Brownian Dynamic simulation in Ageing medium employing Effective Time Transformation

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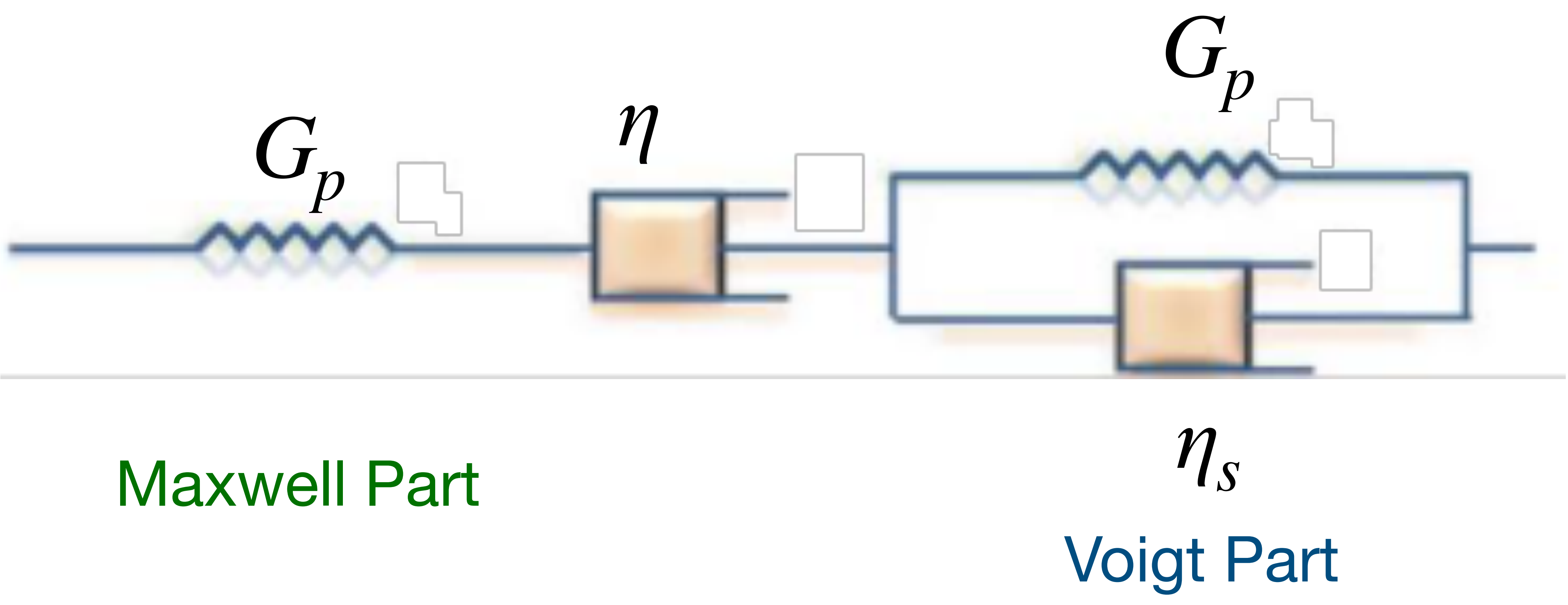
Contents

Brief Summary

- We will start with short description of *Maxwell Voigt Model* of Viscoelasticity.
- This model is combination of two existing models namely, Maxwell model and Kelvin-Voigt model.
- 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)
- We will discuss about Struik's approximation for slowing ageing materials.(This is briefly mentioned in paper by Dr. Joshi.)
- Then, We will take two case as follow-
- In case-I, We will let plateau modulus to remain same and viscous component to to age.
- In case-II, We will let plateau modulus as well as viscous components to age.
- All above listed cases are slowly ageing system. 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)*.

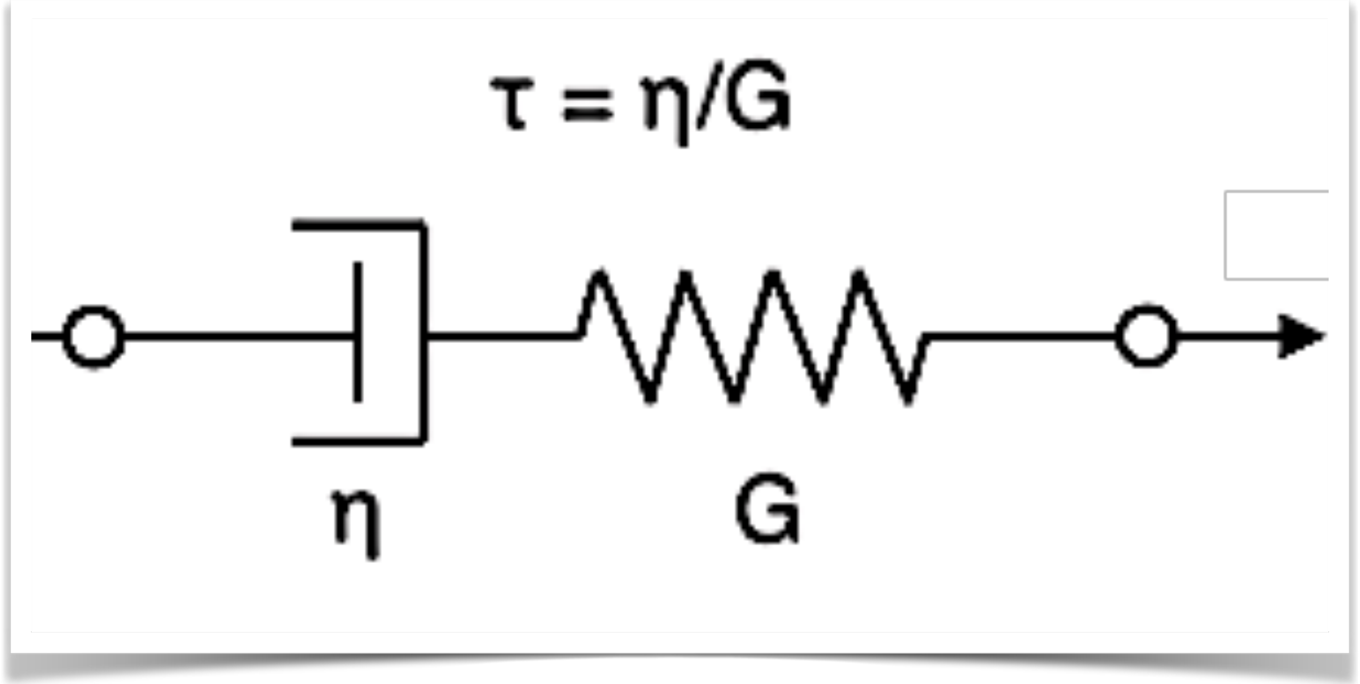
-He used it for analysis of stress relaxation of linear viscoelastic material under varying temperature.

-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, $\tau = \tau_0 a(t)$).

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 , $\dfrac{dt}{a(t)} = d\xi(t)$ *(This definition will resolve the problem.)*
- makes, Equation(ii). as $\tau_0 \cdot \dfrac{dx}{d\xi(t)} = \dfrac{F}{G} - x$ .... Equation(iii)
- Equation(i) and Equation(iii) is similar in form. The difference is that *'dt' is replaced by* $d\xi(t)$.
- $\dfrac{dt}{a(t)} = d\xi(t)$ can be written as $\dfrac{dt}{a(t)} = \tau_0 \cdot \dfrac{dt}{\tau(t)}$
- 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.
- Link to Hopkins(1958) paper

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: $\tau(t_w)$.

- 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., $t - t_w \ll t_w$.

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

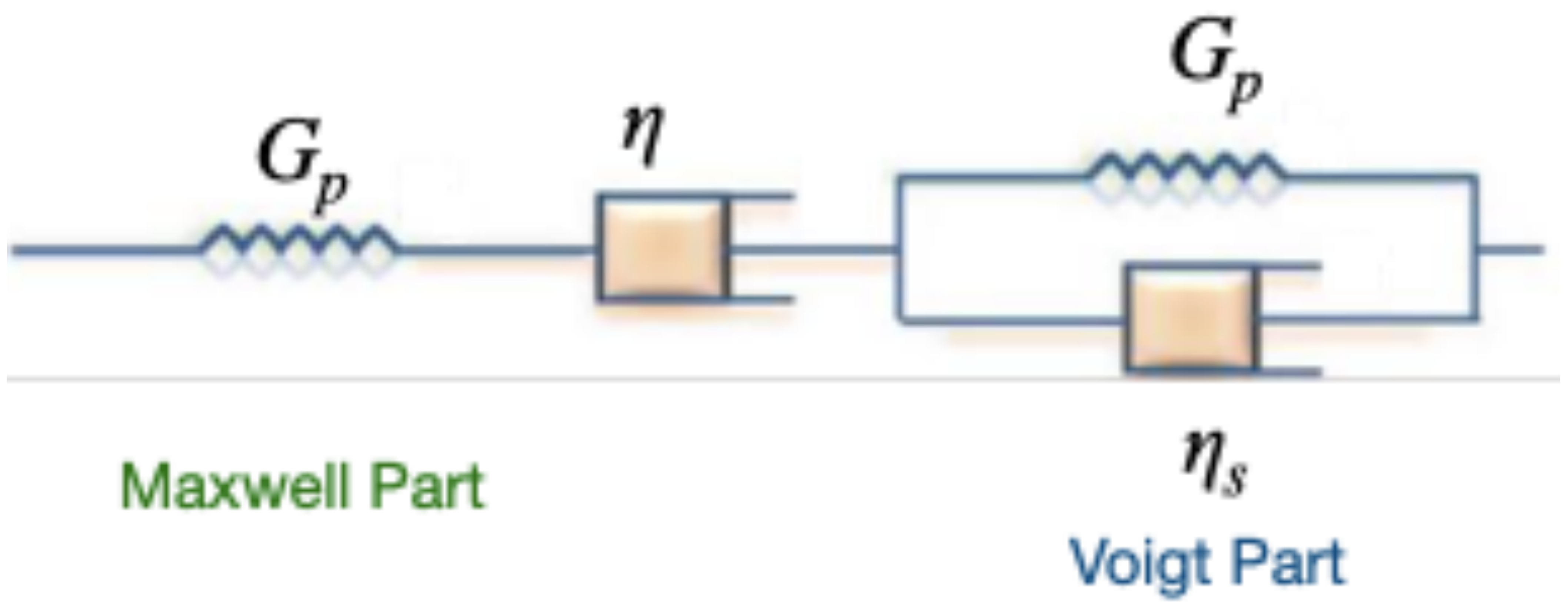
$$\tau_0 \int_{t_w}^{t} \frac{dt'}{\tau(t'_w)} = \frac{\tau_0}{\tau(t'_w)} \int_{t_w}^{t} dt' = \frac{\tau_0}{\tau(t'_w)}[t - t_w]$$

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 .)

Scheme for simulation

An ageing maxwell-voigt system.



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

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

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

	Relaxation time
Maxwell	
Voigt	

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

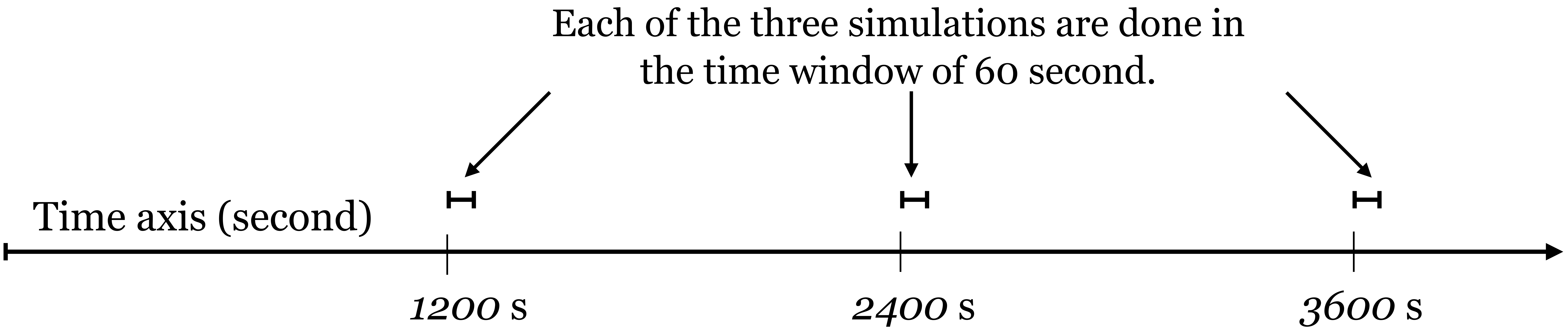
- $\tau(t)$ *and* $\tau_B(t)$ have same time dependent part i.e,

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

-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



- 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 $\quad \eta(t) \approx \eta(t_w) \;\; ; \quad G(t) \approx G(t_w)$

  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 ~ 90,000]

• 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 $\sim$ 90,000]

• 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-

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

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

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

Struik's Approximation

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

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

- $\Delta t \in [10^{-9}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$, [No. of time step in trajectory $\sim$ 90,000]

Mean square displacement for different waiting time

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-9}, 10^{-2}]$ sec ; $t_{max} = 60sec$, [No. of time step in trajectory ~ 80,000]

