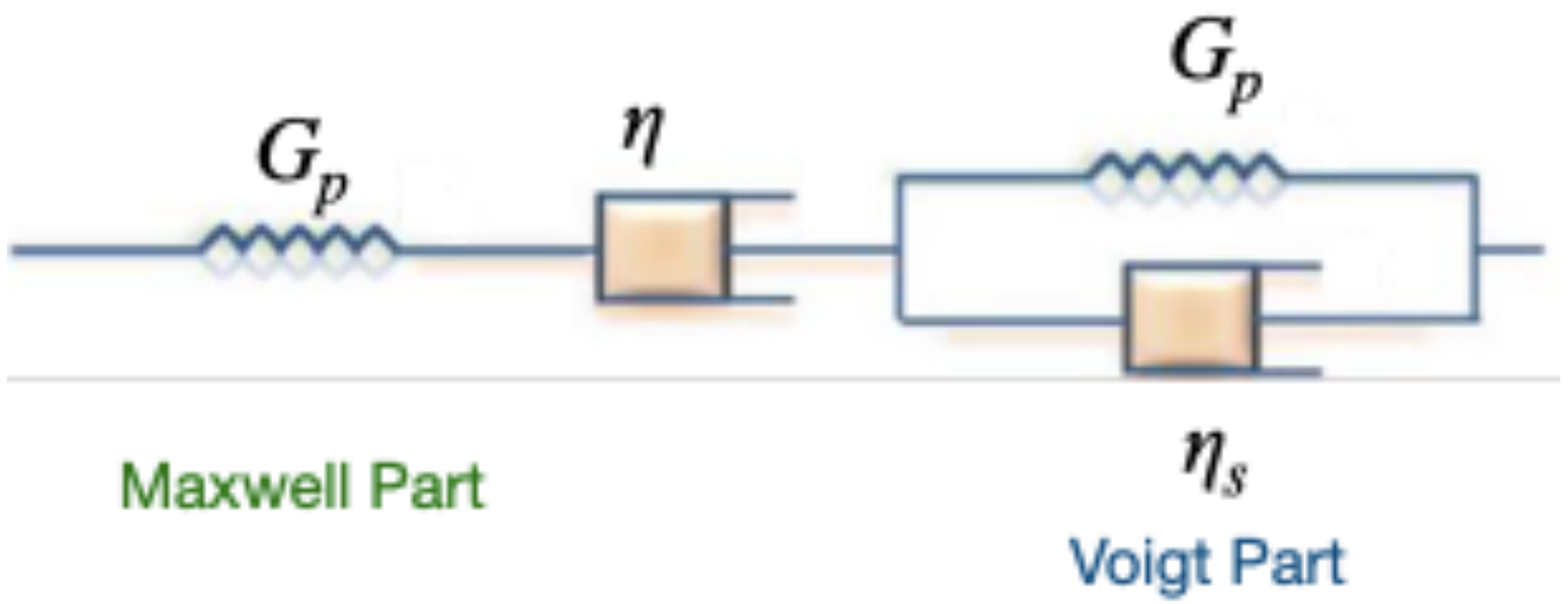
$$\xi(t) - \xi(t_w) = \tau_0 \int_{t_w}^{t} \frac{dt'}{\tau(t_w)}$$

$$\tau_0 \int_{t_w}^{t} \frac{dt'}{\tau(t'_w)} = \frac{\tau_0}{\tau(t'_w)} \int_{t_w}^{t} dt' = \frac{\tau_0}{\tau(t'_w)}[t - t_w] \qquad \text{Q.E.D}$$

- $t - t_w \ll t_w$.(Waiting time is much much larger than simulation time)
- Hence, system can be assumed to be temporally stationary for 60 second of simulation time.
- From here we are simulating the system for each of three waiting time for duration of 60 second like we do for non-ageing cases. .(More discussion in upcoming slides while dealing the MVM system .)

Maxwell-Voigt material: selection of parameters

An ageing maxwell-voigt system.



$G_p \equiv G$ *(To keep notation simple)*

	Time dependent form	constant
$\eta(t)$	$\eta_o \cdot exp(\beta \cdot t)$	$\eta_o = 1\ Pa \cdot s$
$G(t)$	$G_o \cdot exp(\alpha \cdot t)$	$G_0 = 1000\ Pa$
$\eta_s(t)$	$\eta_{so} \cdot exp(\beta \cdot t)$	$\eta_{so} = 10^{-4} Pa \cdot s$

$$\beta = 3.84 \times 10^{-3} \quad [1/s]$$
$$\alpha = 1.92 \times 10^{-3} \quad [1/s]$$

There can be several possible selection of values of η, G, η_s , α, β. We are taking one of such combination as mentioned in above table. This would make the different aspects of the system distinguishable in MSD vs time-lag graph

selection of parameters: continues…

Maxwell relaxation

$$\tau(t) = \lambda(t) = \frac{\eta}{G} = \frac{\eta_o}{G_o} \cdot exp([\beta - \alpha] \cdot t)$$

$$\tau(t) = \lambda(t) = 10^{-3} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)$$

Voigt relaxation

$$\tau_B(t) = \lambda_B(t) = \frac{\eta_s}{G} = \frac{\eta_{so}}{G_o} \cdot exp([\beta - \alpha] \cdot t)$$

$$\tau_B(t) = \lambda_B(t) = 10^{-7} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)$$

Importants Points

- $\tau(t)$ *and* $\tau_B(t)$ have same time dependent part i.e,

  $$exp([1.92 \times 10^{-3} s^{-1}] \cdot t) \equiv a(t)$$

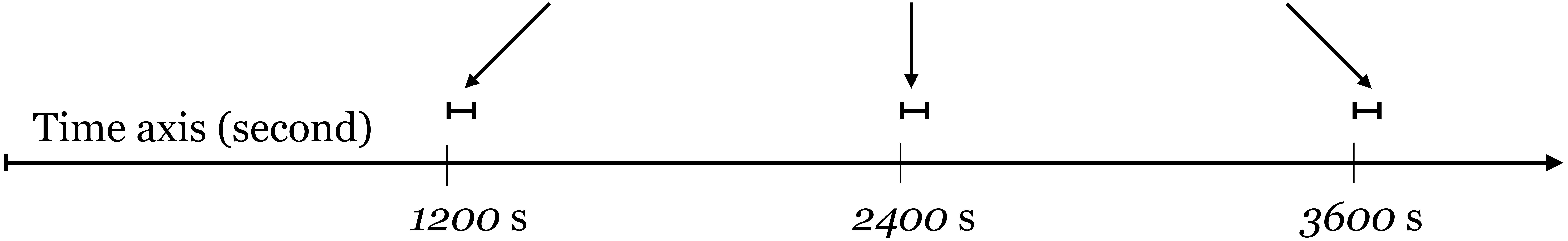
-This is as prescribed in the paper by Shahin and Joshi ‘***PRL 106, 038302 (2011)***

material possesses distribution of modes. Therefore, time-aging time superposition is possible only if all the modes age similarly, preserving the shape of a spectrum of relaxation times [4,8].

Taken from the end of Paragraph-2 in page -2

Scheme for simulation

Each of the three simulations are done in the time window of 60 second.



- We have taken three waiting time :

  $t_{w1} = 1200\ sec, t_{w2} = 2400\ sec, t_{w2} = 3600\ sec,$
- Each simulation is for **60 second ($t - t_w$)**. For each waiting time, in the duration of 60 seconds, sample has not aged considerably.
- Analysis of parameters near $t_w = 1200\ s$. When we see the variation in the values of the parameters due to ageing, we find that the maximum possible change is around 10% only.

$$\frac{G(t_w + 60)\ -\ G(t_w)}{G(t_w)} \sim 0.12 \quad ;for\ t_w = 1200\ s$$

$$\frac{\tau(t_w + 60)\ -\ \tau(t_w)}{\tau(t_w)} \sim 0.12 \quad ;\ t_w = 1200\ s$$

- Coming back to Struik's approximation mentioned in slide no.-10. We will take -

  $\tau(t) \approx \tau(t_w)$, because we have selected the parameters of system such that it qualify as slow ageing system.

  We will take $\eta(t) \approx \eta(t_w)$; $G(t) \approx G(t_w)$

  Which is consistent with $\tau(t) \approx \tau(t_w) \approx \dfrac{\eta(t_w)}{G(t_w)}$.

- **At $t_w = 1200\ s$,**

  $\tau(t) \approx \tau(t_w = 1200\ s)$ [Struik's approximation], because we have selected the parameters of system such that it qualify as slow ageing system.

  We can take $\eta(t) \approx \eta(t_w = 1200\ s)$

  $$G(t) \approx G(t_w = 1200\ s)$$

  $$\eta_s(t) \approx \eta_s(t_w = 1200\ s)$$

• At $t_w = 1200\ s$ (Continue...)