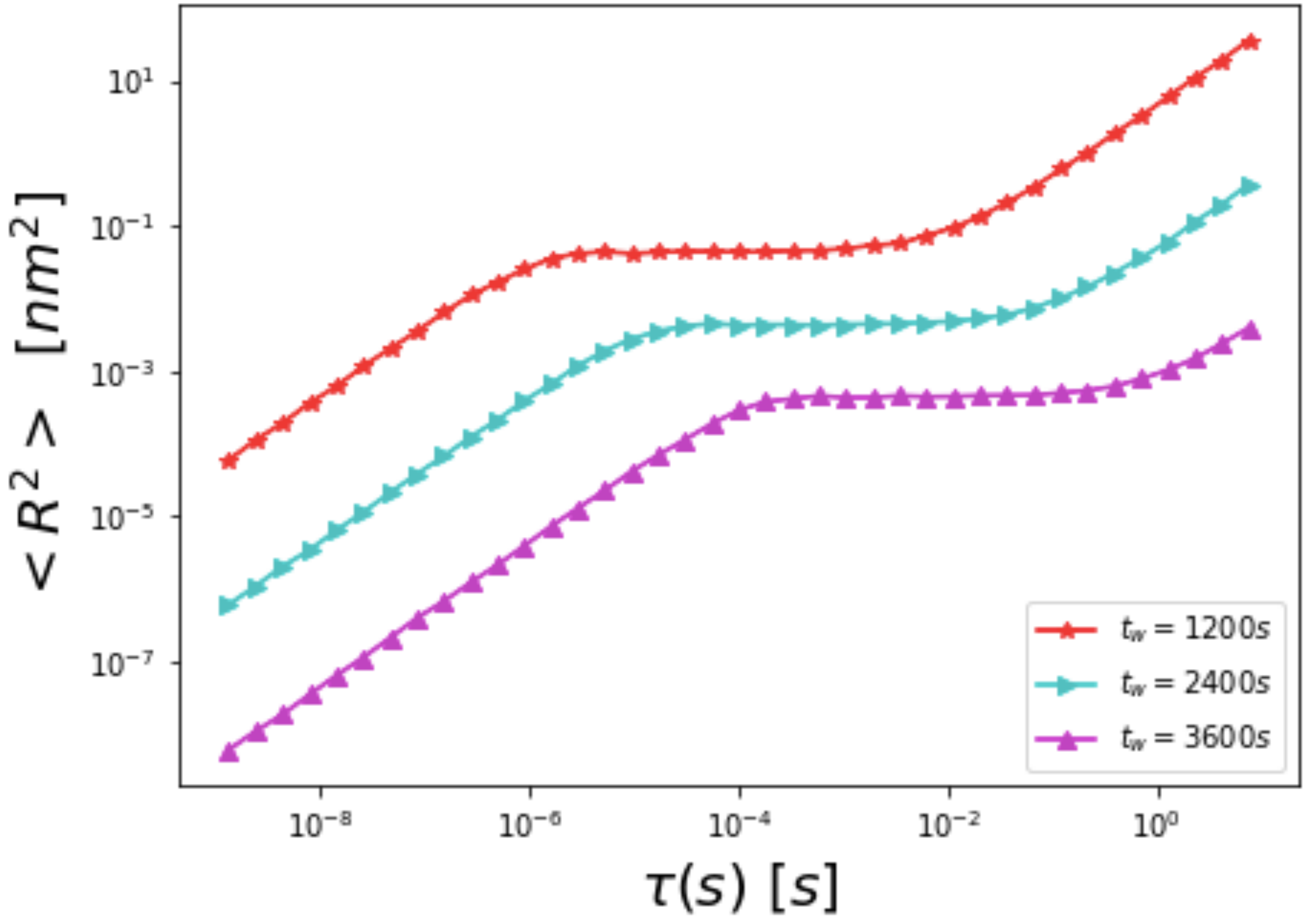


Fig.1 MSD in real time domain for three waiting times

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

τ_0 is not relevant to $\xi - \xi_w$

Applying ETT to Maxwell and Voigt relaxation

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}

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

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-

Result of the Effective time transformation on the system

Real time

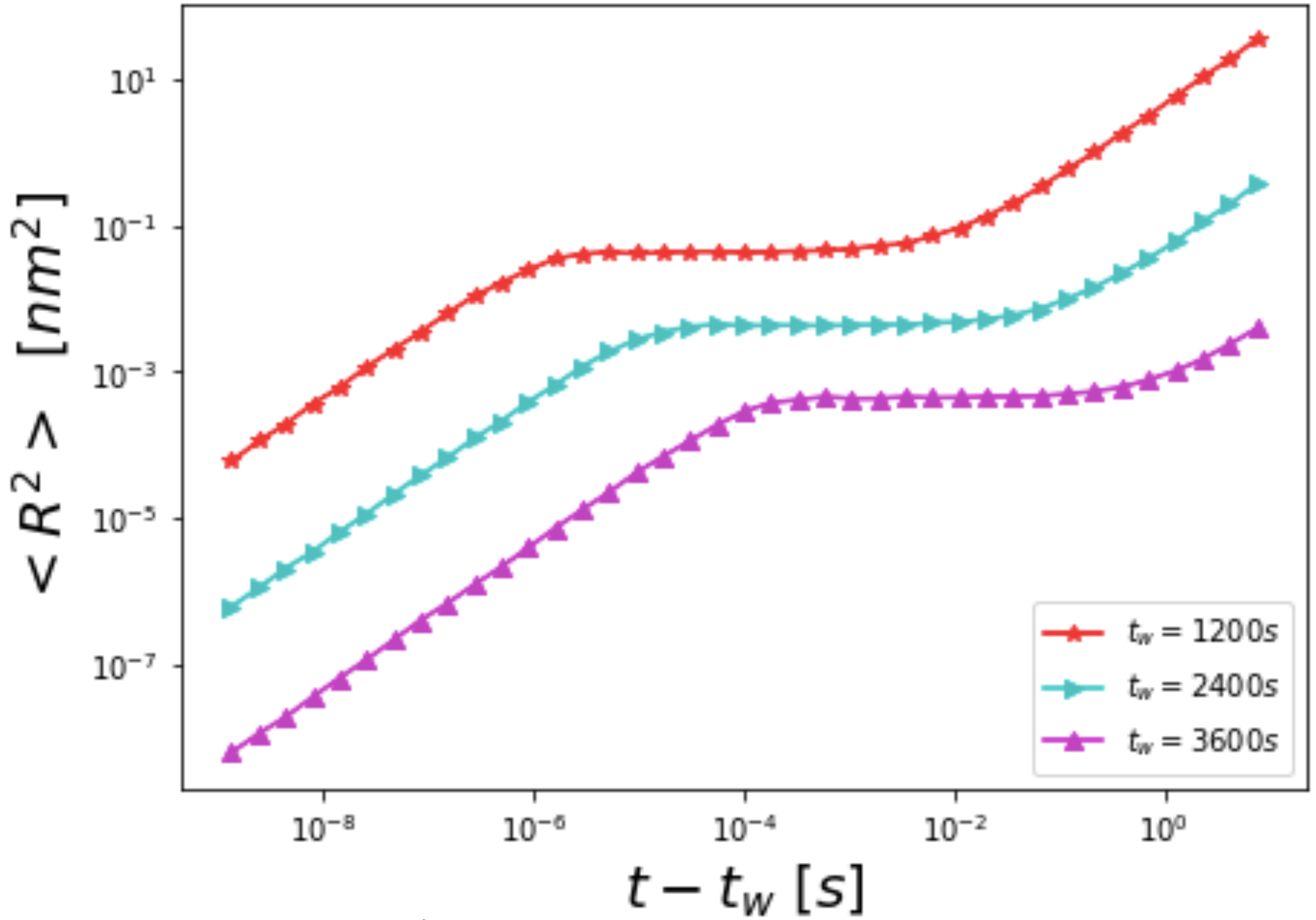


Fig.2

Effective time

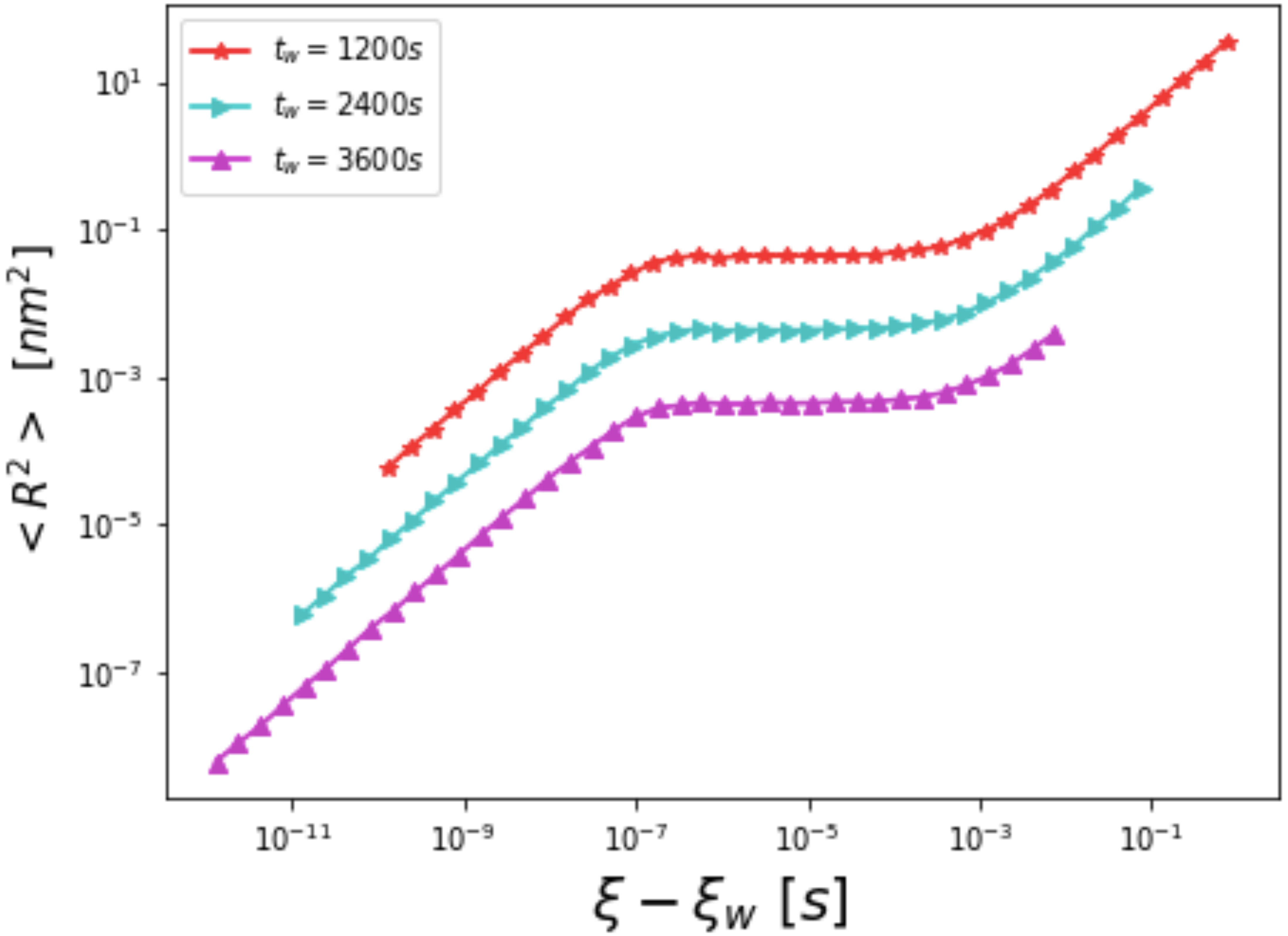


Fig.3

- 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):-

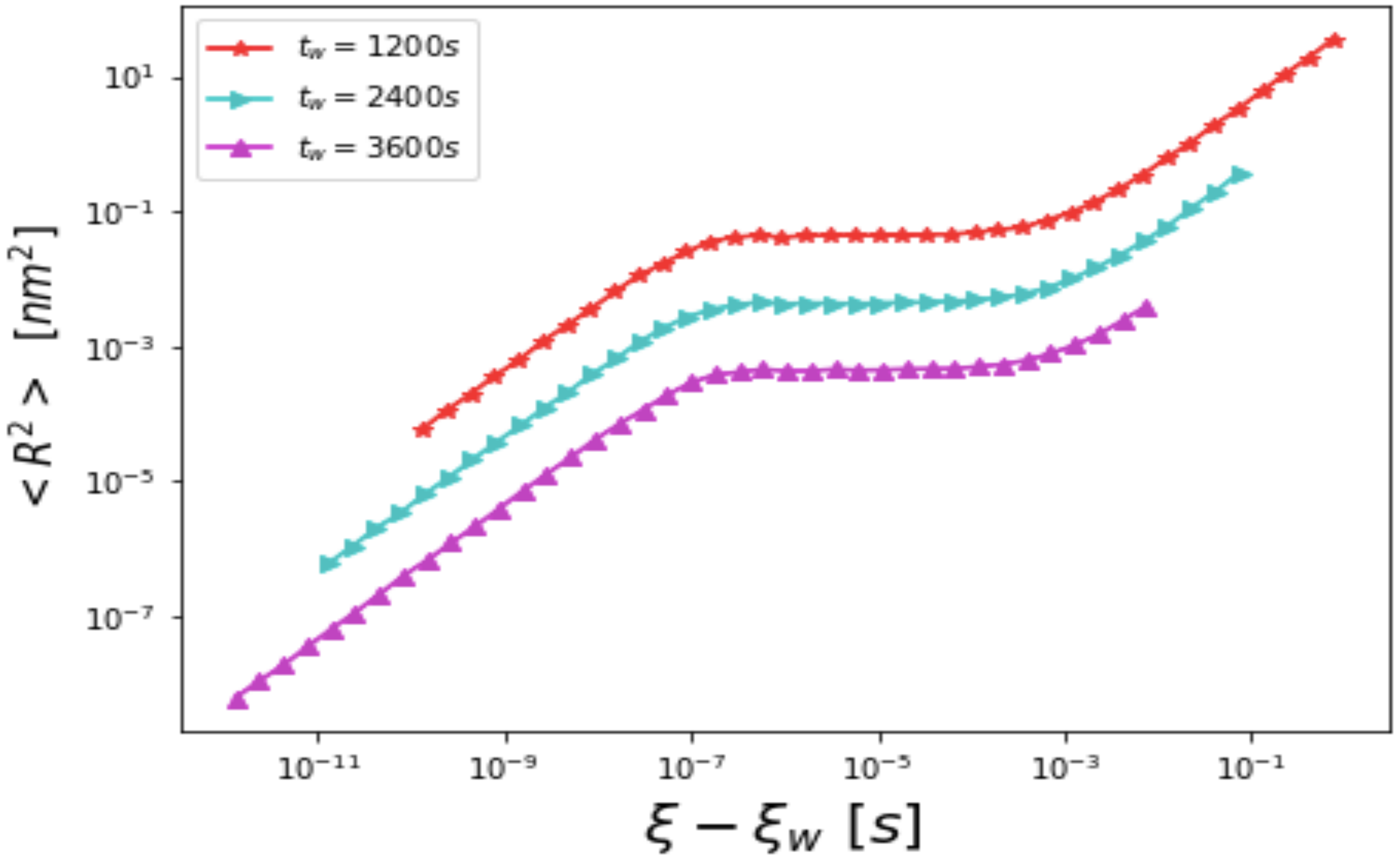


Fig.4

$\times b_{t_w}$

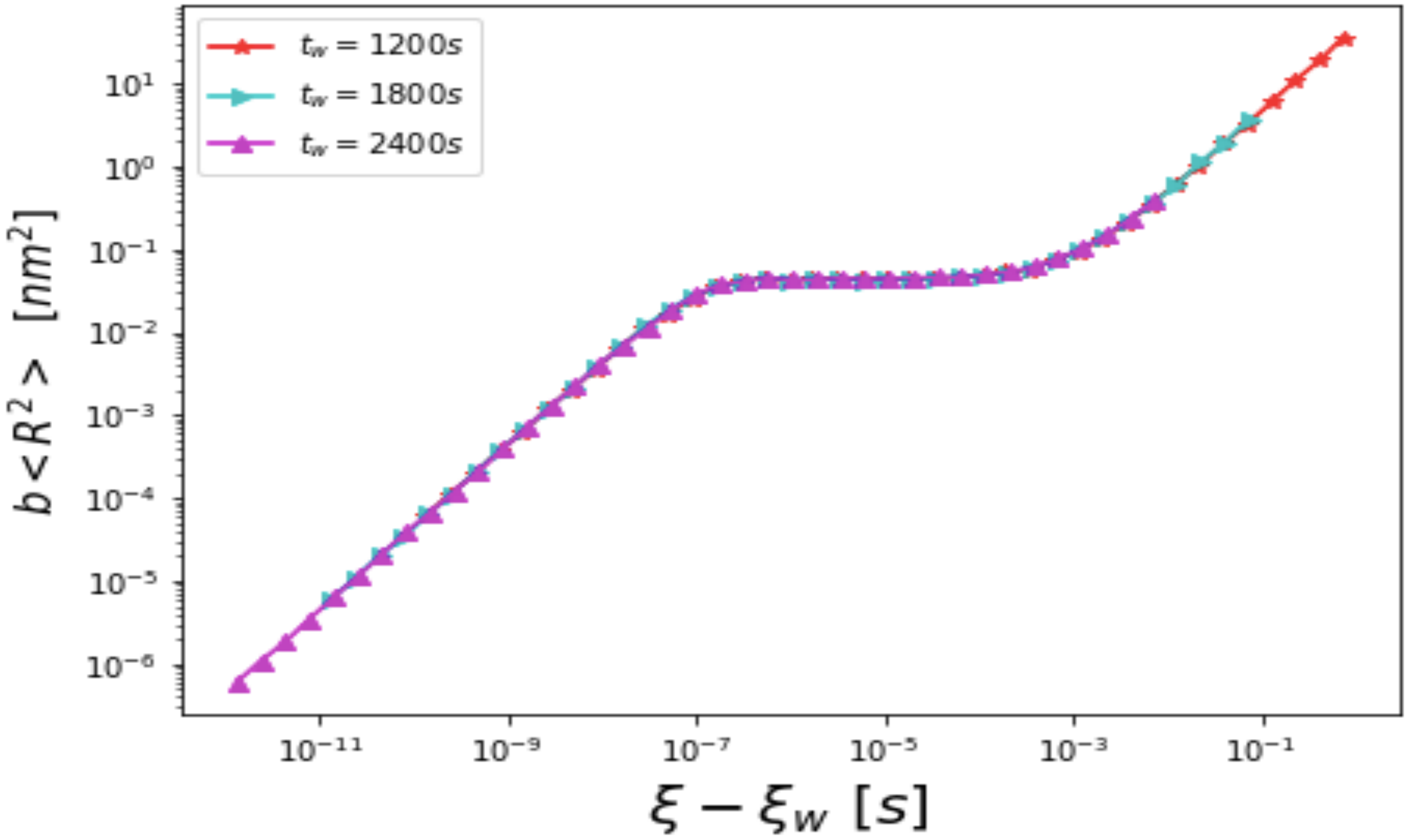


Fig.5: MSD in real Effective Time domain for three waiting times. Reference state is $t_w = 1200s$.

* 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).

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

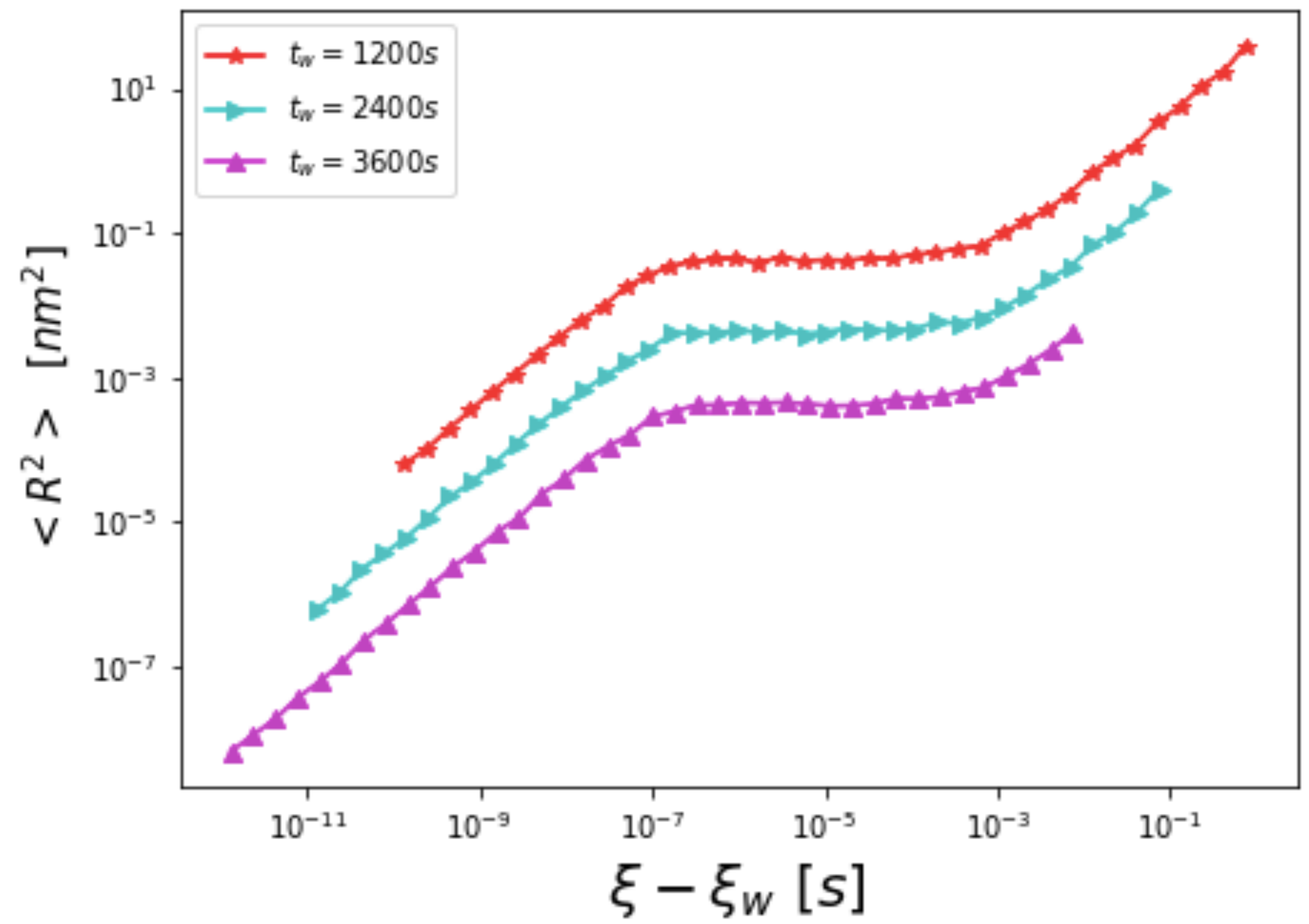
- Steps to get superposition of MSD in Effective Time Domain:

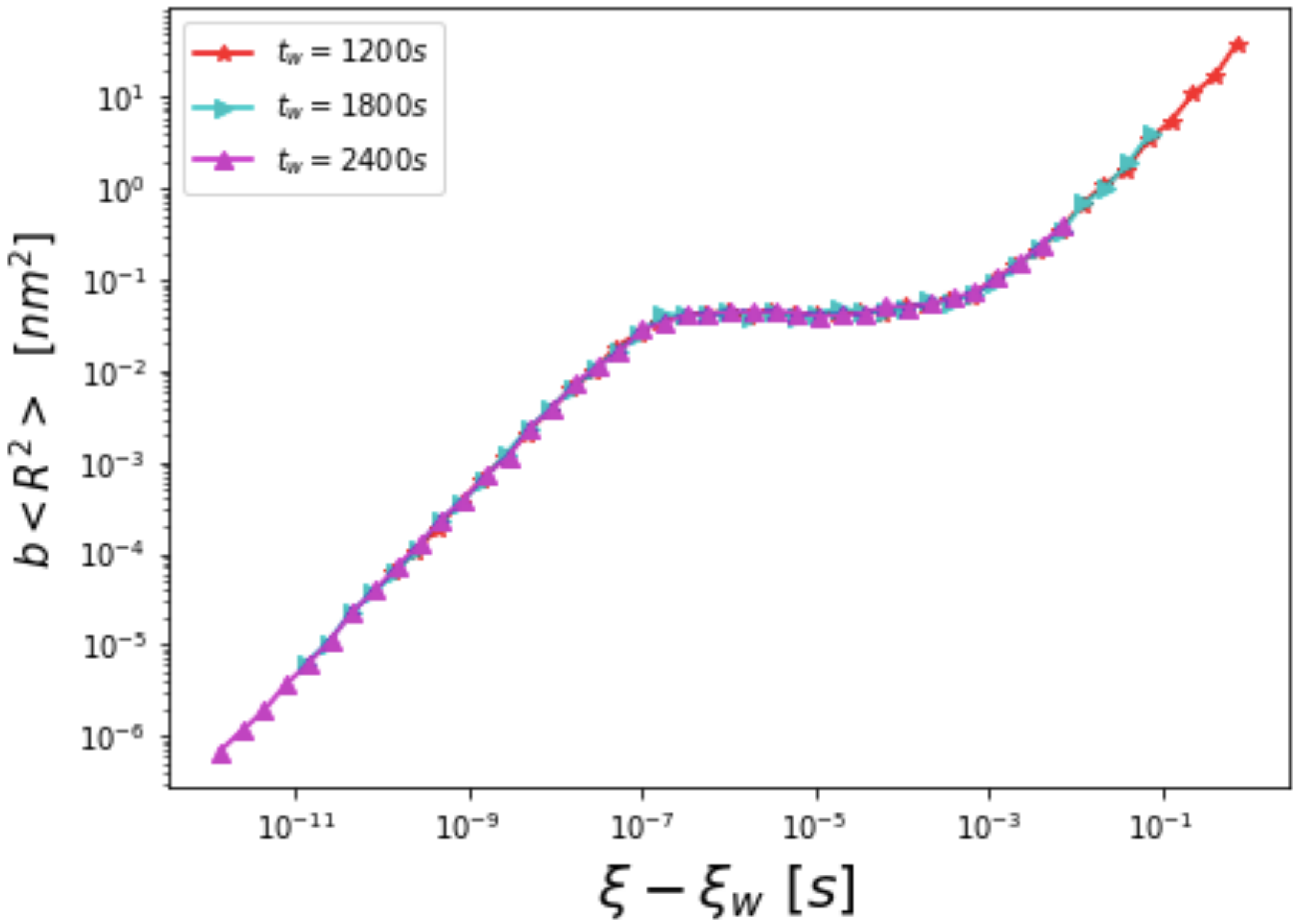
Transform the Real time to Effective time

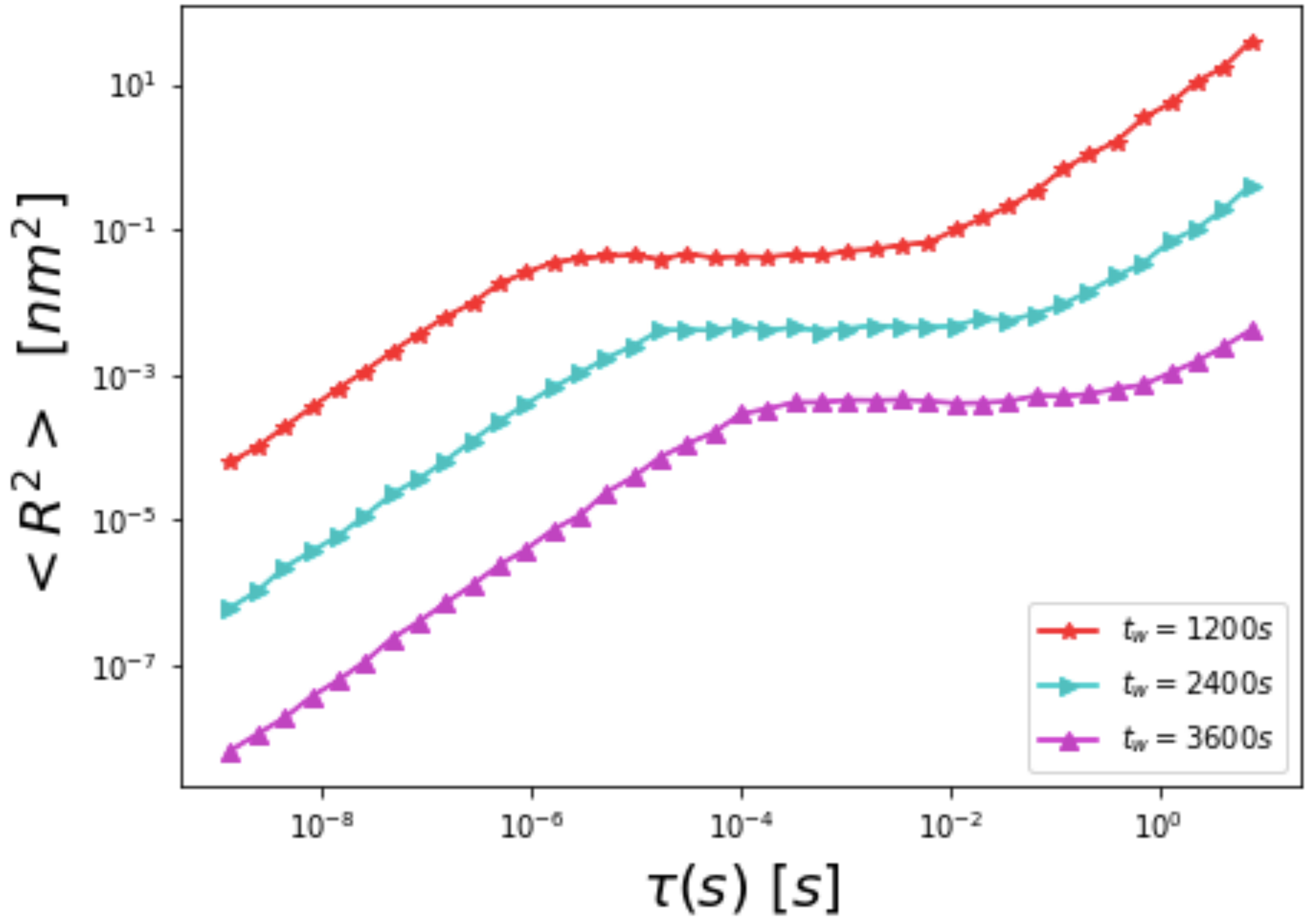
$$[(t - t_w) \rightarrow (\xi - \xi_w)]$$

$$\downarrow$$

Superimposed curve in Effective Time Domain


$t_w = 1200s$
$t_w = 2400s$
$t_w = 3600s$
$< R^2 > \quad [nm^2]$
$\xi - \xi_w \ [s]$


$t_w = 1200s$
$t_w = 1800s$
$t_w = 2400s$
$b < R^2 > \quad [nm^2]$
$\xi - \xi_w \ [s]$



$< R^2 > \quad [nm^2]$
10^{1}
10^{-1}
10^{-3}
10^{-5}
10^{-7}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^{0}
$\tau(s)\ [s]$
$t_w = 1200s$
$t_w = 2400s$
$t_w = 3600s$

Transformation of time data

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

$t - t_w \rightarrow$	τ_1	τ_2	τ_3							τ_{39}	τ_{40}

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

There are corresponding 40 bins for time-lag in *effective time domain*

(placed on time axis, graph-y)

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

- 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 10% only in this case too.
- Same is true fro $t_w = 3600\ s$.