- So basically, we will do the simulation as mentioned in the paper 'Random-Walk Trajectories of Probe Particles in Viscoelastic Complex Fluids by Manas Khan and Thomas G. Mason '(Phys. Rev. E **89**, 042309)
- The parameters for simulation would be as follow-

$$\tau(t) \approx \tau(t_w = 1200\ s)$$
$$\tau_B(t) \approx \tau_B(t_w = 1200\ s)$$
$$\eta(t) \approx \eta(t_w = 1200\ s)$$
$$G(t) \approx G(t_w = 1200\ s)$$
$$\eta_s(t) \approx \eta_s(t_w = 1200\ s)$$

Struik's Approximation

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-9}, 10^{-2}]\ sec$; $t_{max} = 60 sec$, [No. of time step in trajectory $\sim$ 1,00,000]

• At $t_w = 2400\ s$

- Analysis of parameters near $t_w = 2400\ s$. When we see the variation in the values of the parameters due to ageing, we find that the maximum possible change is around 12% only in this case too.

$$\frac{\tau(t_w + 60)\ -\ \tau(t_w)}{\tau(t_w)} \sim 0.12 \quad ;\ t_w = 2400\ s$$

$$\frac{G(t_w + 60)\ -\ G(t_w)}{G(t_w)} \sim 0.12 \quad ; for\ t_w = 2400\ s$$

- The parameters for simulation in this case would be as follow-

$$\tau(t) \approx \tau(t_w = 2400\ s)$$

$$\tau_B(t) \approx \tau_B(t_w = 2400\ s)$$

$$\eta(t) \approx \eta(t_w = 2400\ s)$$

$$G(t) \approx G(t_w = 2400\ s)$$

$$\eta_s(t) \approx \eta_s(t_w = 2400\ s)$$

Struik's Approximation

- $\Delta t \in [10^{-9}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$, [No. of time step in trajectory ~ 1,00,000]

• At $t_w = 3600\ s$

- Analysis of parameters near $t_w = 3600\ s$. When we see the variation in the values of the parameters due to ageing, we find that the maximum possible change is around 12% only in this case too.

$$\frac{\tau(t_w + 60)\ -\ \tau(t_w)}{\tau(t_w)} \sim 0.12 \quad ;\ t_w = 3600\ s$$

$$\frac{G(t_w + 60)\ -\ G(t_w)}{G(t_w)} \sim 0.12 \quad ; for\ t_w = 3600\ s$$

- The parameters for simulation in this case would be as follow-

$$\tau(t) \approx \tau(t_w = 3600\ s)$$

$$\tau_B(t) \approx \tau_B(t_w = 3600\ s)$$

$$\eta(t) \approx \eta(t_w = 3600\ s)$$

$$G(t) \approx G(t_w = 3600\ s)$$

$$\eta_s(t) \approx \eta_s(t_w = 3600\ s)$$

Struik's Approximation

- $\Delta t \in [10^{-9}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$, [No. of time step in trajectory ~ 1,00,000]

Mean square displacement for different waiting time

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-9}, 10^{-2}]$ sec ; $t_{max} = 60 sec$, [No. of time step in trajectory ~ 1,00,000]