- 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.

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

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

Case-I : AgeingMaxwell-Voigt Model

- In this particular case Kelvin-Voigt material having **time dependent elastic modulus.** while its visas component is temporally constant.
- The elastic modulus (G) of material is increasing with time as per following equation:-

$$G(t) = G_O \cdot exp(\beta \cdot t) \qquad hence,\ \tau(t) = \frac{\eta_0}{G(t)} = \tau_o \cdot exp(-\beta \cdot t)$$

$\beta = 1.9 \times 10^{-3} \quad [1/s]$ [This value is to achieve the goal for slow Ageing.]

- Summarising this particular case:-

Component	Temporal Nature	Functional form
Elastic	Time dependent	$G(t) = G_O \cdot exp(\beta \cdot t)$
Viscous	Constant	η_o

$$\tau(t) = \frac{\eta_o}{G(t)}$$

$$\tau(t) = \tau_o \cdot exp(-\beta \cdot t)$$

- Parameters value of the system : $G_0 = 1000Pa$ and $\eta_0 = 1Pa \cdot s \quad \Rightarrow \tau_0 = 10^{-3}[s]$

Case-I : Ageing Kelvin-Voigt Model (Continue…)

- We have taken three waiting time :
  $t_{w1} = 1200\ sec, t_{w2} = 1800\ sec, t_{w2} = 2400\ sec,$
- Each simulation is for **60 second($t - t_w$)**. For each waiting time, in duration of 60 second, sample has not aged considerable. Or relative change in elasticity is ,

$$\frac{G(t_w + 60) \ - \ G(t_w)}{G(t_w)} \sim 0.09 \quad ; for\ all\ t_w$$

- $t - t_w \ll t_w$.(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.

Case-I : Mean square displacement for different waiting time

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-8}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$, [No. of time step in trajectory ~ 80,000]

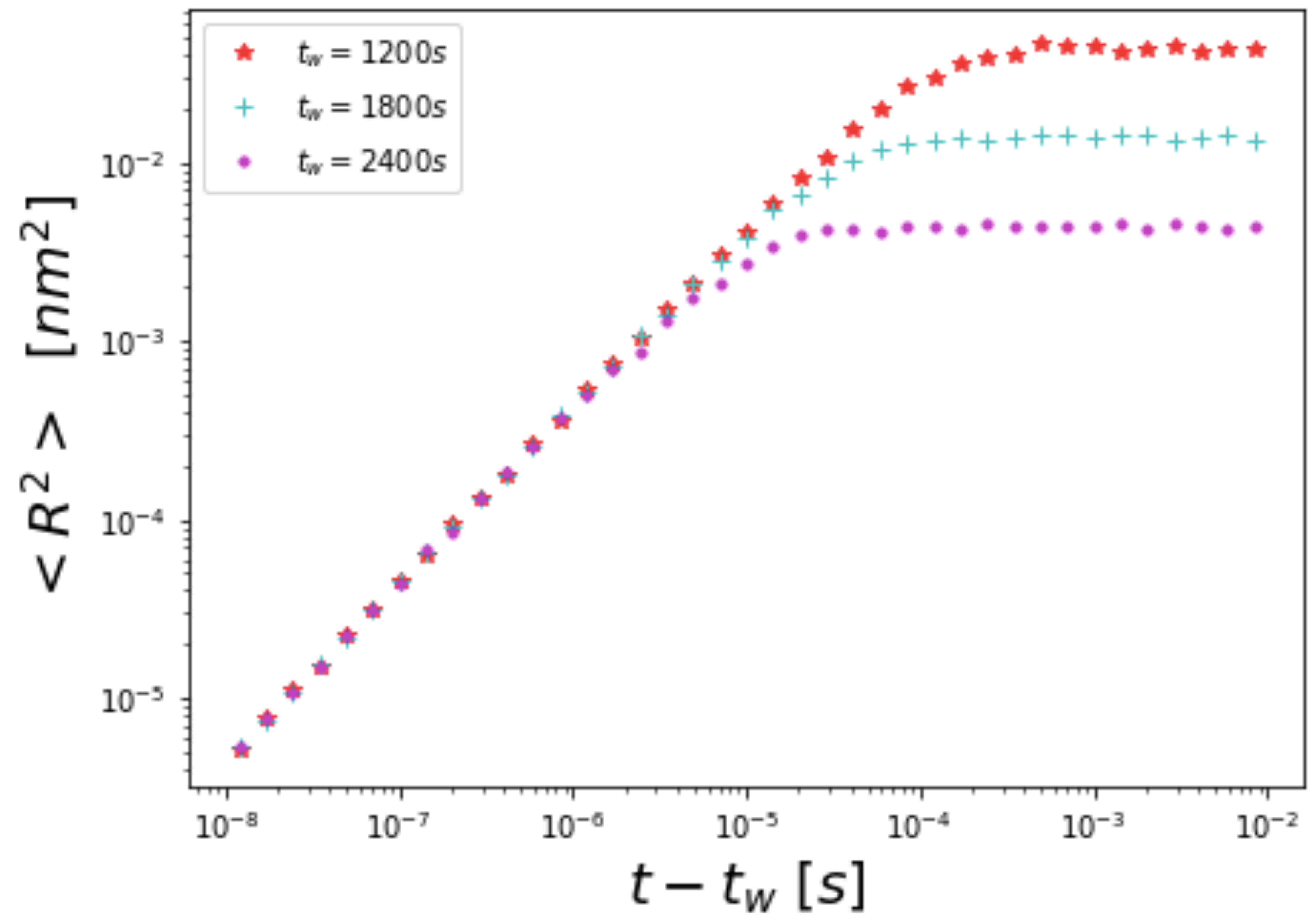


Fig.1 MSD in real time domain for three waiting times

- Here, $t - t_w$ is used with sense of time-lag (τ).
- As material ages, -Plateau value decreases, and

  -Relaxation time decreases
- Plateau value $= r_{t_w}^2 = \dfrac{k_B T}{6\pi a G(t_w)}$ $(\downarrow)$ as, $G(t_w)$ $(\uparrow)$.
- $\tau(t_w) = \dfrac{\eta_0}{G(t_w)}$ hence, $\tau(\downarrow)\ as\ G(t_w)\ (\uparrow)$.

NOTE : This curve can be extended upto time-lag = 60s. I released it very later while self reviewing this PPT. I will rectify it soon.

Case-I : Mean square displacement and sub-trajectories

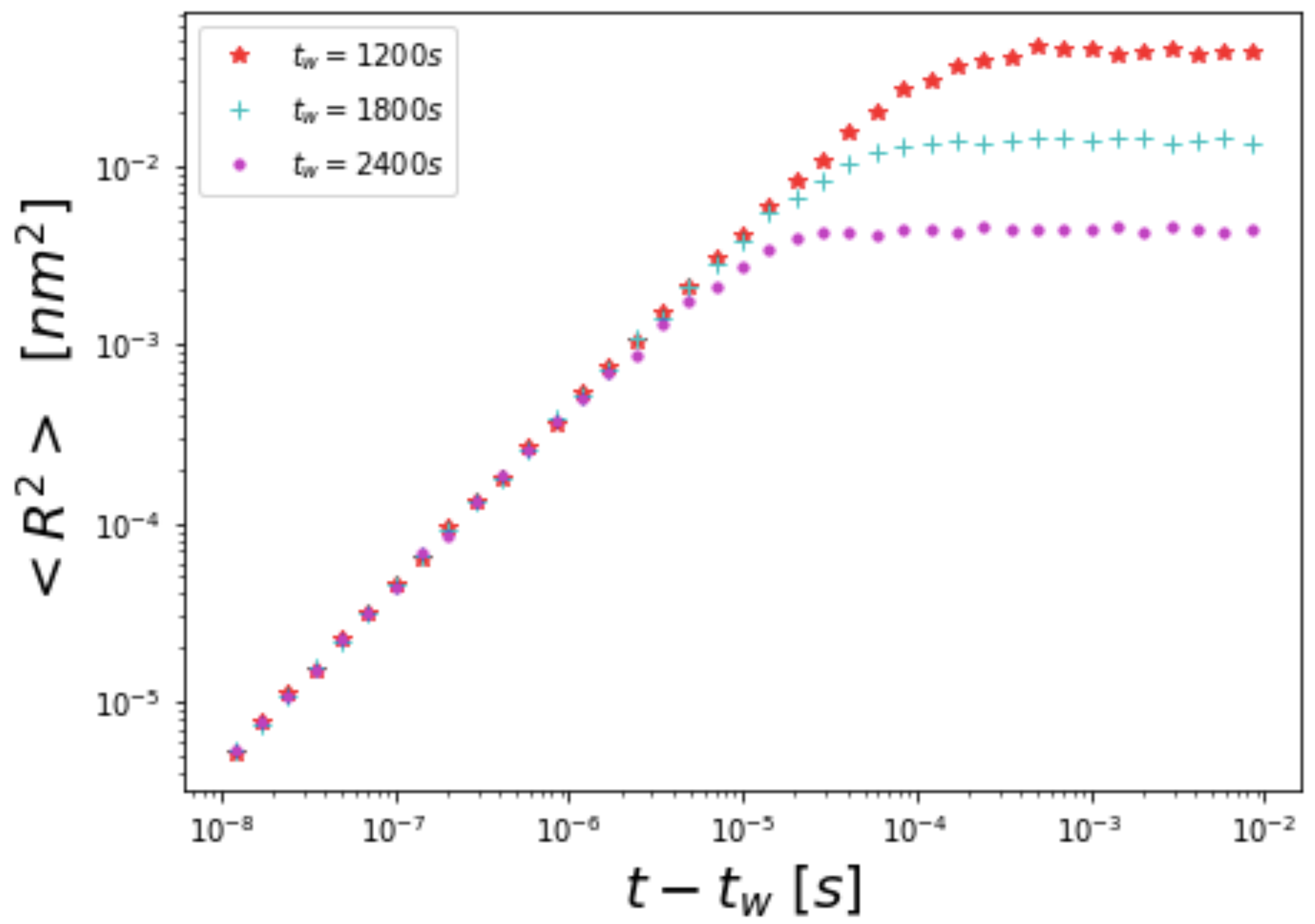
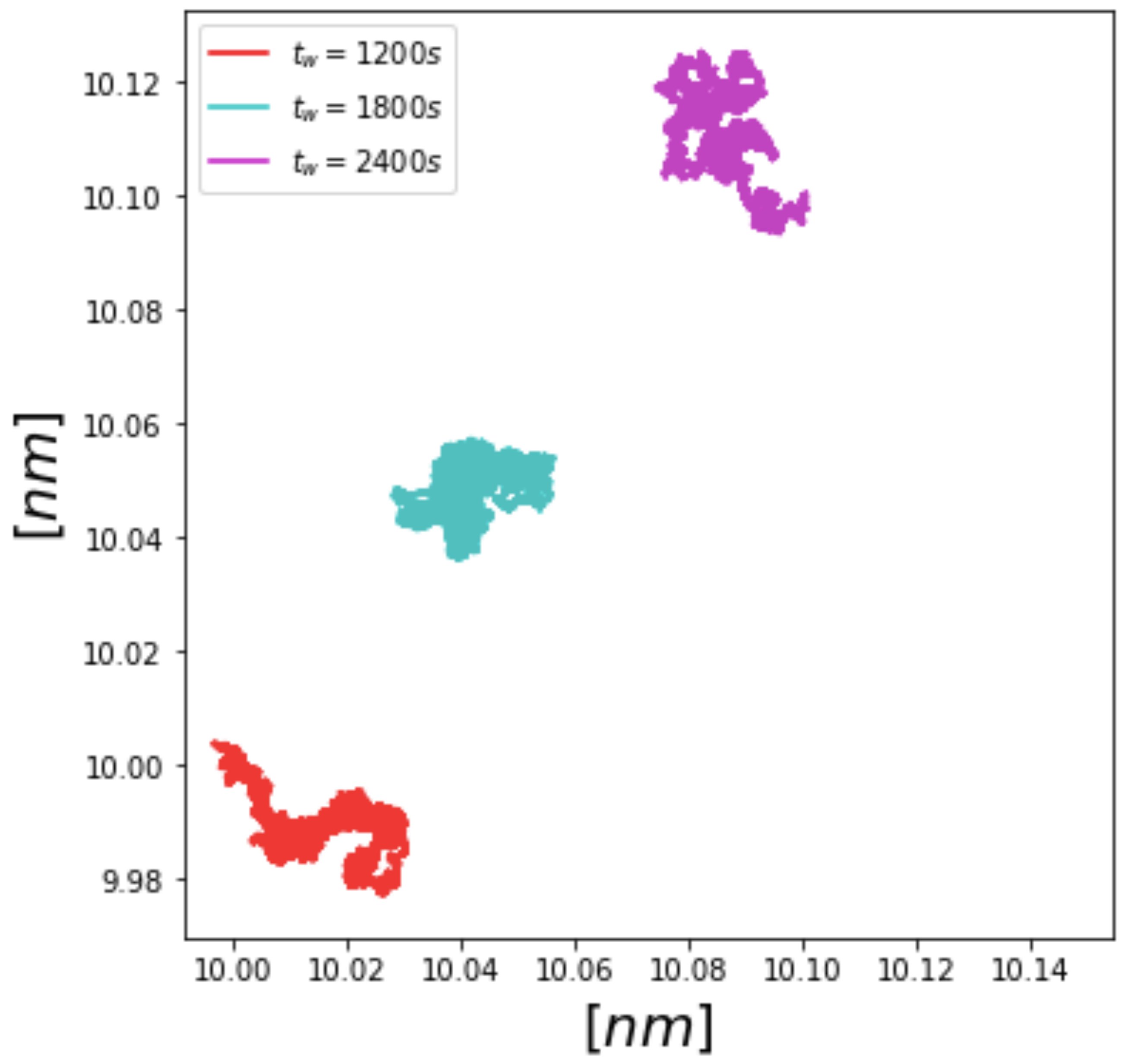
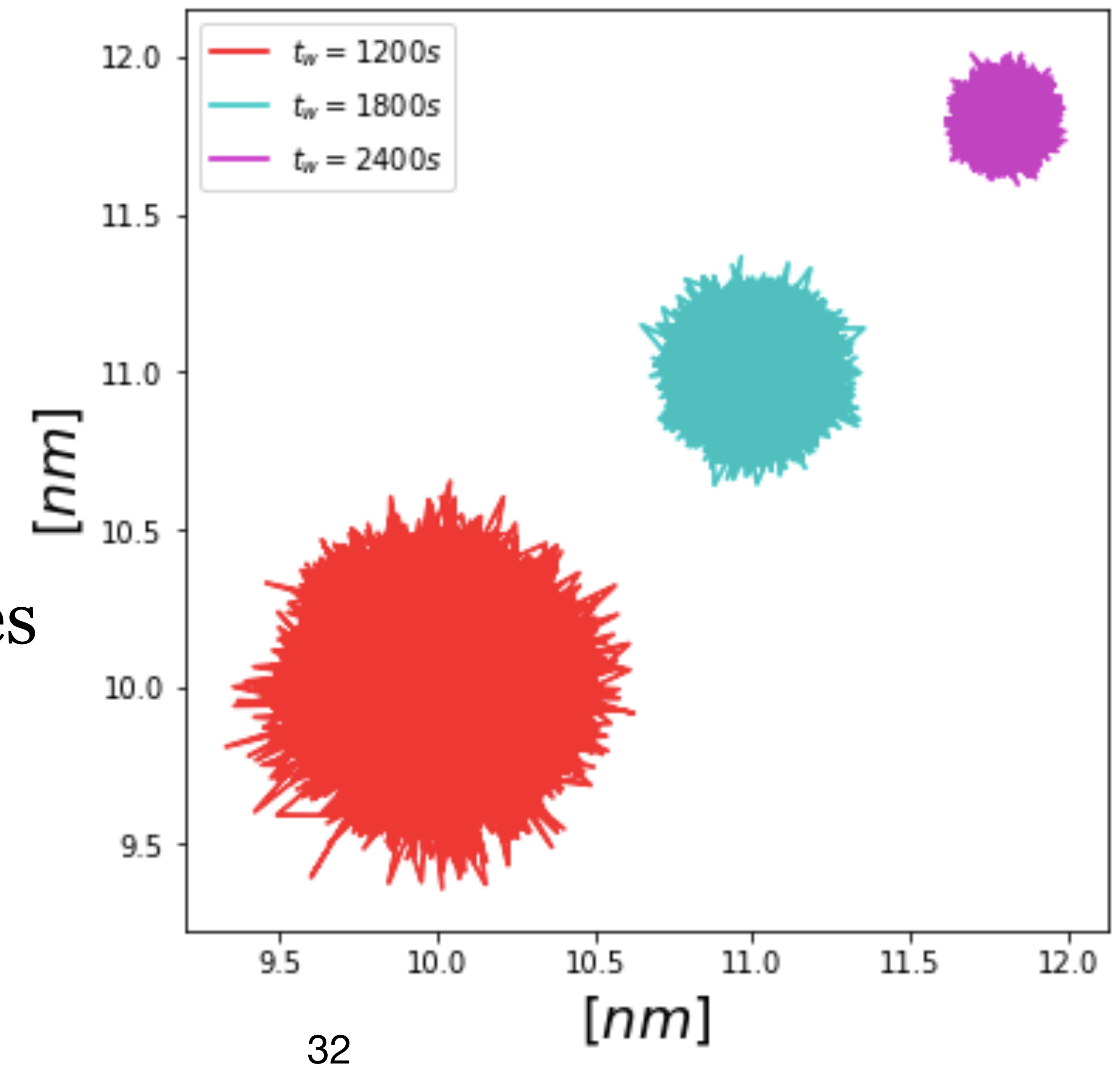


Fig.2: MSD in real time domain for three waiting times



- $t_{max} = 10^{-5}s; No.\ of\ steps = 10^5$
- The extent of spread at each ageing time is same.
- This is due to non ageing in viscous component of the material.



- $t_{max} = 10^{-2}s; No.\ of\ steps = 10^5$
- The confinement space is getting smaller with increase in time.
- This is due to ageing in elastic component of the material.

Case-I : Effective Time Transformation(ETT)

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

- Hence, $\tau(t) = \tau_0 \cdot exp(-\beta \cdot t) \Rightarrow \xi - \xi_w = \frac{exp(\beta \cdot t) - exp(\beta \cdot t_w)}{\beta}$

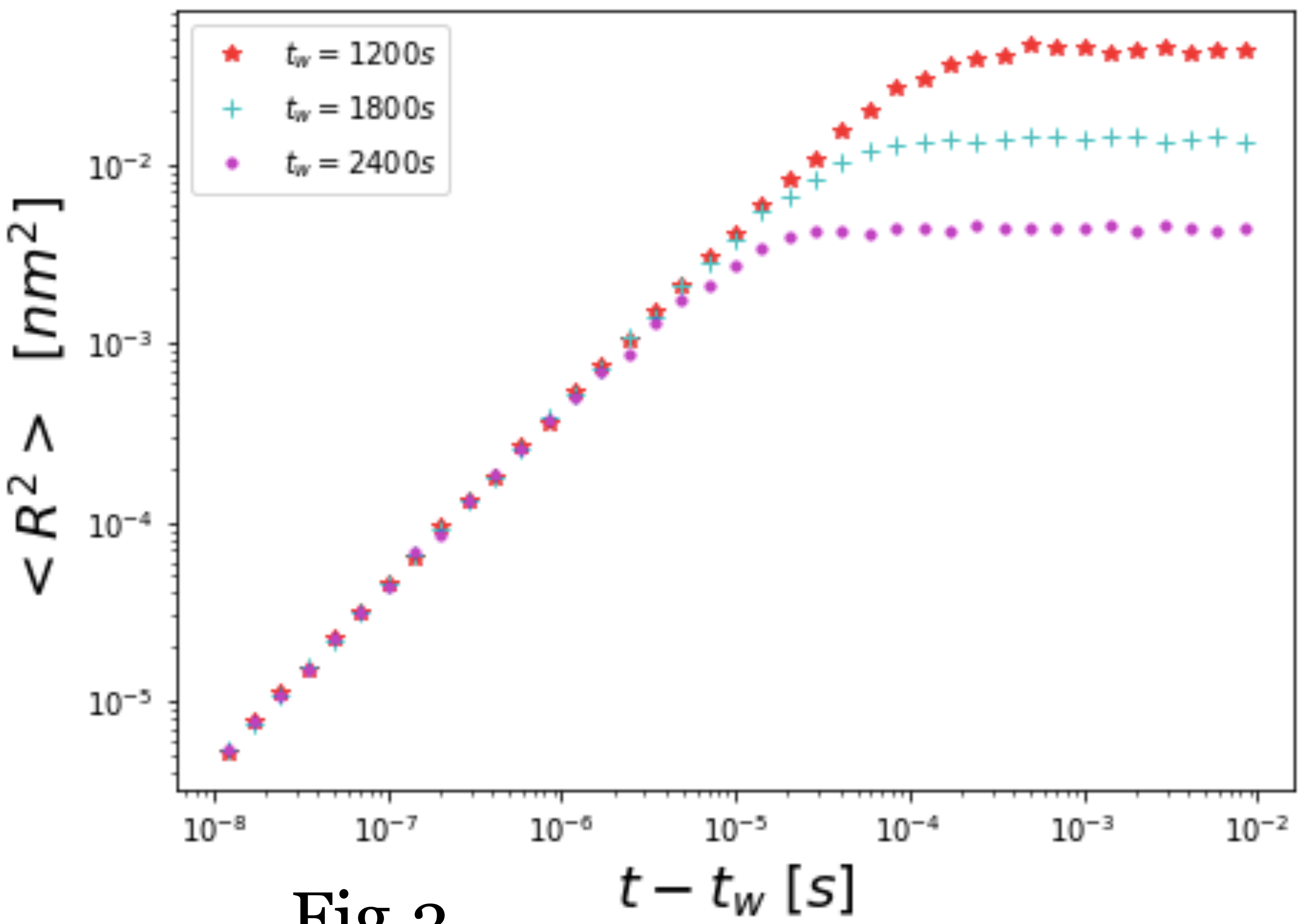


Fig.3

$\rightarrow$

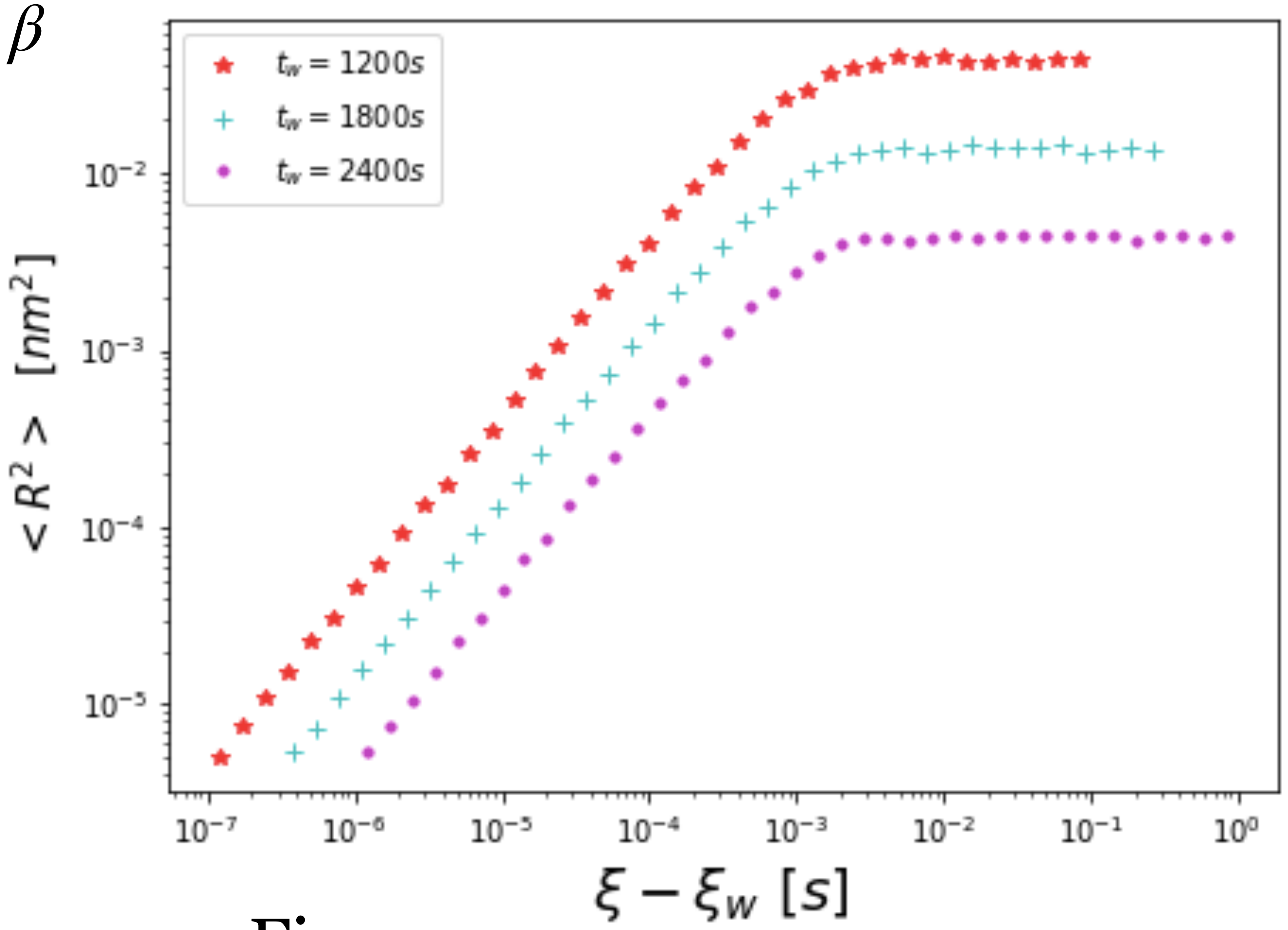


Fig.4

- 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:-

$$b_{t_w=1200s} = \frac{G(t = t_w = 1200s)}{G(t = t_w = 1200s)} = 1\ ,\quad b_{t_w=1800s} = \frac{G(t = t_w = 1800s)}{G(t = t_w = 1200s)} = 3.16\ ,\quad b_{t_w=2400s} = \frac{G(t = t_w = 2400s)}{G(t = t_w = 1200s)} = 10$$

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

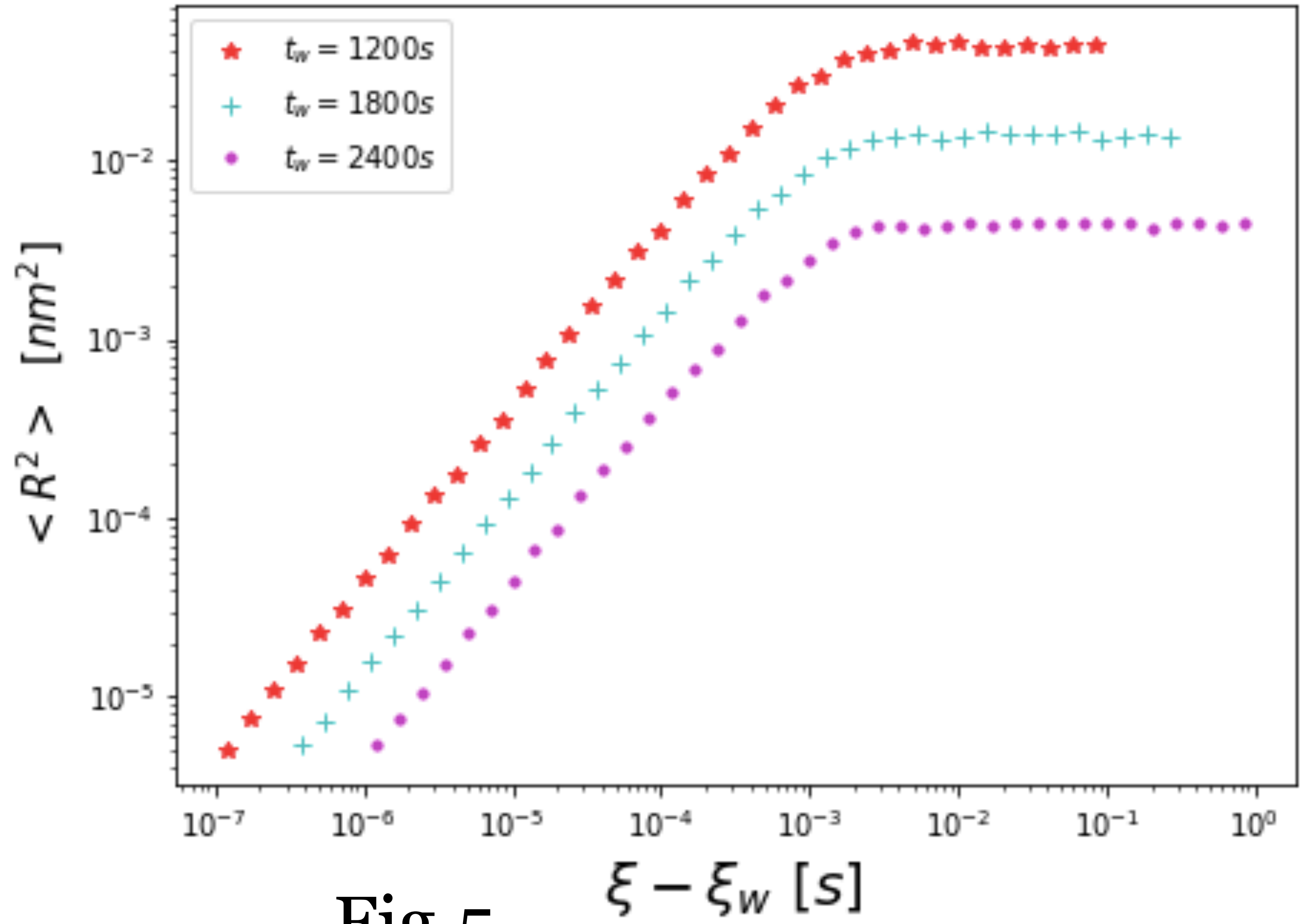


Fig.5

$\times b_{t_w}$

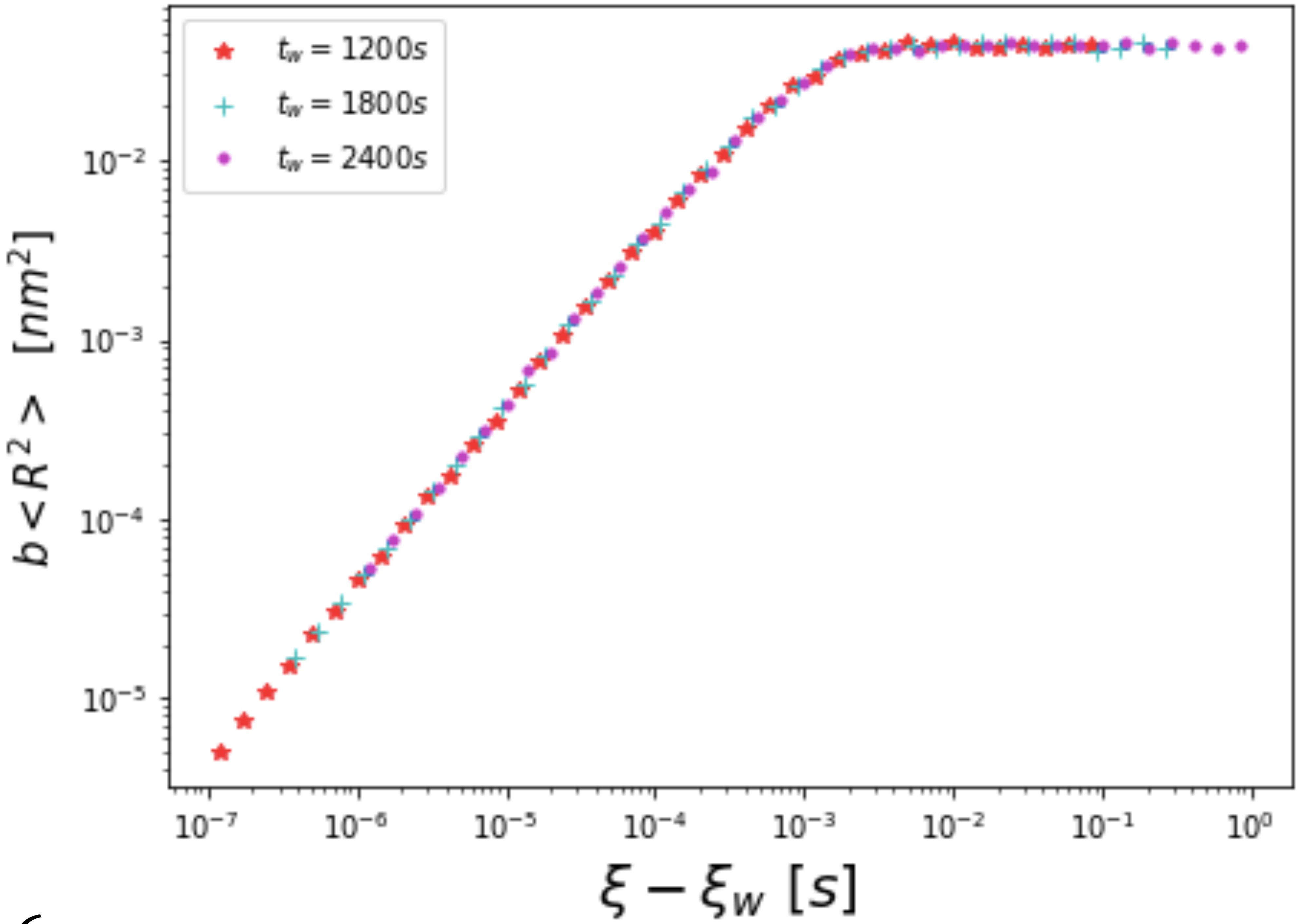


Fig.6:MSD in real Effective Time domain for three waiting times. Reference state is $t_w = 1200s$.

* 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-I

- We are only considering (slow) ageing in Elastic 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 $\beta = 1.9 \times 10^{-3}$ $[1/s]$ is to make sure of slow ageing.
- This is to make sure that system remain temporary stationary while simulation.
- Steps to get superposition of MSD in Effective Time Domain:

Transform the Real time to Effective time

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

↓

Multiply by Vertical shift Factor ('b')

$$[\times b_{t_w}]$$

↓

Superimposed curve in Effective Time Domain

Case-II : Ageing Kelvin-Voigt Model

- In this particular case Kelvin-Voigt material having **time dependent Viscous modulus.** while its elastic component is temporally constant.
- The viscous modulus (η) of material is increasing with time as per following equation:-

$$\eta(t) = \eta_o \cdot exp(\alpha \cdot t) \qquad hence,\ \tau(t) = \frac{\eta(t)}{G_o} = \tau_o \cdot exp(\alpha \cdot t)$$

$$\alpha = 1.9 \times 10^{-3} \quad [1/s]$$

- Summarising this particular case:-

Component	Temporal Nature	Functional form
Elastic	Constant	G_o
Viscous	Time dependent	$\eta(t) = \eta_o \cdot exp(\alpha \cdot t)$

$$\tau(t) = \frac{\eta(t)}{G_o}$$

$$\Rightarrow \tau(t) = \tau_o \cdot exp(\alpha \cdot t)$$

$$\alpha = 1.9 \times 10^{-3} \quad [1/s]$$

- Parameters value of the system : $G_0 = 1000Pa$ and $\eta_0 = 10^{-3}Pa \cdot s \ \Rightarrow \tau_0 = 10^{-6}[s]$

Case-II : Ageing Kelvin-Voigt Model (Continue...)

- We have taken three waiting time :
  $t_{w1} = 1200\ sec, t_{w2} = 1800\ sec, t_{w2} = 2400\ sec,$
- Each simulation is for **60 second**. For each waiting time, in duration of 60 second, sample has not aged considerable. Or,

$$\frac{\eta(t_w + 60) - \eta(t_w)}{\eta(t_w)} \sim 0.09 \quad ; for\ all\ t_w$$

- $t - t_w \ll t_w$ is mentioned here too.
- 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.

Case-II : Mean square displacement

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-8}, 10^{-2}]\ sec\ ; t_{max} = 60sec$ • [No. of time step in trajectory ~ 80,000]

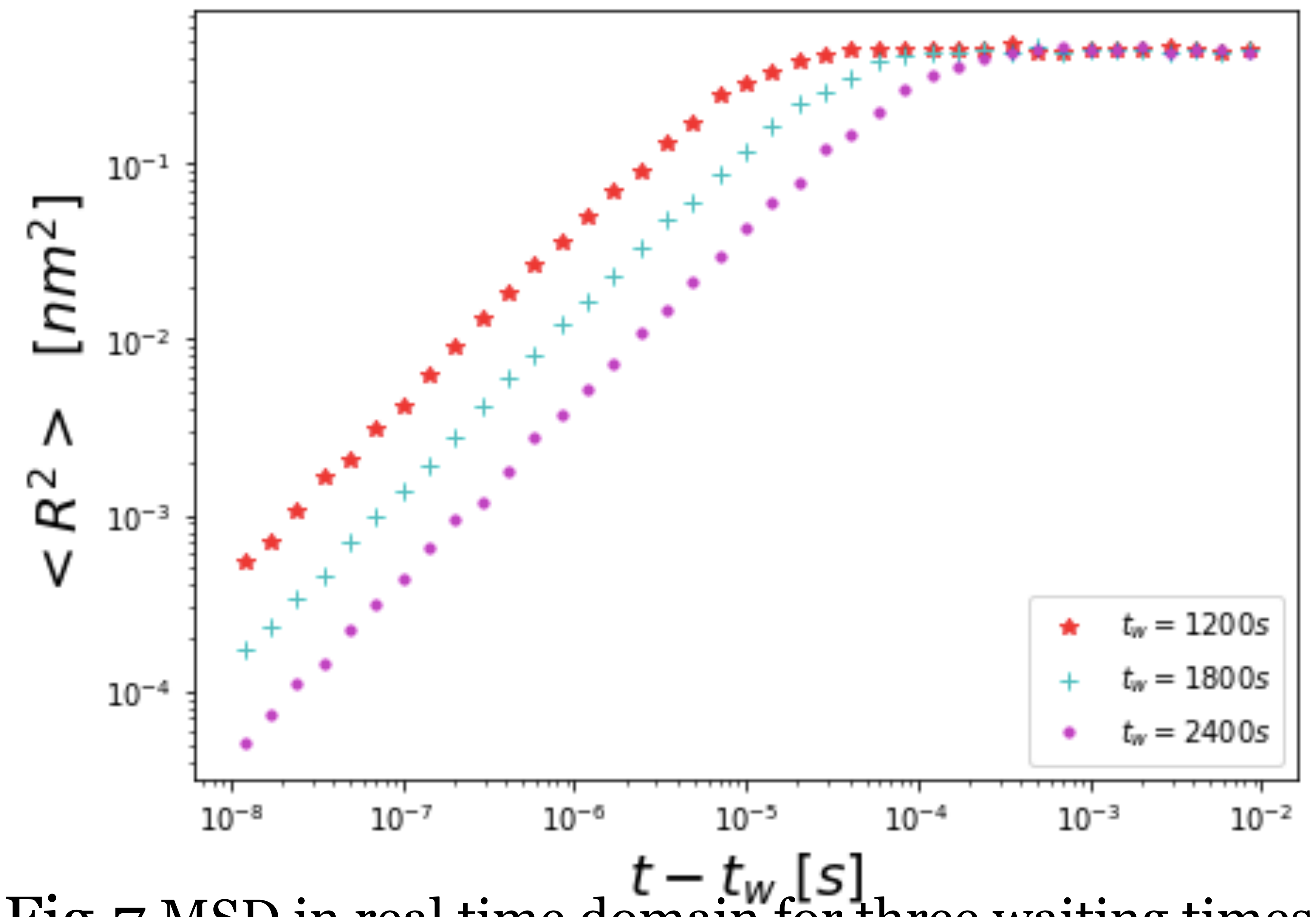


Fig.7 MSD in real time domain for three waiting times

- Here, $t - t_w$ is used in sense of time-lag (τ).
- As material ages, -Plateau value remain same, and
  -Relaxation time increases
- Plateau value = $r_0^2 = \dfrac{k_B T}{6\pi a G_0}$ $(is\ constant)$ as, G_0 $[is\ constant]$.
- $\tau(t) = \dfrac{\eta(t)}{G_0}$, hence, $\tau(\uparrow)\ as\ \eta(t)\ (\uparrow)$.