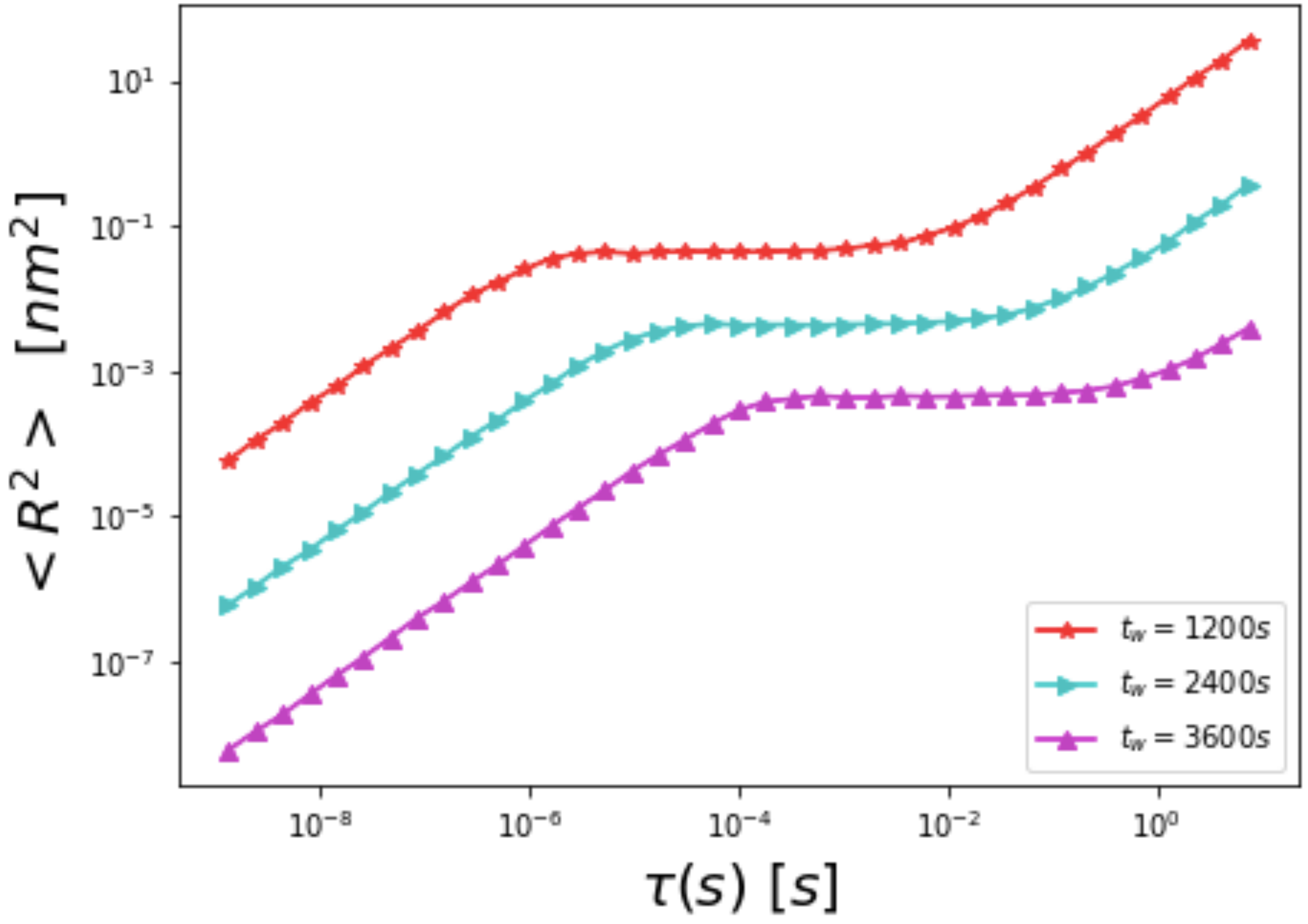


Fig.1 MSD in real time domain for three waiting times

- Some literature mention, $t - t_w$ in place of time-lag (τ).
- As material ages, -Plateau value decreases, and
  -τ and τ_B increases.
- Plateau value $= r_{t_w}^2 = \dfrac{k_B T}{6\pi a G(t_w)}$ ($\downarrow$) as, $G(t_w)$ ($\uparrow$).

Effective Time Transformation(ETT)

- Since, transformation is defined as: $\xi(t) - \xi(t_w) = \tau_o \int_{t_w}^{t} \frac{dt'}{\tau(t')}$

- For arbitrary $\tau(t) = \tau_0 \cdot exp(\gamma \cdot t) \Rightarrow \ \xi - \xi_w = \frac{exp(\gamma \cdot t_w) - exp(\gamma \cdot t)}{\gamma}$

This shows τ_0 is not relevant for $\xi - \xi_w$

Applying ETT to Maxwell and Voigt relaxations

Maxwell relaxation

$$\tau(t) = \lambda(t) = \frac{\eta}{G} = \frac{\eta_o}{G_o} \cdot exp([\beta - \alpha] \cdot t)$$

$$\tau(t) = \lambda(t) = 10^{-3} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)$$

$$\xi(t) - \xi(t_w) = \tau_o \int_{t_w}^{t} \frac{dt'}{\tau(t')}$$

$$\xi(t) - \xi(t_w) = 10^{-3} \int_{t_w}^{t} \frac{dt'}{10^{-3} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)}$$

$$[\beta - \alpha] = exp([1.92 \times 10^{-3})$$

$$\xi - \xi_w = \frac{exp([\beta - \alpha] \cdot t_w) - exp([\beta - \alpha] \cdot t)}{[\beta - \alpha]}$$

Voigt relaxation

$$\tau_B(t) = \lambda_B(t) = \frac{\eta_s}{G} = \frac{\eta_{so}}{G_o} \cdot exp([\beta - \alpha] \cdot t)$$

$$\tau_B(t) = \lambda_B(t) = 10^{-7} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)$$

$$\xi(t) - \xi(t_w) = \tau_o \int_{t_w}^{t} \frac{dt'}{\tau(t')}$$

$$\xi(t) - \xi(t_w) = 10^{-7} \int_{t_w}^{t} \frac{dt'}{10^{-7} \cdot exp([1.92 \times 10^{-3} s^{-1}] \cdot t)}$$

$$[\beta - \alpha] = exp([1.92 \times 10^{-3})$$

$$\xi - \xi_w = \frac{exp([\beta - \alpha] \cdot t_w) - exp([\beta - \alpha] \cdot t)}{[\beta - \alpha]}$$

Transformation of time data points from real to effective time domain

*Convention is as per the paper-(Bhavna and Joshi, Soft Matter, 2016, 12, 8167)**

There are 40 bins for time-lag in *real time domain* (placed on time axis, graph-x)