Case-II : Mean square displacement and sub-trajectories

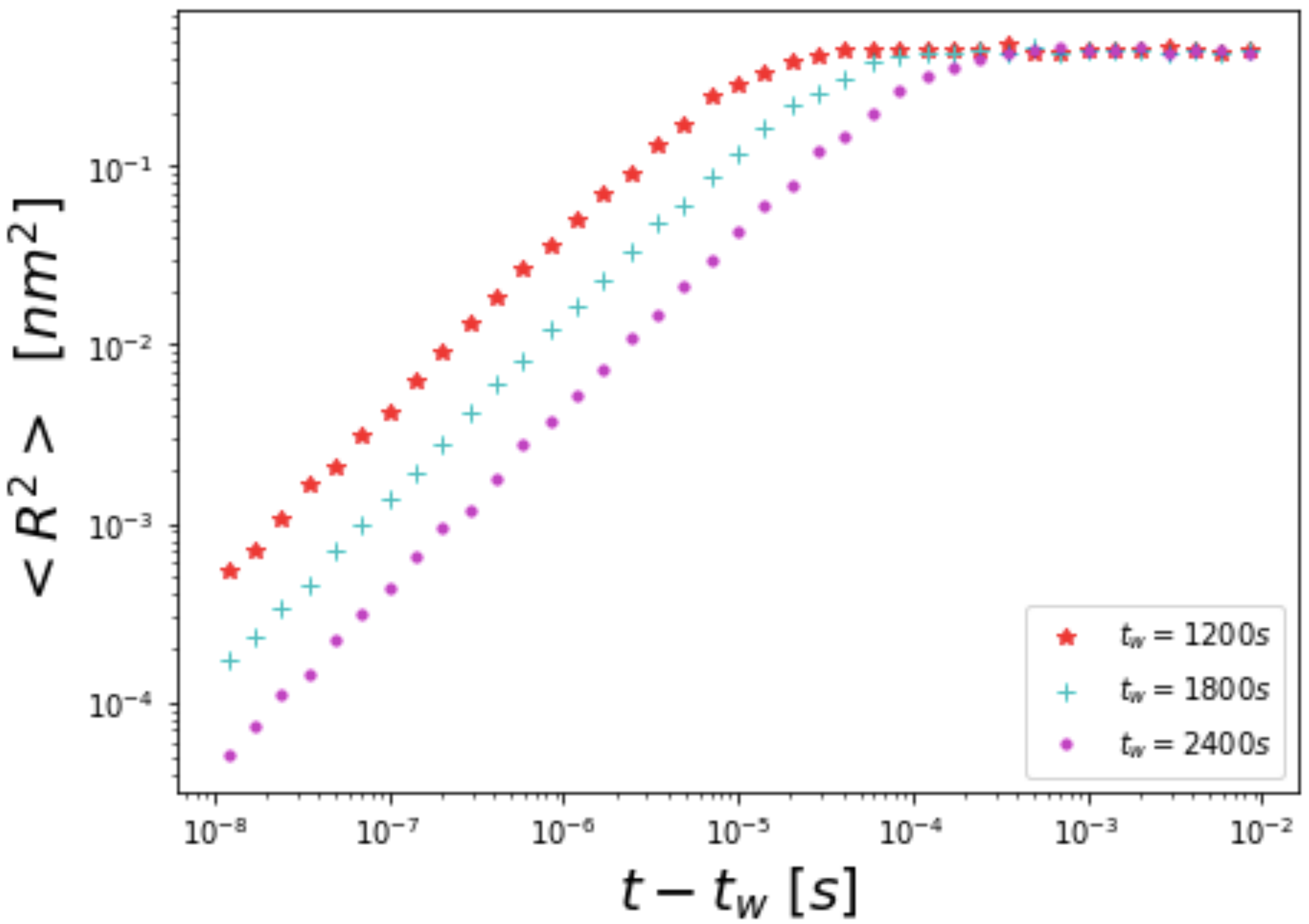
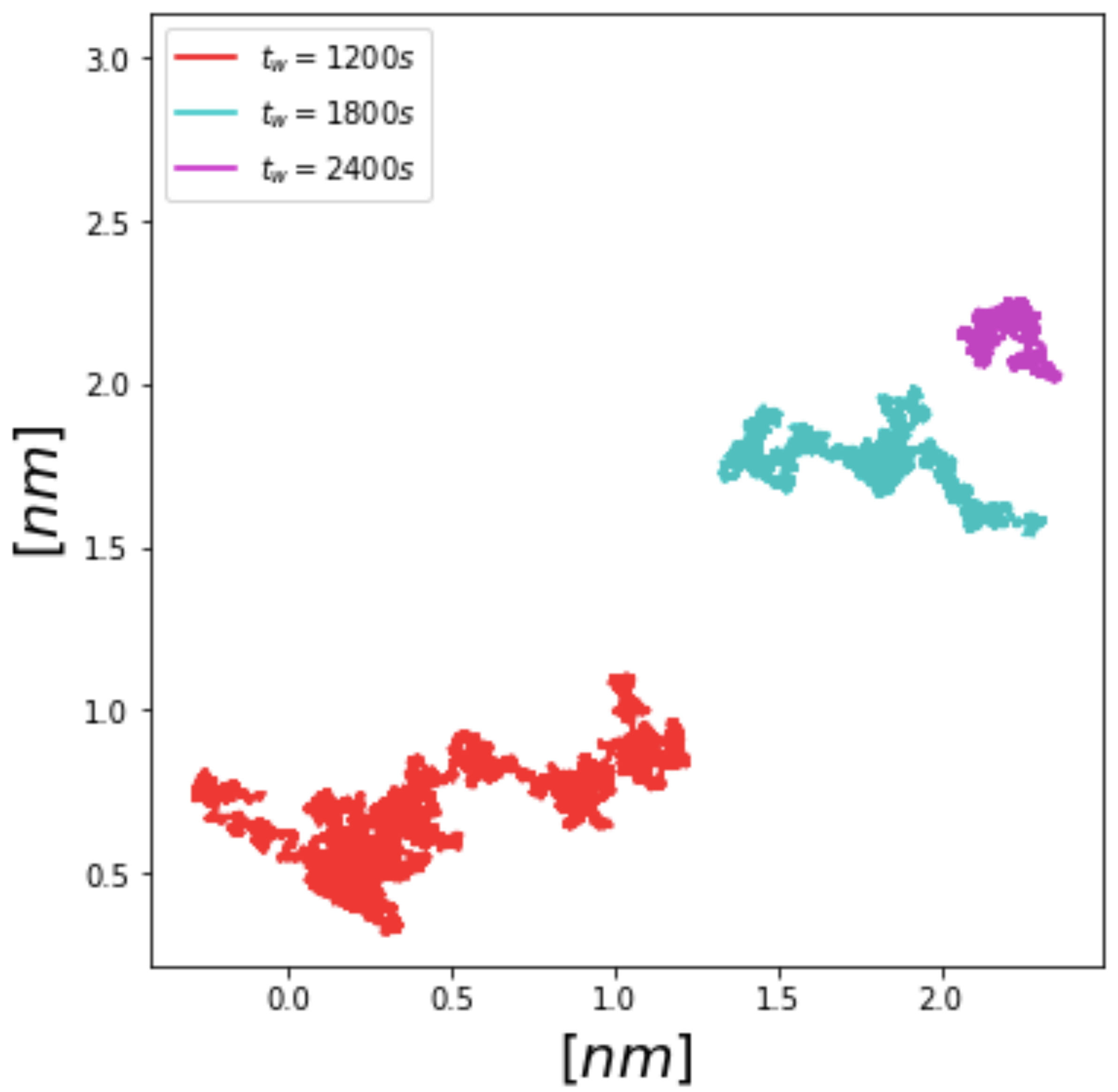
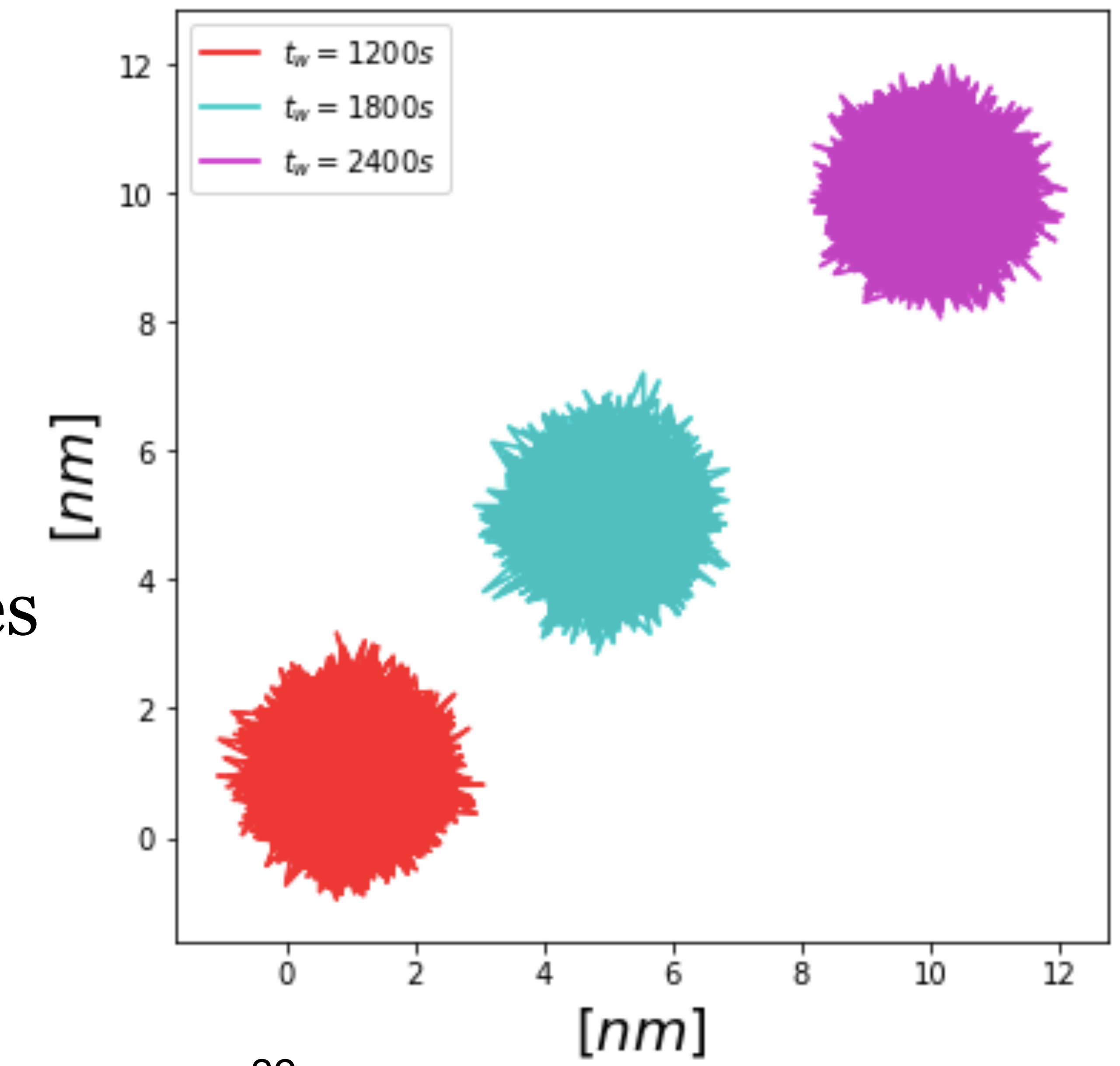


Fig.8: MSD in real time domain for three waiting times



- $t_{max} = 10^{-5}s$; $No.\ of\ steps = 10^5$
- The extent of diffusion is decreasing as time progress.
- This is due to ageing in viscous component of the material.



- $t_{max} = 10^{-2}s$; $No.\ of\ steps = 10^5$
- The confinement space is same with increase in time.
- This is due to non- ageing in elastic component of the material.

Case-II : Effective Time Translation

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

- Hence, $$\tau(t) = \tau_0 \cdot exp(\alpha \cdot t) \Rightarrow \xi - \xi_w = \frac{exp(-\alpha \cdot t_w) - exp(-\alpha \cdot t)}{\alpha}$$

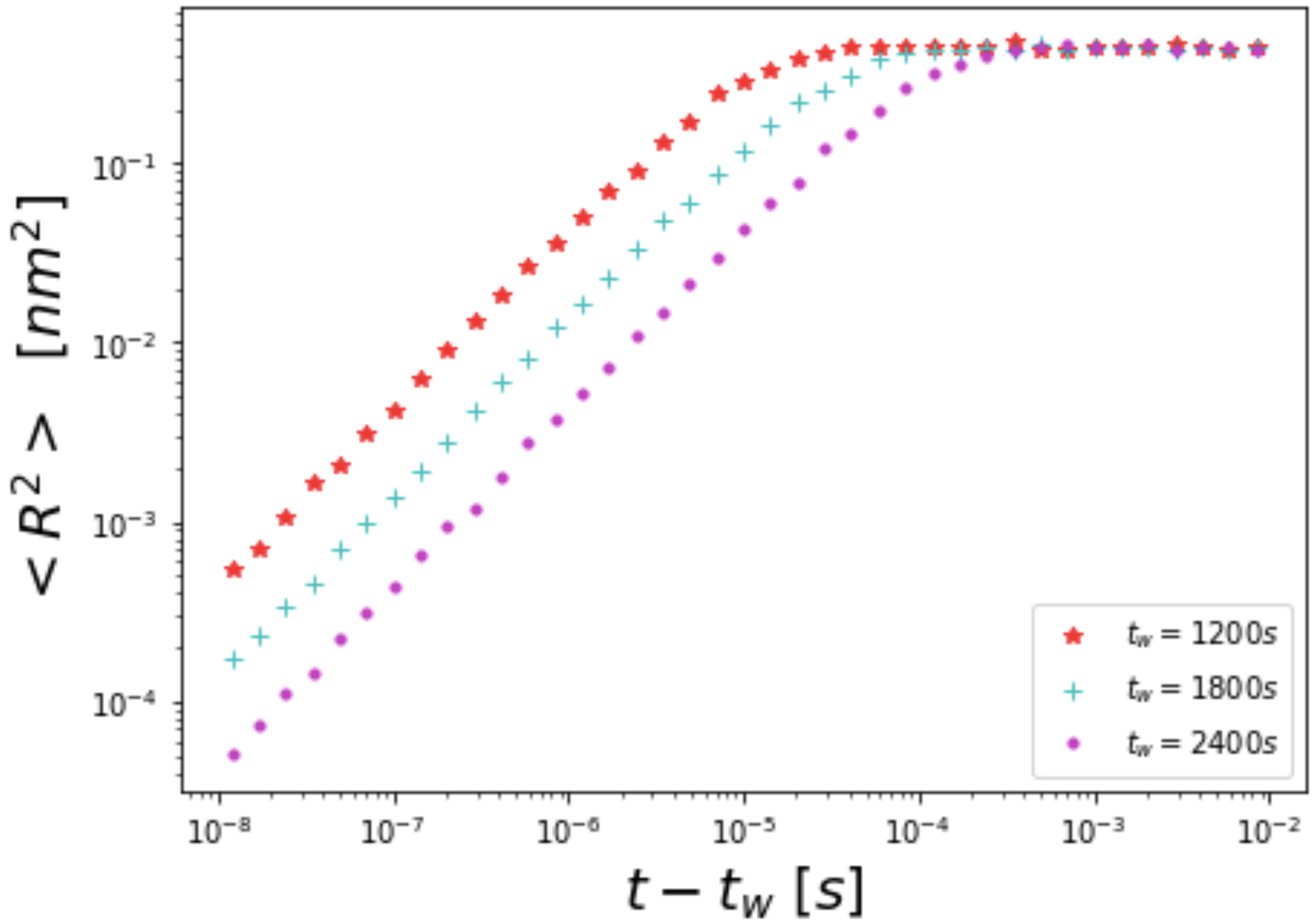


Fig.9:MSD in real time domain for three waiting times

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

$\longrightarrow$

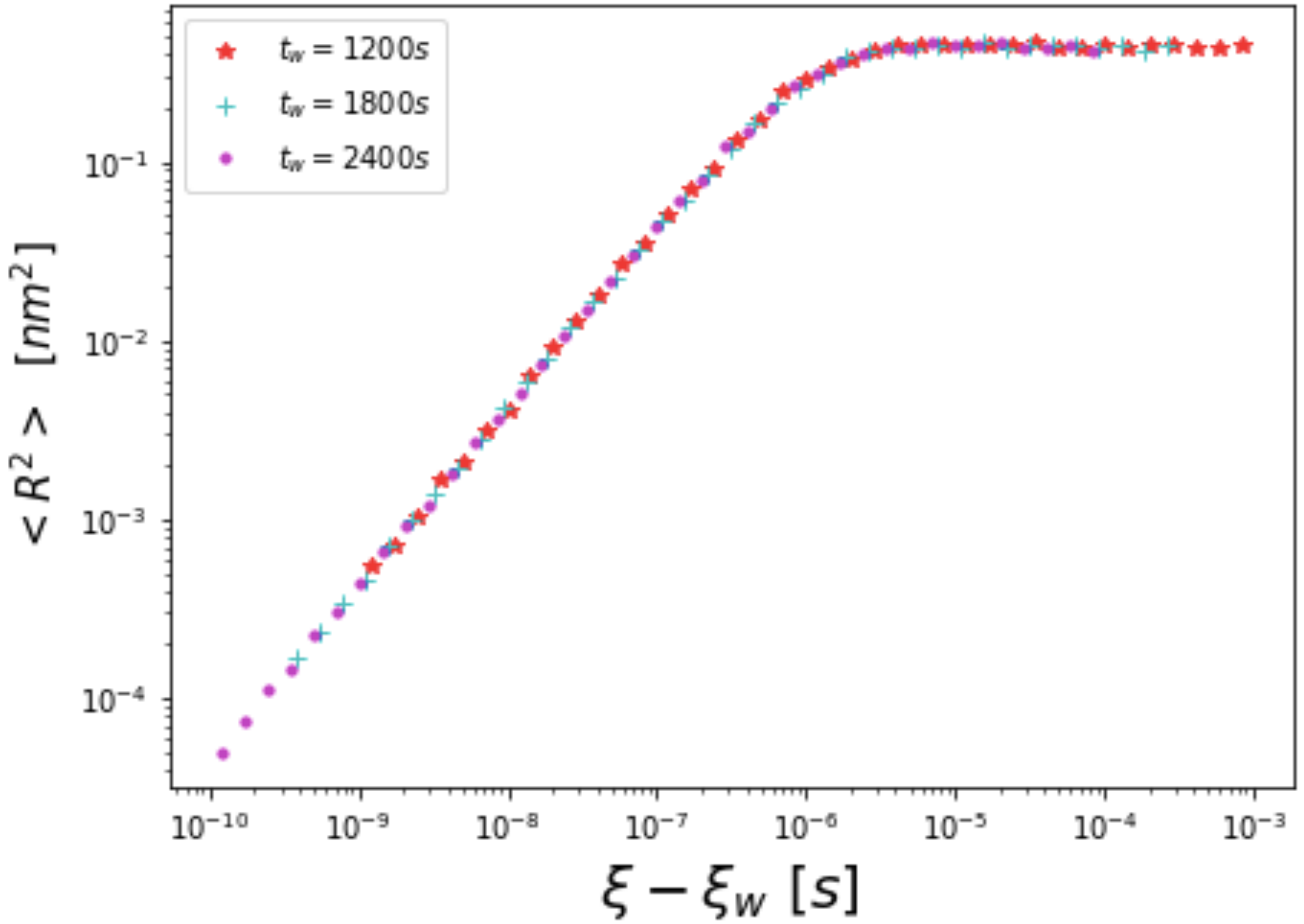


Fig.10: MSD in real Effective Time domain for three waiting times.

Reference state is $t_w = 1200s$.

- In this case time transformation is enough to get superposition without any need to multiply by vertical shift factor ['b']. This is because in this case elastic component is non ageing hence, $b_{t_w=1200s} = b_{t_w=1800s} = b_{t_w=2400s} = 1$(discussed in next slide).

⭐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

Case-III : Ageing Kelvin-Voigt Model

- In this particular case Kelvin-Voigt material having **time dependent Viscous as well as elastic modulus.** It is most general case for ageing in Kelvin Voigt Material.
- The viscous modulus (η) of material is increasing with time as per following equation: -
- The elastic modulus (η) of material is increasing with time as per following equation: -

$$\eta(t) = \eta_o \cdot exp(\alpha \cdot t) \quad ; \; and \quad G(t) = G_O \cdot exp(\beta \cdot t)$$

$$hence, \; \tau(t) = \frac{\eta(t)}{G(t)} = \tau_o \cdot exp((\alpha - \beta) \cdot t)$$

$$\alpha = 3.8 \times 10^{-3} \;\; [1/s] \qquad and \;\; \beta = 1.9 \times 10^{-3} \;\; [1/s]$$

- Summarising this particular case:-

Component	Temporal natare	Functional form
Elastic	Time Dependent	$\eta(t) = \eta_o \cdot exp(\alpha \cdot t)$
Viscous	Time Dependent	$G(t) = G_O \cdot exp(\beta \cdot t)$

- Parameters value of the system : $G_0 = 1000 Pa$ and $\eta_0 = 10^{-4} Pa \cdot s \;\; \Rightarrow \tau_0 = 10^{-7} [s]$

Case-III : Ageing Kelvin-Voigt Model (Continue…)

- We have taken three waiting time :

  $t_{w1} = 1200\ sec, t_{w2} = 1800\ sec, t_{w2} = 2400\ sec,$
- Each simulation is for **60 second**. For each waiting time, in duration of 60 second, sample has not aged considerable. Or,

$$\frac{\eta(t_w + 60)\ -\ \eta(t_w)}{\eta(t_w)} \sim 0.18 \quad ; for\ all\ t_w$$

$$\frac{G(t_w + 60)\ -\ G(t_w)}{G(t_w)} \sim 0.09 \quad ; for\ all\ t_w$$

- $t - t_w \ll t_w$ is mentioned here too.
- 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.

Case-III : Mean square displacement

- Simulation by Uniformly Distributed Logarithmic time (UDLT) method
- $\Delta t \in [10^{-8}, 10^{-2}]\ sec$; $t_{max} = 60 sec$ • [No. of time step in trajectory ~ 80,000]

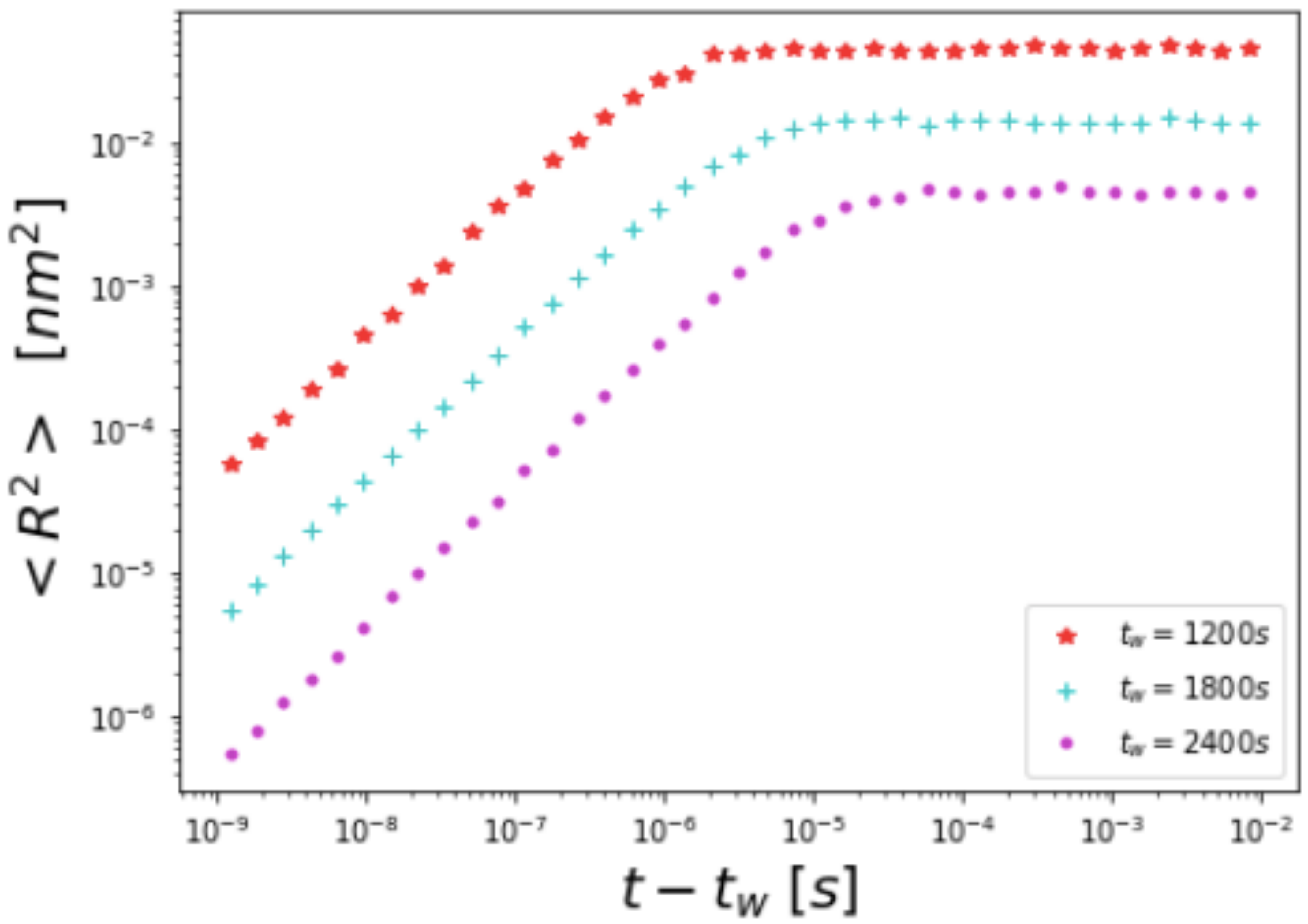


Fig.11: MSD in real time domain for three waiting times

- Here, $t - t_w$ is used in sense of time-lag (τ).
- As material ages, -Plateau value decreases
  -Relaxation time increases
- Plateau value $= r_{t_w}^2 = \dfrac{k_B T}{6\pi a G(t_w)}$ (↓) as, $G(t)$ (↑).
- $\tau(t) \propto \dfrac{\eta(t)}{G(t)}$ hence, $\tau(\uparrow)\ as\ \eta(t)\ (\uparrow)$.
- Rate of increase of Viscous component is twice the rate of increase of Elastic Component ($\alpha = 2\beta$).

$$\eta(t) = \eta_o \cdot exp(\alpha \cdot t)$$
$$G(t) = G_O \cdot exp(\beta \cdot t)$$

Case-III : Mean square displacement and sub-trajectory

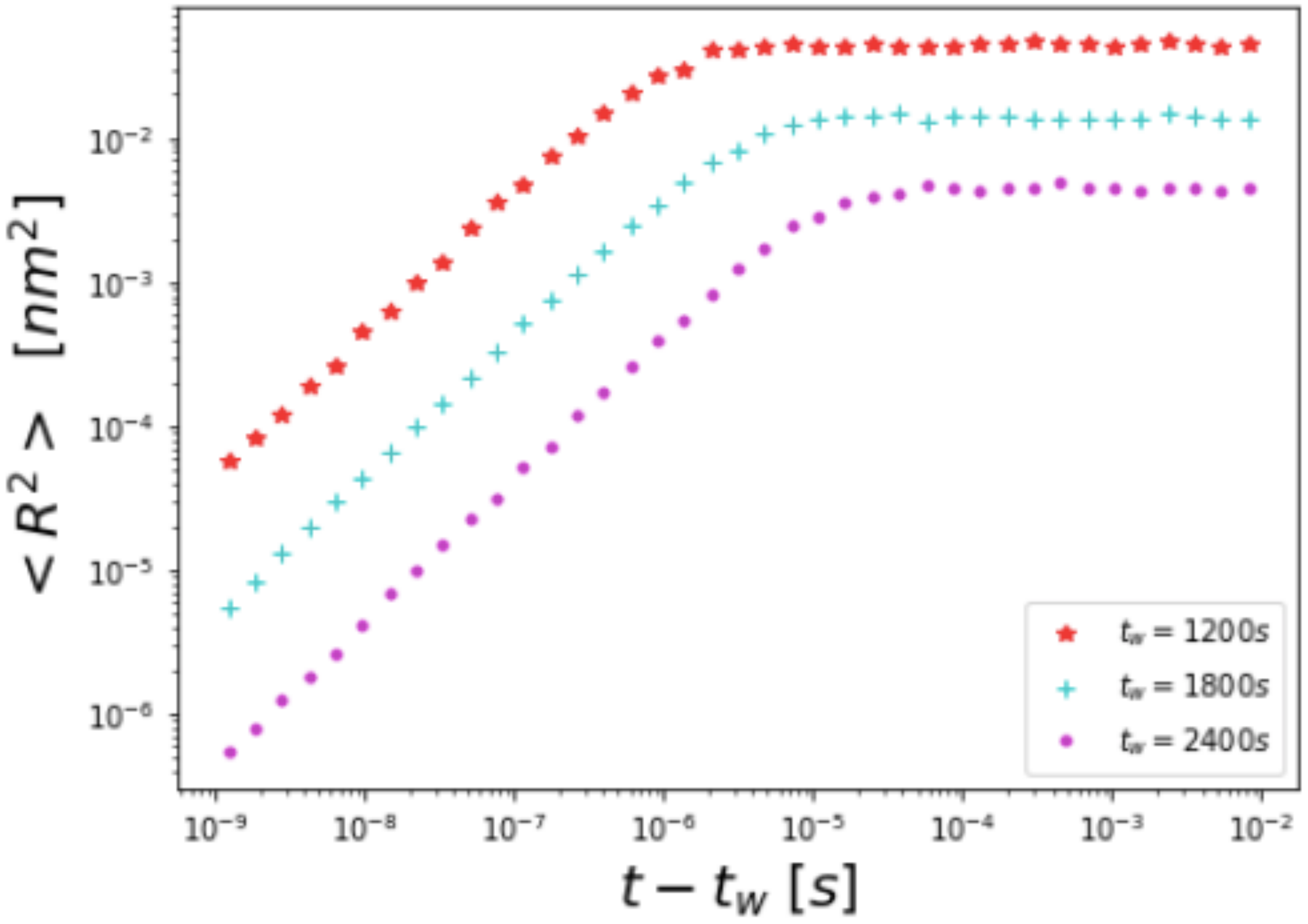
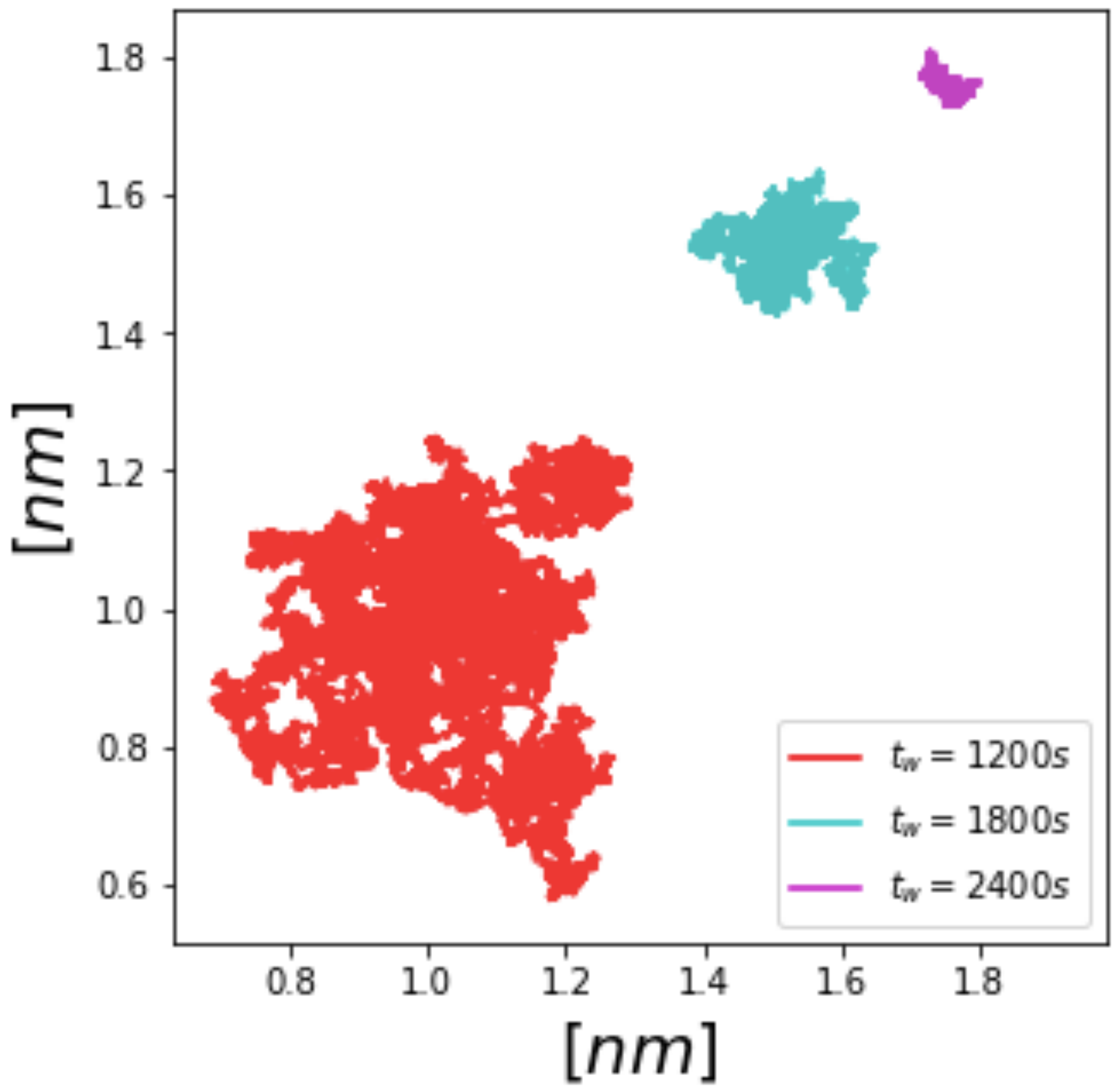
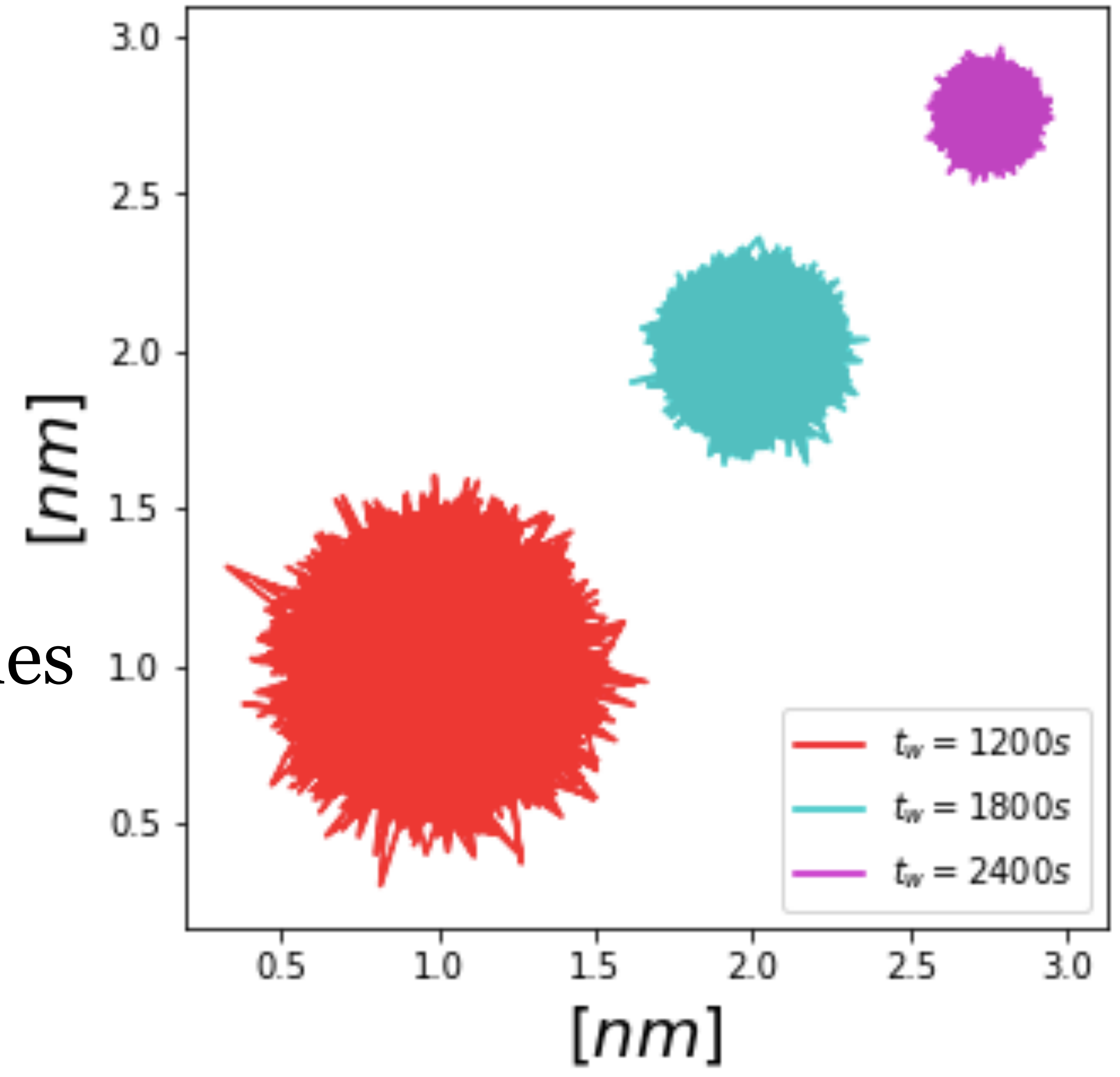


Fig.11: MSD in real time domain for three waiting times



- $t_{max} = 10^{-5}s; No.\ of\ steps = 10^5$
- The extent of diffusion at each ageing time is decreasing as time progress.
- This is due to ageing in viscous component of the material making it more viscous as time passes.



- $t_{max} = 10^{-2}s; No.\ of\ steps = 10^5$
- The confinement space is getting smaller with increase in time.
- This is due to ageing in elastic component of the material.

Case-III : Effective Time Transformation (ETT)

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

- Hence, $$\tau(t) = \tau_0 \cdot exp([\alpha - \beta] \cdot t) \Rightarrow \ \xi - \xi_w = \frac{exp([\alpha - \beta] \cdot t_w) - exp([\alpha - \beta] \cdot t)}{[\alpha - \beta]}$$

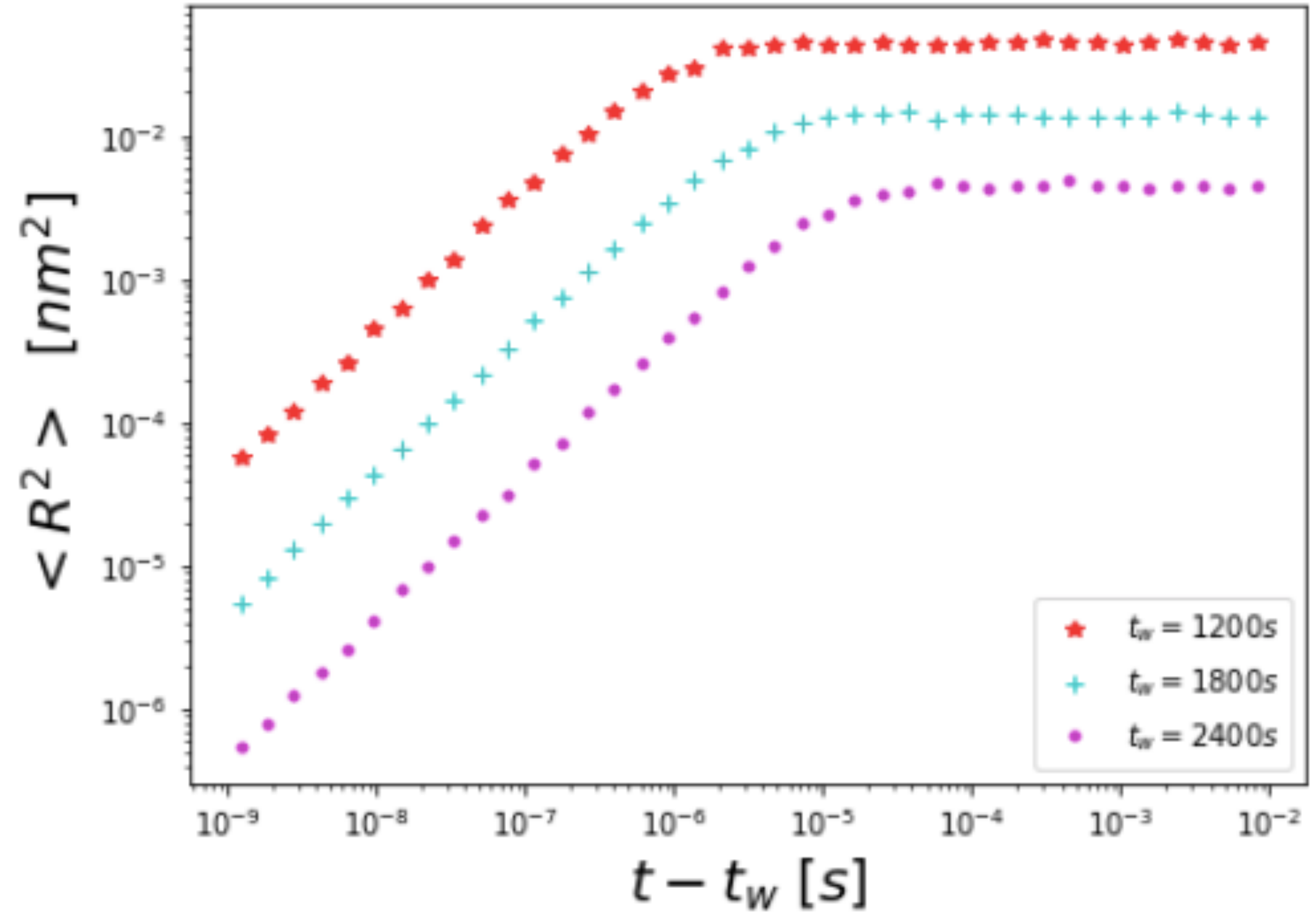


Fig.12: MSD in real time domain for three waiting times

$\rightarrow$

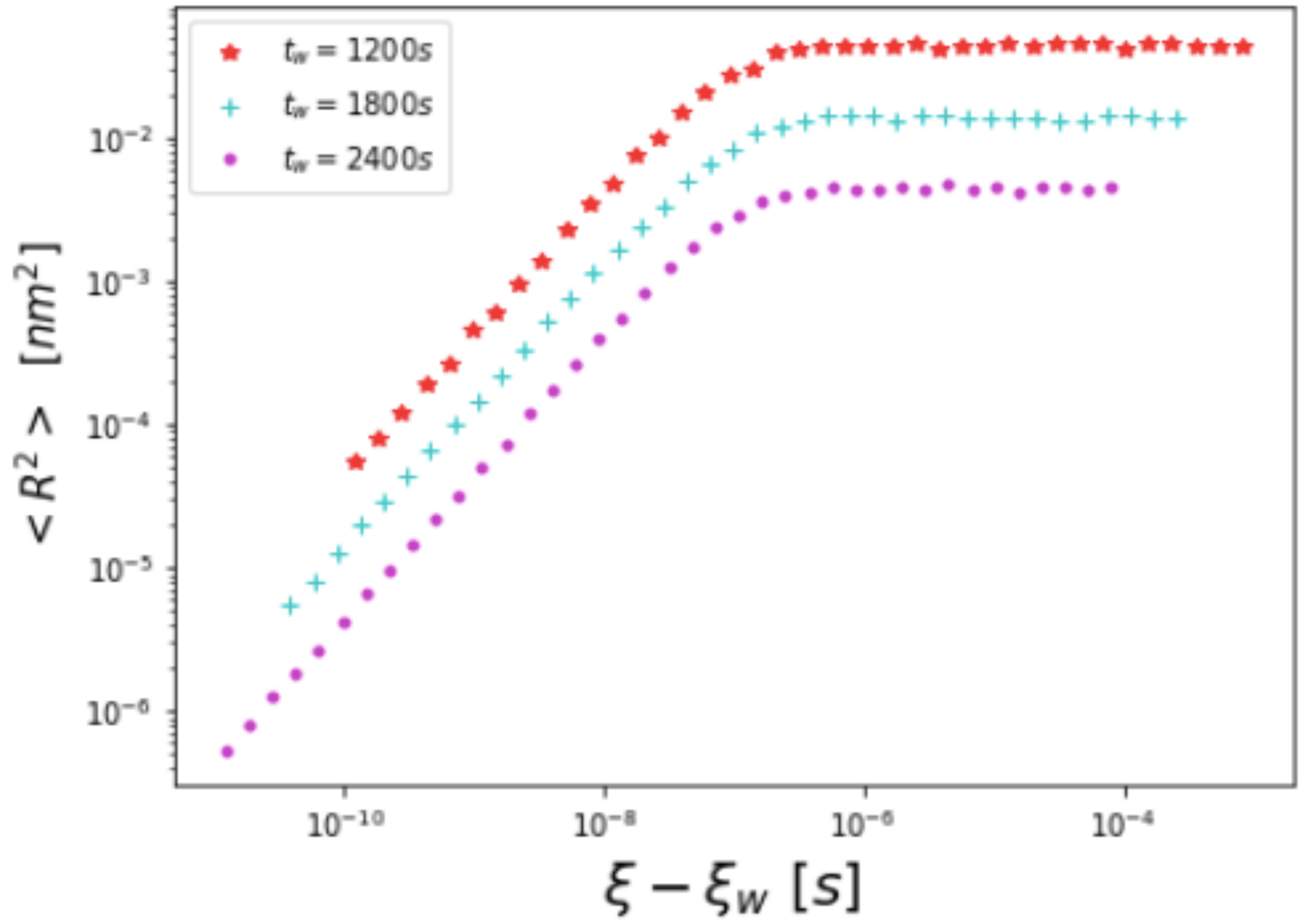


Fig.13: MSD in Effective time domain for three waiting times

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

Case-III : Effective Time Translation (Continue…)