$t - t_w \rightarrow$											
	t_1	t_2	t_3	.	.	.	.	.	.	t_{39}	t_{40}

$$\xi_i - \xi_w = \frac{exp(\beta \cdot t_i) - exp(\beta \cdot t_w)}{\beta} \; ; \; i \in (1,40)$$

There is one to one relation between real and effective time domain data points

$\xi - \xi_w \rightarrow$											
	ξ_1	ξ_1	ξ_1	.	.	.	.	.	.	ξ_{39}	ξ_{40}

There are corresponding 40 bins for time-lag in *effective time domain*
(placed on time axis, graph-y)

We repeat this procedure to each of the waiting time i.e., $t_w = 1200\ s,\ 2400\ s,\ 3600\ s$

The result of the process is as follow-

* https://iitk-my.sharepoint.com/:b:/g/personal/maniskmr_iitk_ac_in/EeSLgHVoGiRHnoxcOOAPMuEBIhkZArFTMIPF5TX0cc7HVw?e=9CJ3tP

Result of the Effective time transformation on the system

Real time

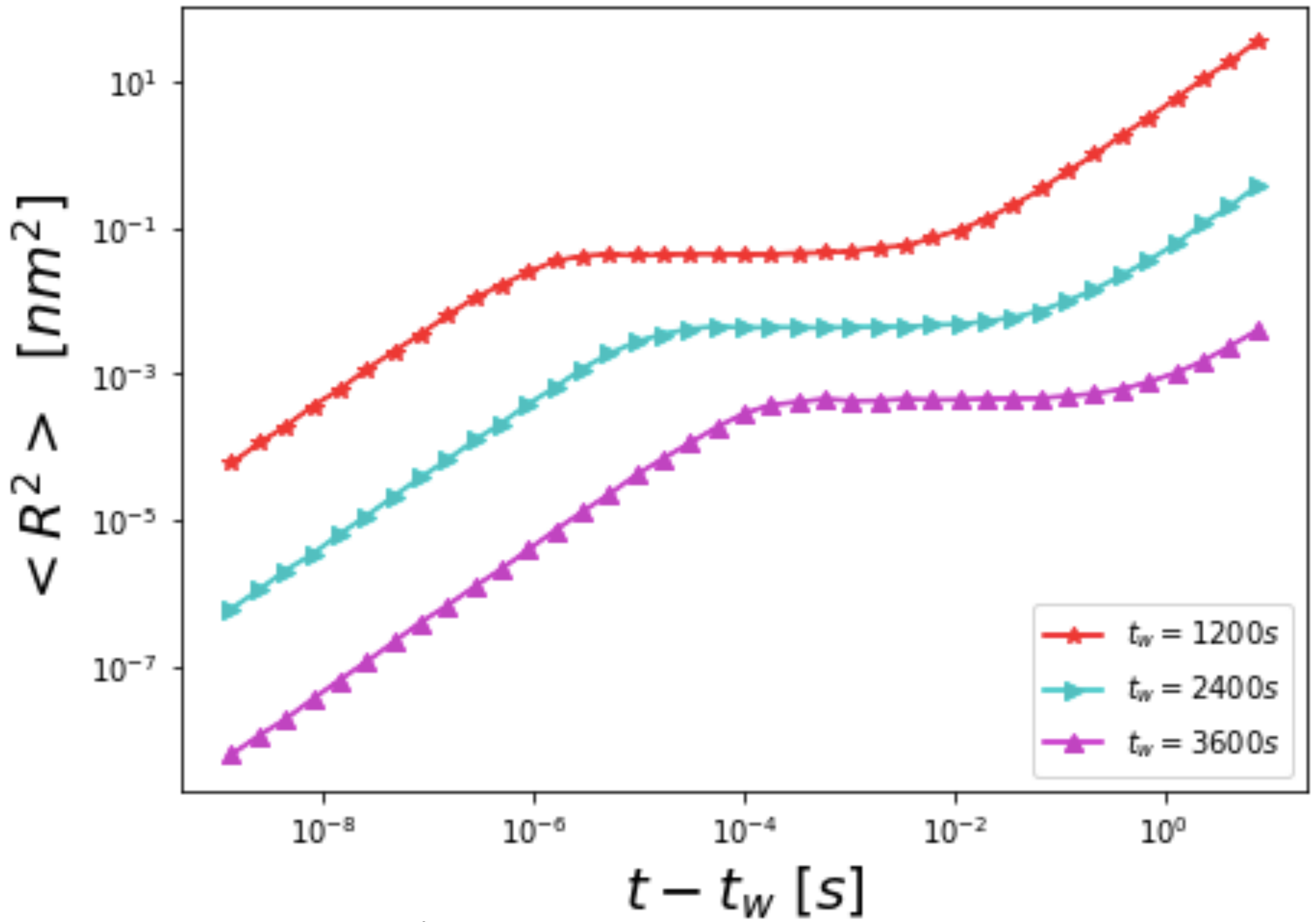


Fig.2

Effective time

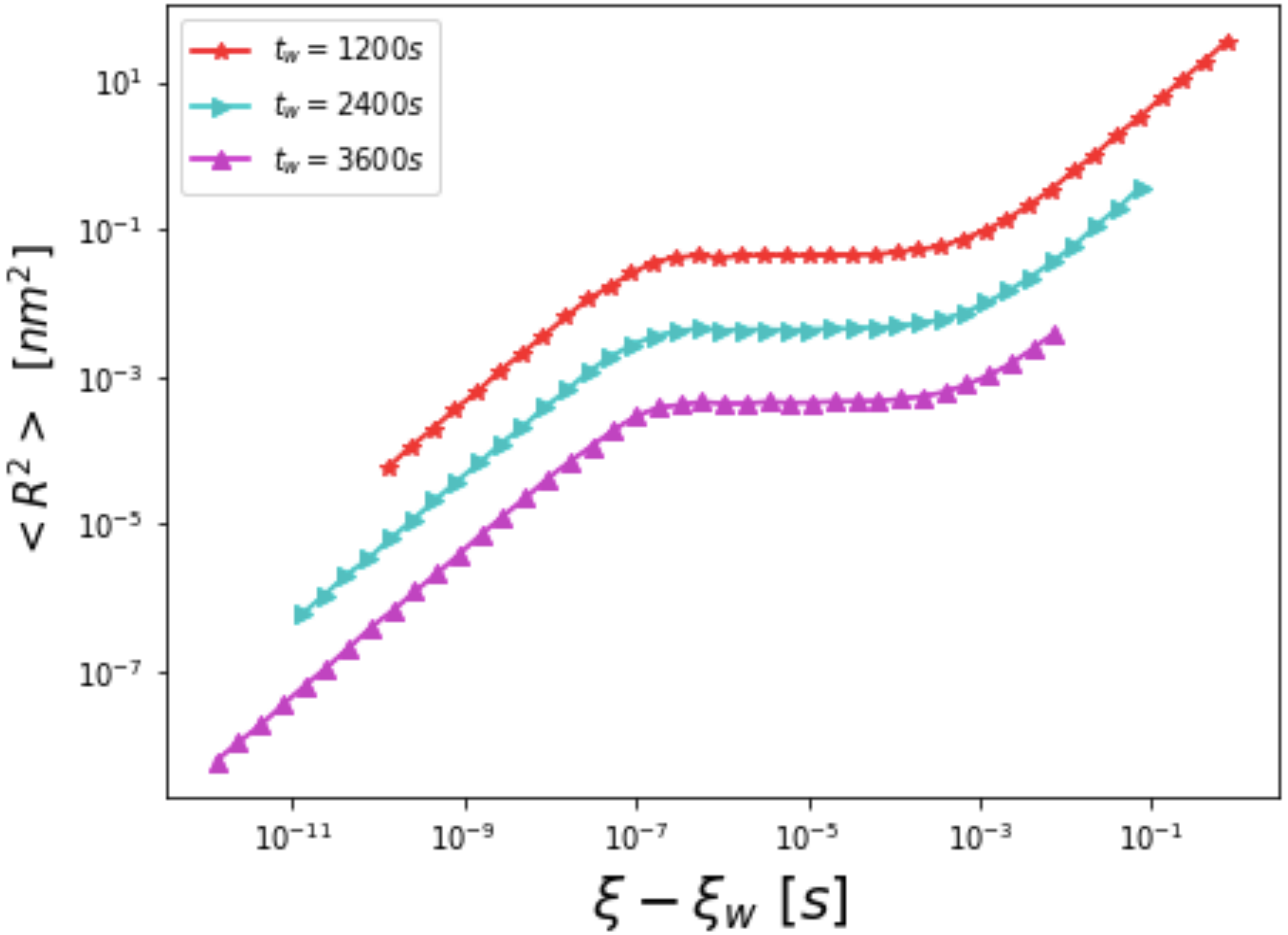


Fig.3

- Comparing both the graphs makes it clear that the time domain transformation change each of the MSD curve in such a way that in effective time domain they have matching relaxation time.

Case-I : Effective Time Translation (Continue...)