- For 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 then :-

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

- Now multiplying each MSD curve with their respective ‘b’ values gives :-

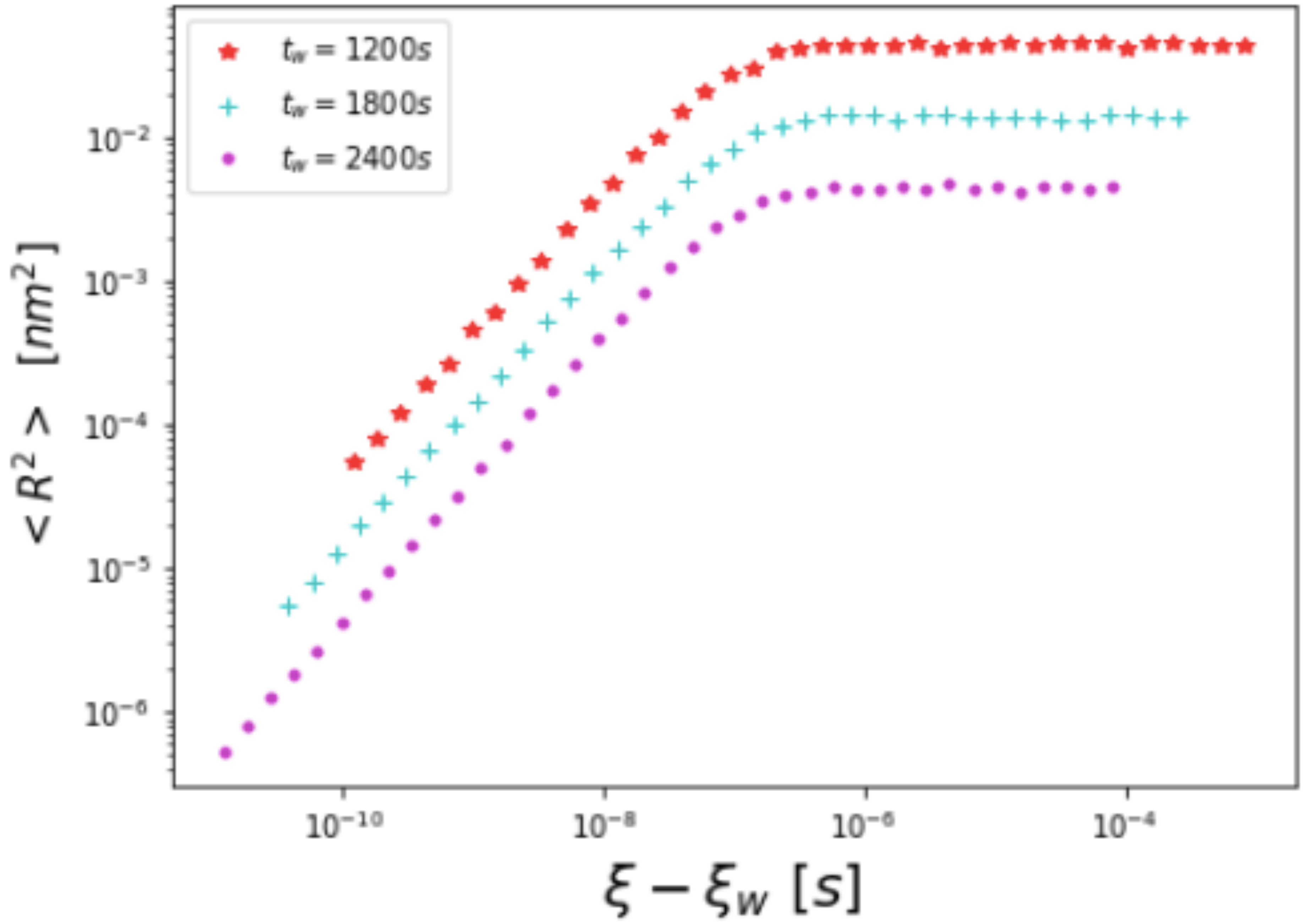


Fig.14: MSD in Effective time domain for three waiting times

$$\times b_{t_w} \longrightarrow$$

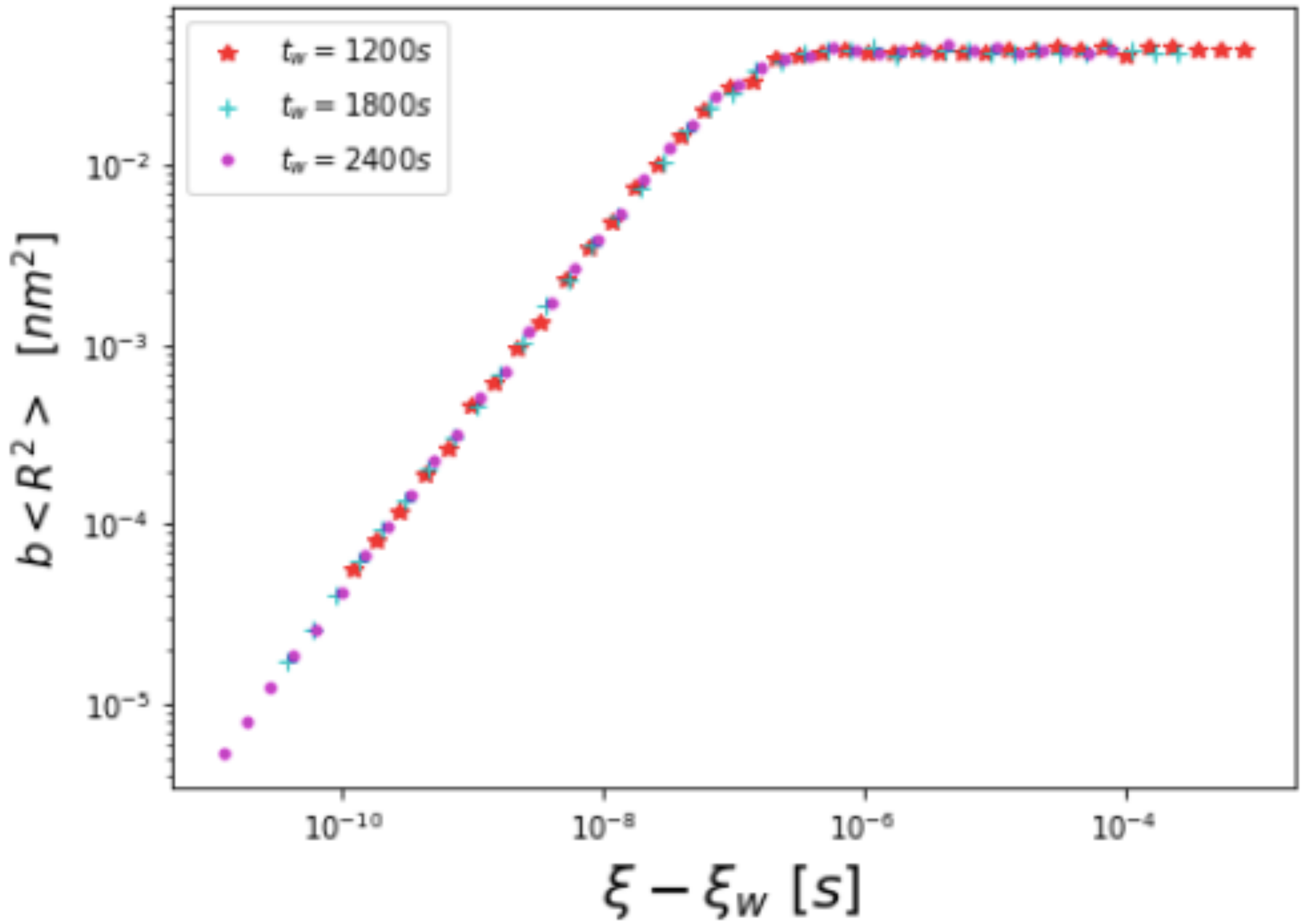


Fig.15: MSD in real Effective Time domain for three waiting times.

Reference state is $t_w = 1200s$.

⭐Brief Summary of Case-III

- We are considering (slow) ageing in each of the material components (η, G, *and* η_s) of *Maxwell-Voigt Model.*
- *We selected ageing parameter such that we can apply Struik's approximation.*
- We selected three waiting times(t= 1200s, 2400s and 3600s), and all are relatively high when compared to simulation time ($t_{max} = 60\ s$). $\boxed{\text{Or, } t - t_w \ll t_w}$
- Steps to get superposition of MSD in Effective Time Domain:

Transform the Real time to Effective time

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

$$\downarrow$$

Multiply by Vertical shift Factor ('b')

$$[\ \times b_{t_w}]$$

$$\downarrow$$

Superimposed curve in Effective Time Domain

Prediction of long term MSD behaviour using ETT

- This is similar to the last Case in terms of ageing behaviour.
- The only difference is selection of waiting time as :

$$t_{w1} = 1200 \ sec, t_{w2} = 1800 \ sec, t_{w3} = 3600 \ sec,$$

- For above scenario we get following MSD in real time domain:

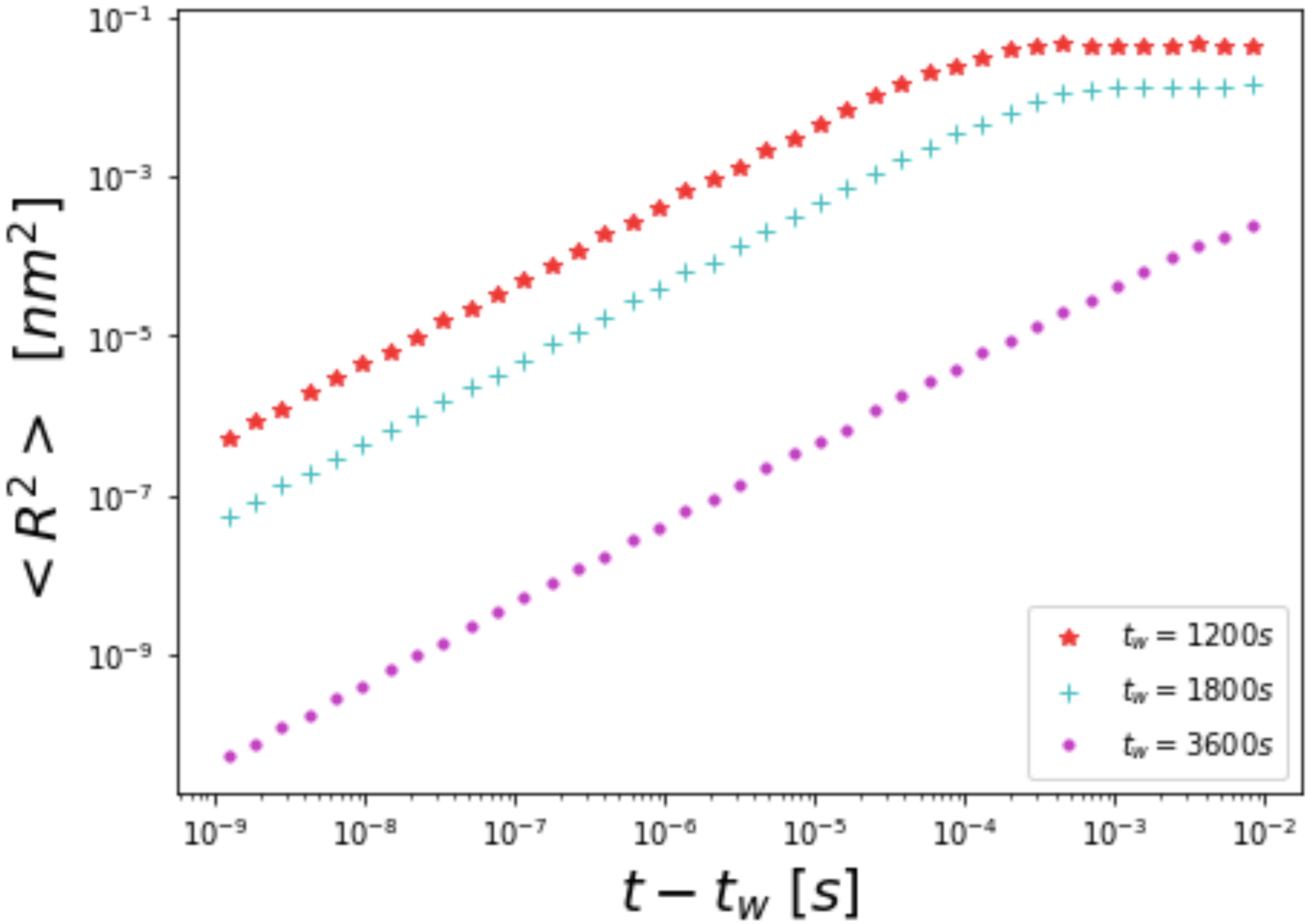


Fig.16: MSD in real time domain for three waiting times

- UDLT method.
- $\Delta t \in [10^{-8}, 10^{-2}] \ sec \ ; t_{max} = 60 sec.$
- The above simulation time is not enough to show Plateau for $t_w = 3600s$. (Short time simulation)
- But we can predict it using MSD graph in Effective time domain as discussed in next couple of slides .

Effective Time Transformation (ETT)

- We are following the Time Transformation protocol very similar to case-III.
- It gives the following result after *time domain transformation* and *vertical shift factor [b] multiplication*.
- *We have taken reference state as* $t_w = 1200s$. *Hence, Each Curve is superimposed on it.*

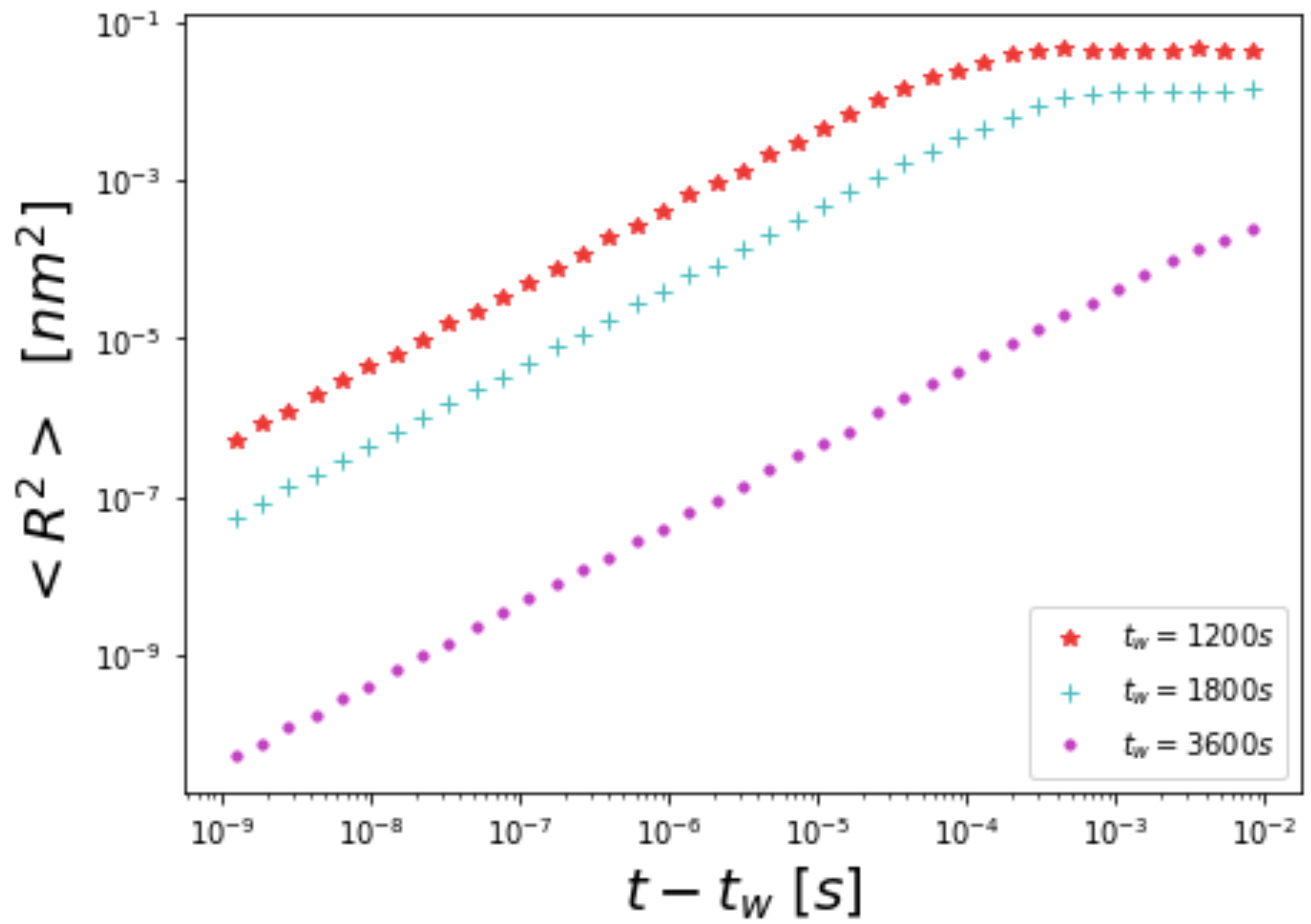


Fig.17: MSD in real time domain for three waiting times

→

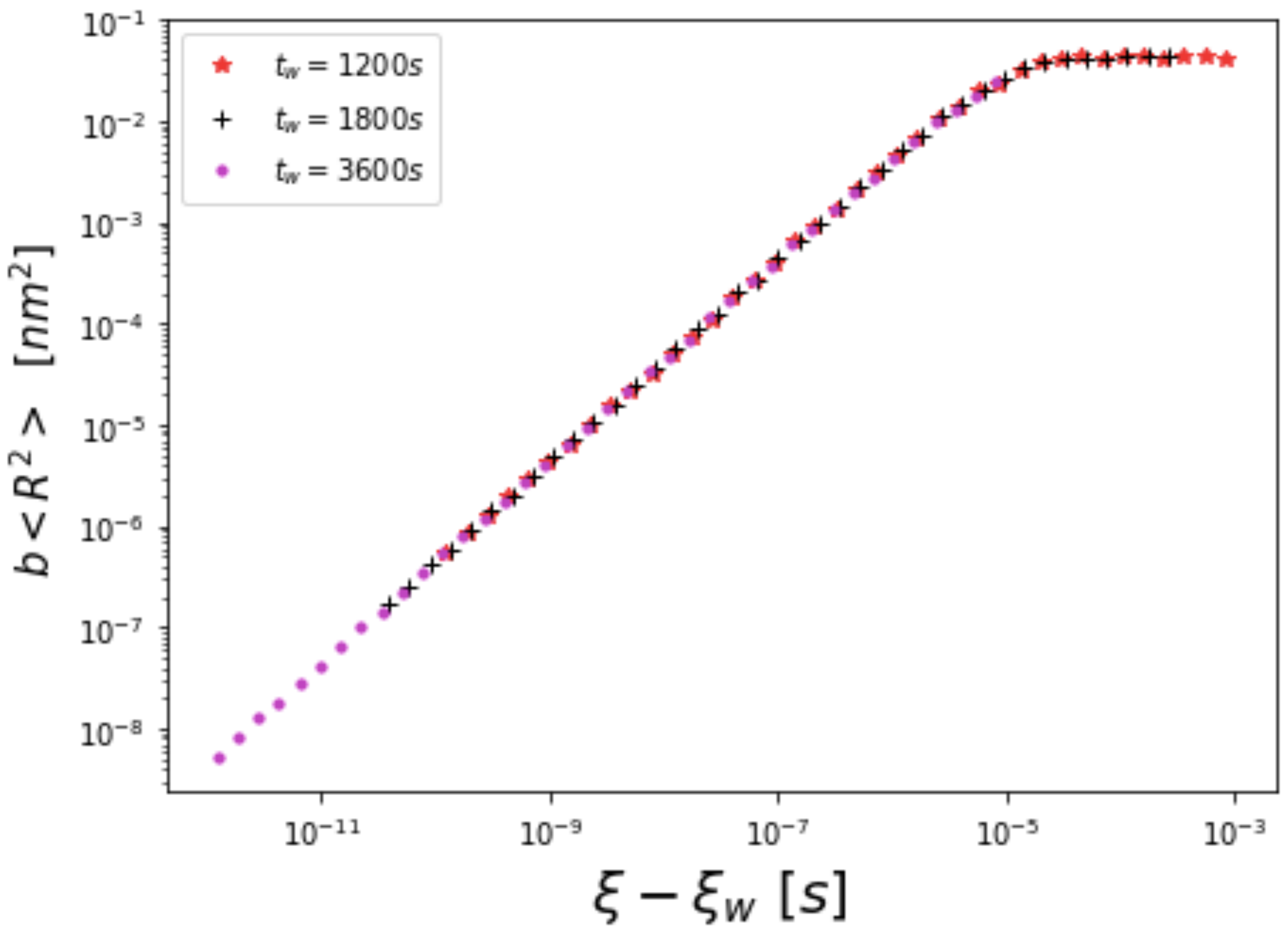


Fig.18:MSD in real Effective Time domain for three waiting times.

Reference state is $t_w = 1200s$.