- To superpose all the curve, we need to multiply each curve by ***vertical shift factor ['b']**** : -
- Factor 'b' depends on elastic modulus for each waiting time.
- For calculating 'b', we need to take a **reference curve** and then proceed like this:-

Taking $t_w = 1200s$ as reference state (we can take any one of three as reference state) then:-

$$b_{t_w=1200s} = \frac{G(t = t_w = 1200s)}{G(t = t_w = 1200s)} = 1\ , \quad b_{t_w=1800s} = \frac{G(t = t_w = 2400s)}{G(t = t_w = 1200s)} = 10\ , \quad b_{t_w=2400s} = \frac{G(t = t_w = 2400s)}{G(t = t_w = 3600s)} = 100$$

- Now multiplying each MSD curve(Left side Figure) with their respective 'b' values gives (Right side Figure):-

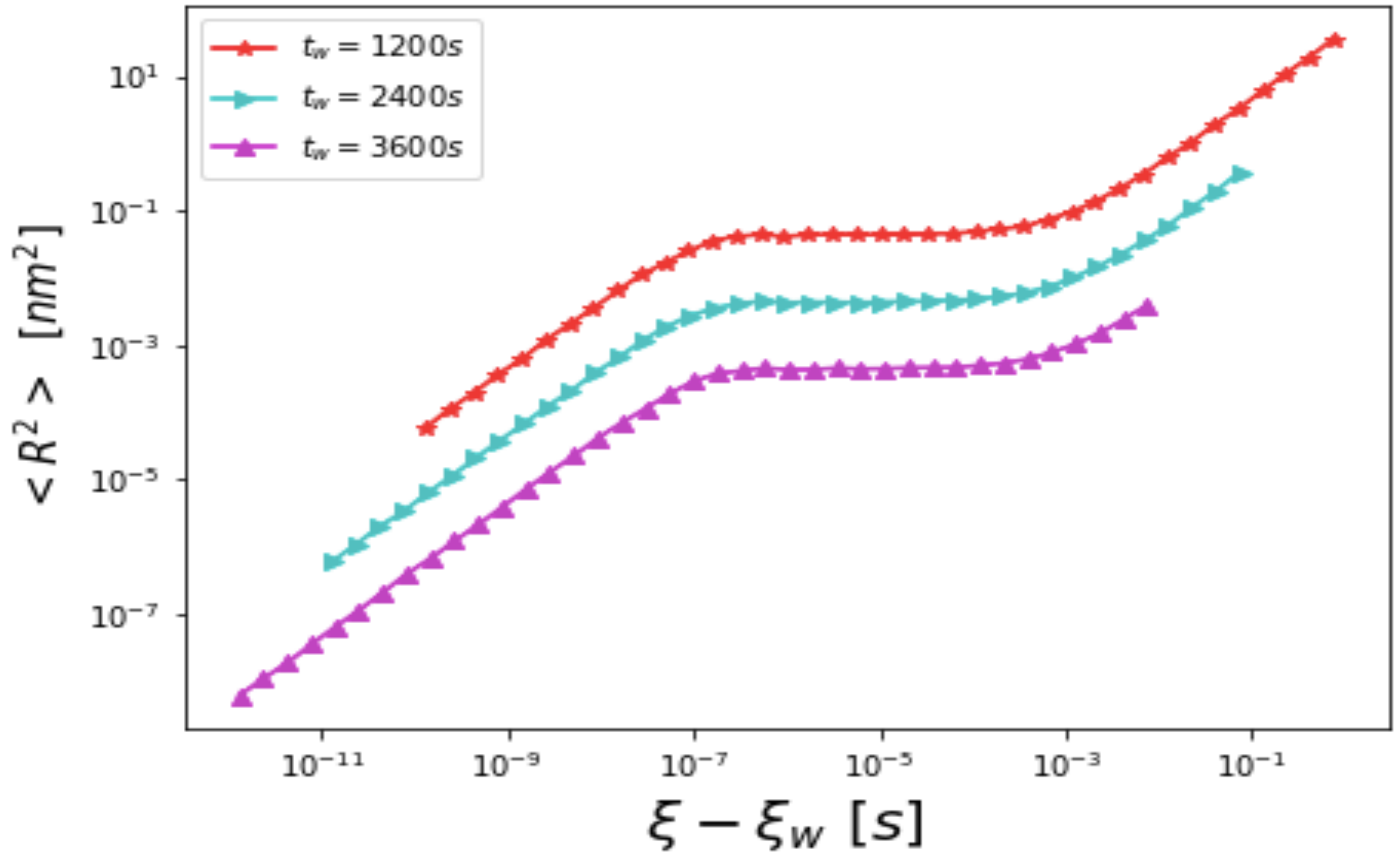


Fig.4

$\times b_{t_w}$

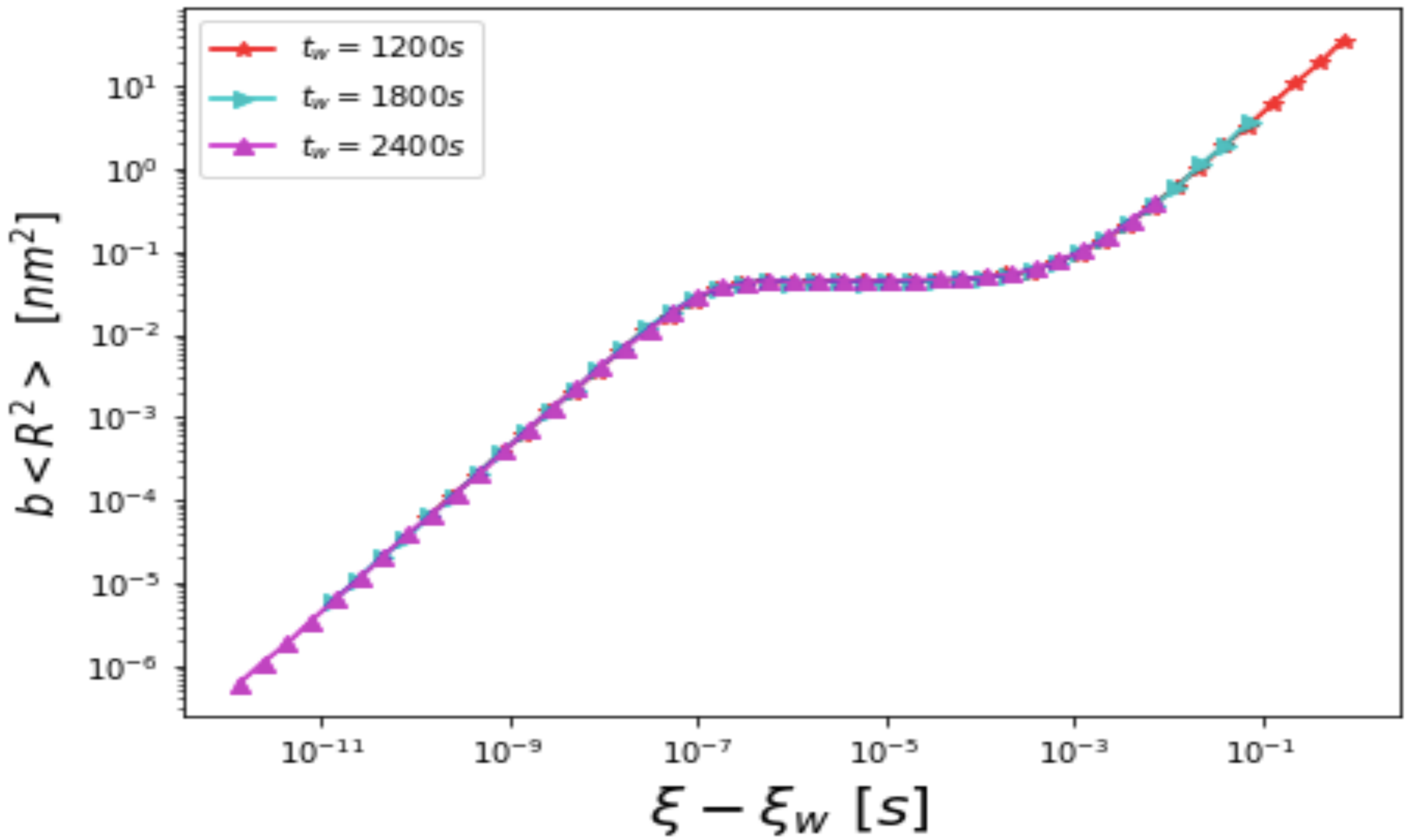


Fig.5: MSD in real Effective Time domain for three waiting times. Reference state is $t_w = 1200s$.

* Soft Matter, 2012, 8, 4171 ('b' factor to compensate changing Elastic modulus is mentioned in several papers of Dr. Joshi et. al.)

Brief Summary of Case-II

- We are only considering (slow) ageing in Viscous component of *Kelvin Voigt Model.*
- We selected three waiting times, and all are relatively high when compared to simulation time. Or, $t - t_w \ll t_w$
- Selection of value of $\alpha = 1.9 \times 10^{-3} s$ is to make sure of slow ageing.
- This is to make sure that system remain temporary stationary while simulation.
- In this case vertical shift factor is identical for all waiting time and equal to unity due non ageing in elastic component (G_0).

$$b_{t_w=1200s} = \frac{G(t = t_w = 1200s)}{G(t = t_w = 1200s)} = 1, \quad b_{t_w=1800s} = \frac{G(t = t_w = 1800s)}{G(t = t_w = 1200s)} = 1, \quad b_{t_w=2400s} = \frac{G(t = t_w = 2400s)}{G(t = t_w = 1200s)} = 1$$

- Steps to get superposition of MSD in Effective Time Domain:

Transform the Real time to Effective time

$$[(t - t_w) \rightarrow (\xi - \xi_w)]$$

$$\downarrow$$

Superimposed curve in Effective Time Domain