Inverse Transformation from Effective Time Domain of MSD data

- Effective Time Transformation is defined as : $\xi - \xi_w = \dfrac{exp[-(\alpha-\beta)\cdot t_w] - exp[-(\alpha-\beta)\cdot t]}{(\alpha-\beta)}$

- Inverse Transformation from above equation gives :

$$t - t_w = \frac{-1}{(\alpha-\beta)} \cdot log[exp(-(\alpha-\beta)\cdot t_w) - (\alpha-\beta)(\xi-\xi_w)] - t_w$$

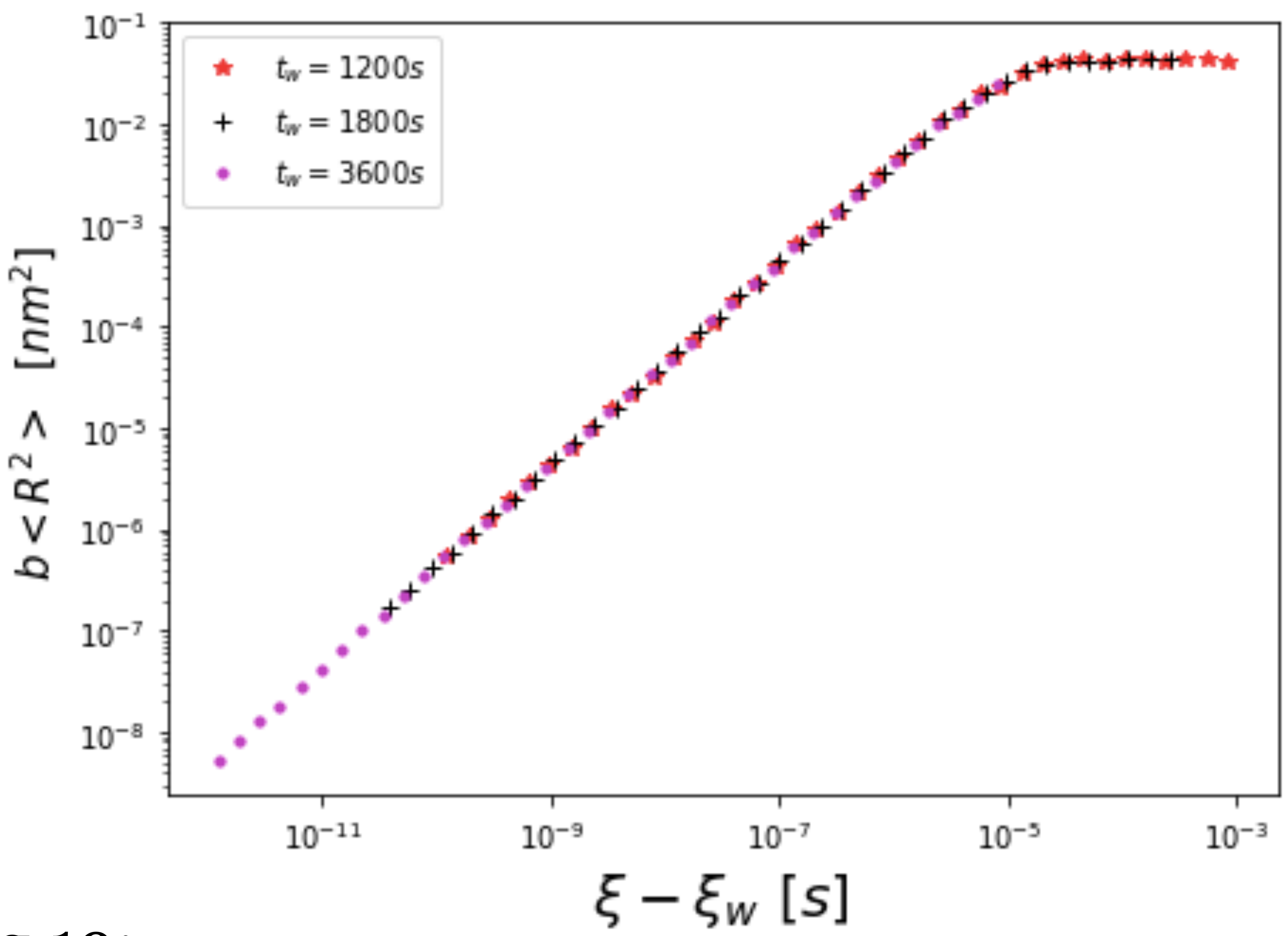


Fig.19: MSD in Effective Time domain for three waiting times. Reference state is $t_w = 1200s$.

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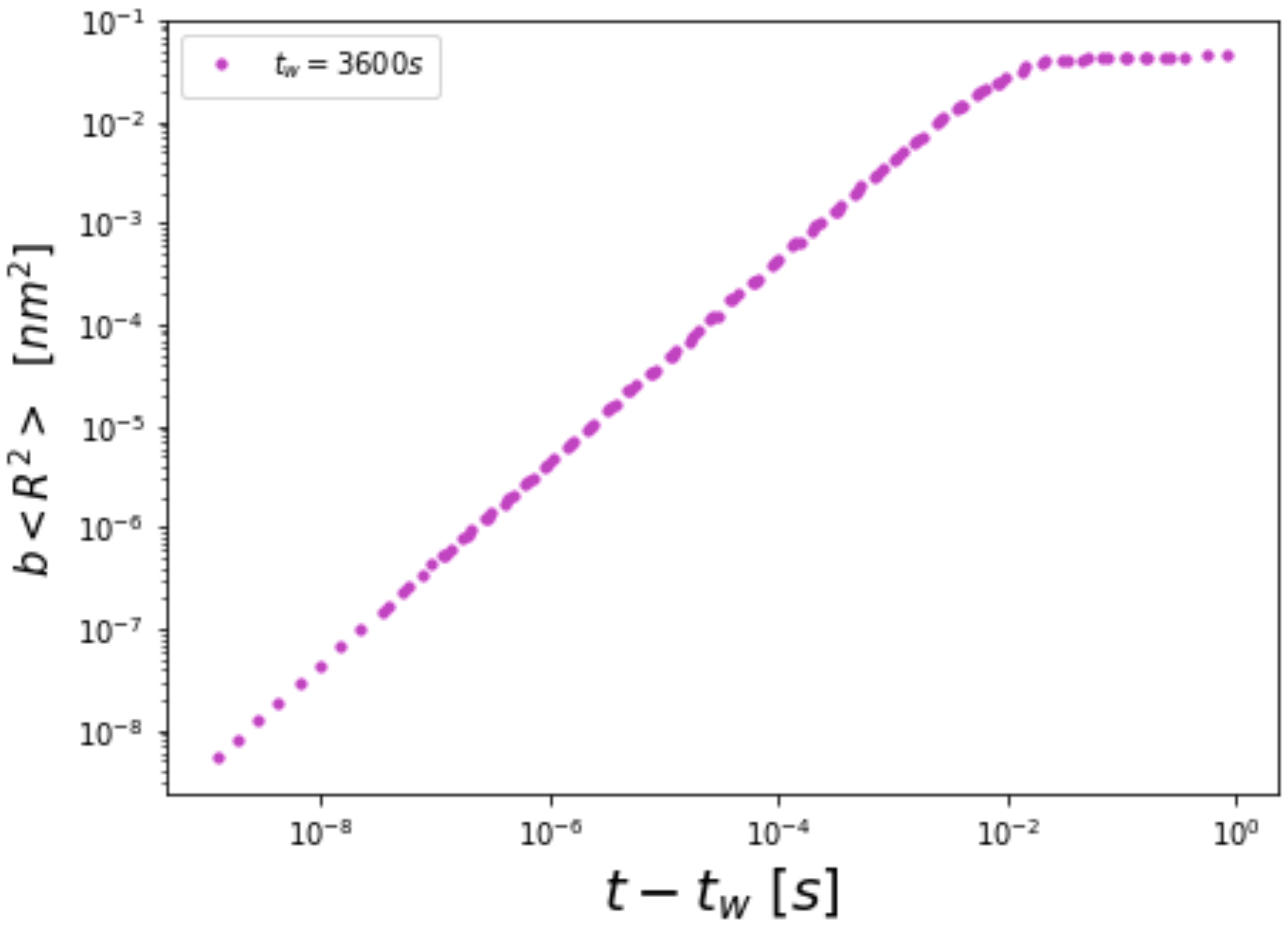


Fig.20: Combined single curve after inverting from Effective time Domain for long time prediction

Adjustment using Vertical Shift factor to retrieve the MSD curve

- Vertical shift factor for $t_w = 3600s$ is : $b_{t_w=3600s} = \dfrac{G(t = t_w = 3600s)}{G(t = t_w = 1200s)} = 100$
- Hence we will divide the MSD data by 'b' factor to get the MSD data for $t_w = 3600s$.

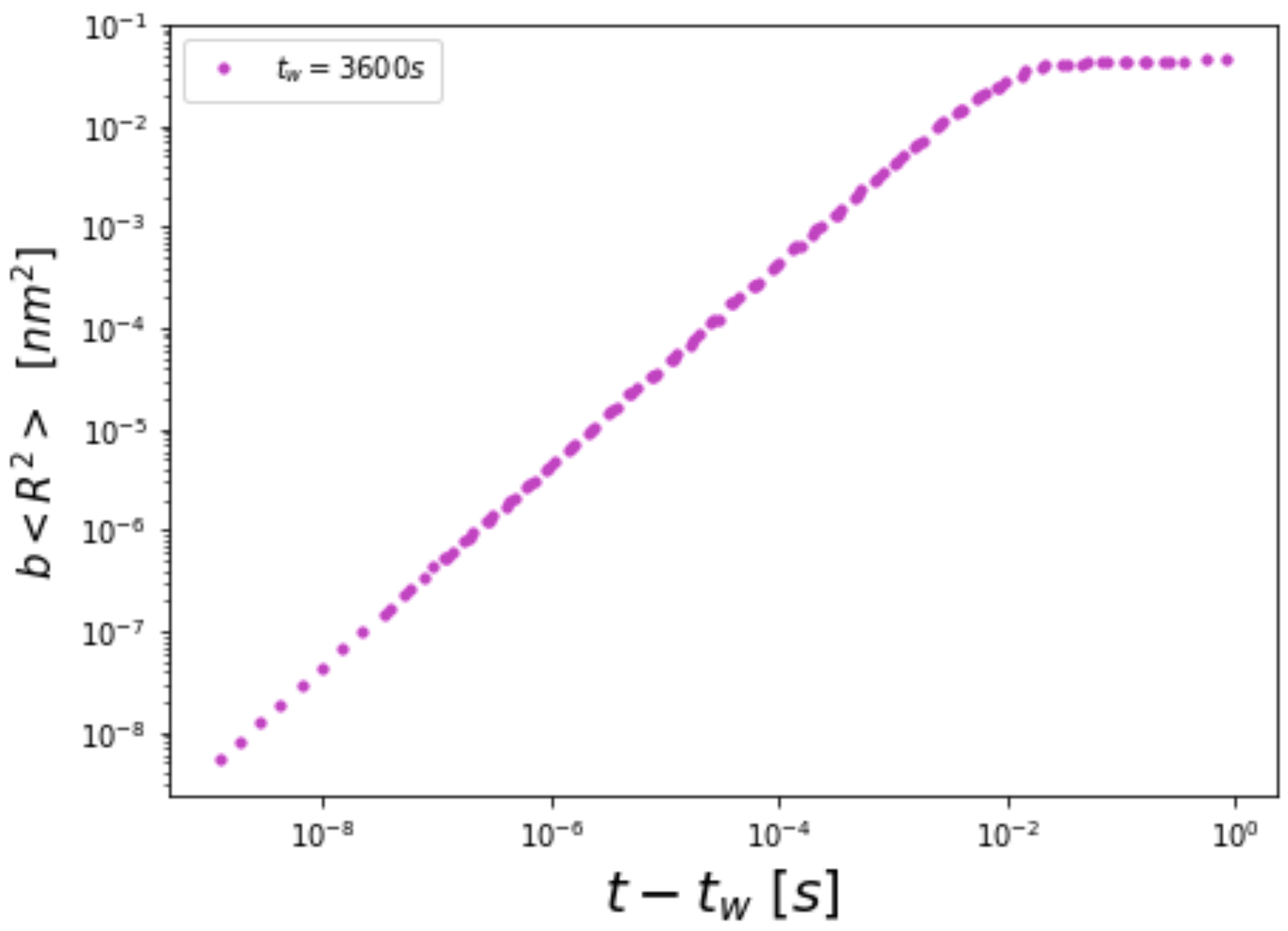


Fig.20: Combined single curve after inverting from Effective time Domain for long time prediction

$$\times \frac{1}{b_{t_w=3600s}} \longrightarrow$$

Fig.9:

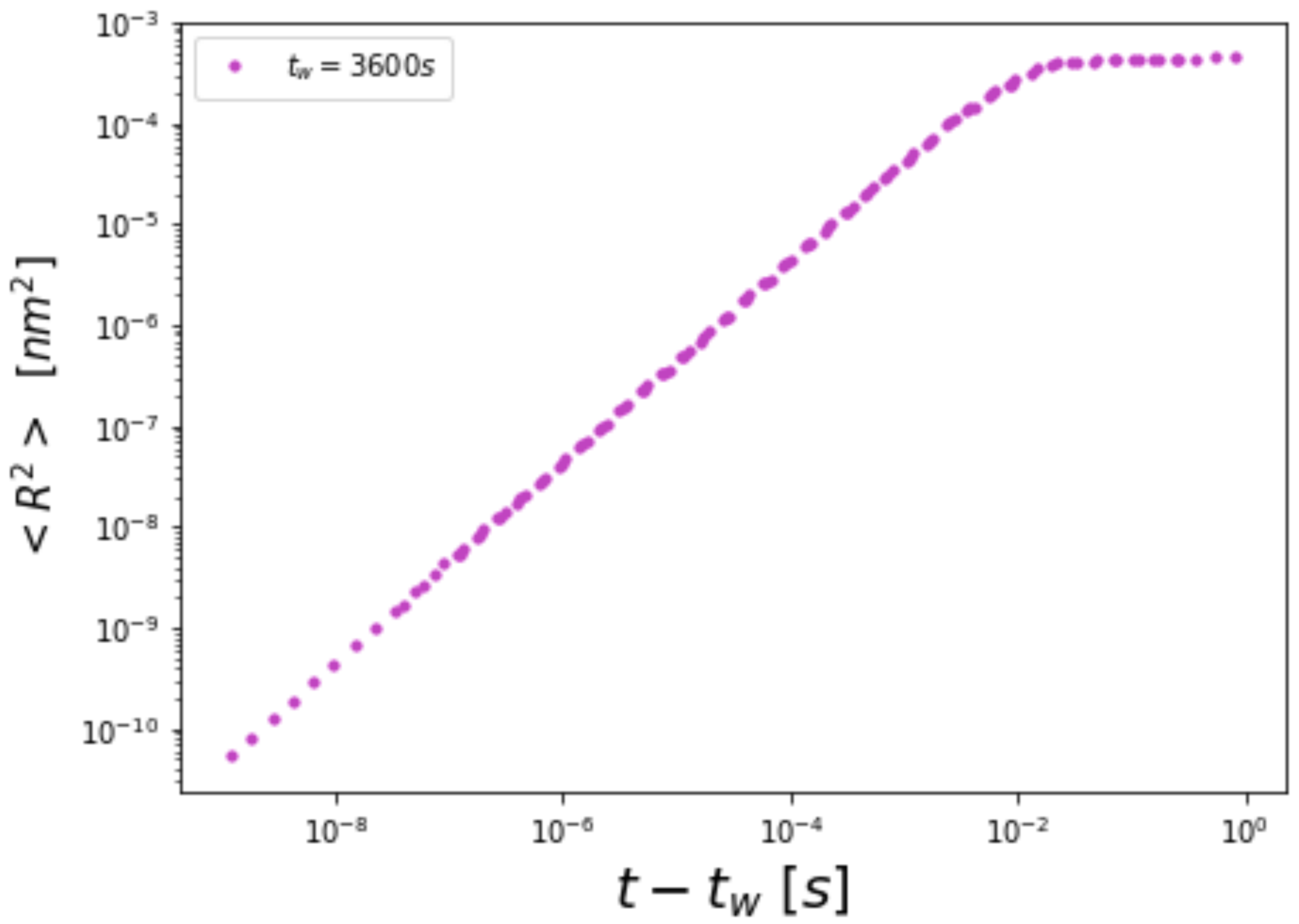


Fig.21: Combined single curve Scaled Down to get MSD for $t_w = 3600s$ in Real time domain.

Verifying the MSD graph features for predicted MSD

- Since, $\tau(t) = \tau_0 \cdot exp[(\alpha - \beta) \cdot t]$. Where,$\tau_0 = 10^{-7}, \alpha = 3.8 \times 10^{-3}s, \beta = 1.9 \times 10^{-3}s$.
- Hence, for $\tau(t = t_w = 3600s) = 10^{-2}s$.
- Plateau Value = $r_0^2 = \dfrac{k_B T}{6\pi a G(t)}$.

Fig.1

- $G(t) = G_O \cdot exp(\beta \cdot t) \Rightarrow G(t = t_w = 3600s) = 2.2 \times 10^{-4}[nm]^2$
- Both $\tau(t = t_w = 3600s) = 10^{-2}s$ and $G(t = t_w = 3600s) = 2.2 \times 10^{-4}[nm]^2$

  is matching from values predicted from the graph.
- We can similarly predict MSD behaviour of very long waiting time like $t_w = 10000s$ or show if we know the MSD behaviour for short waiting time (like $t_w = 1200s$ and $t_w = 1800s$).

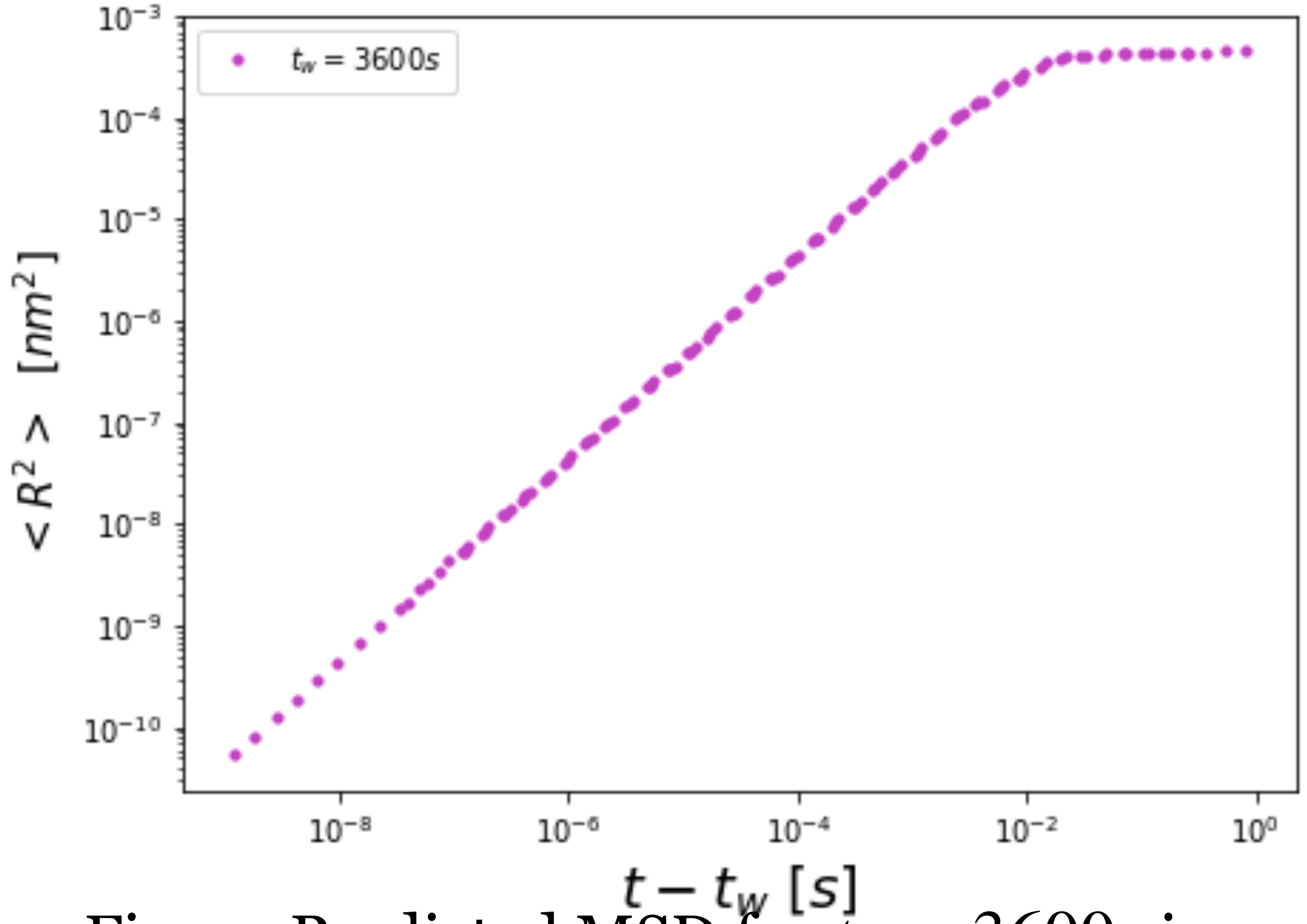


Fig.21: Predicted MSD for $t_w = 3600s$ in real time domain.

Ageing Viscous medium

- We are taking a viscous medium which shows time dependent viscosity coefficient.
- The viscosity (η) of medium is increasing with time as per following equation:-

$$\eta(t) = \eta_o exp(\alpha \cdot t) \quad ; \qquad \alpha = 2.3 \times 10^{-3}\ [1/s]$$

- Basically, we are dealing with a medium with shows **slow** time dependent change in viscosity.
- We have taken five different waiting time:

$t_{w1} = 1200\ sec, t_{w2} = 1800\ sec, t_{w2} = 2400\ sec, t_{w2} = 3000\ sec, t_{w2} = 3600\ sec$.

- For all these five cases simulation has been done for $60\ sec$.
- In those simulation time of $60\ sec$ change in viscosity is almost negligible or,

$$\frac{\eta(t_w + 60) - \eta(t_w)}{\eta(t_w)} \ll 1$$

- Hence, System behave locally as a **stationary system.** In our case for all five waiting times, the value is:- $\dfrac{\eta(t_w + 60) - \eta(t_w)}{\eta(t_w)} \sim 0.13$

Defining Effective Time Transformation for Viscous Medium

- For a viscous medium we define Friction coefficient $\zeta(t) = 6\pi \cdot a \cdot \eta(t)$.
- We define, $\dfrac{dt'}{\zeta(t')} = d\xi \;\; \Rightarrow \;\; \displaystyle\int_{t_w}^{t} \frac{dt'}{\zeta(t')} = \int_{\xi_w}^{\xi} d\xi$.
- The motivation for this transformation is coming from Langevin equation of spherical particle in viscous medium (over-damped Case):

$$\zeta(t)\frac{dx}{dt} = F_r(t)\;; \qquad (F_r(t) \text{ is delta correlated random force})$$

$$\Rightarrow \frac{dx}{dt\,/\,\zeta(t)} = F_r(t)$$

- From here, We are altogether taking $\dfrac{dt}{\zeta(t)} = d\xi$. This is similar to the approach we mentioned for kelvin Voigt Material in this present work. Hopkins(1958) who used similar approach for the case of time dependent Maxwell Material.

Ageing Viscous medium : Trajectory

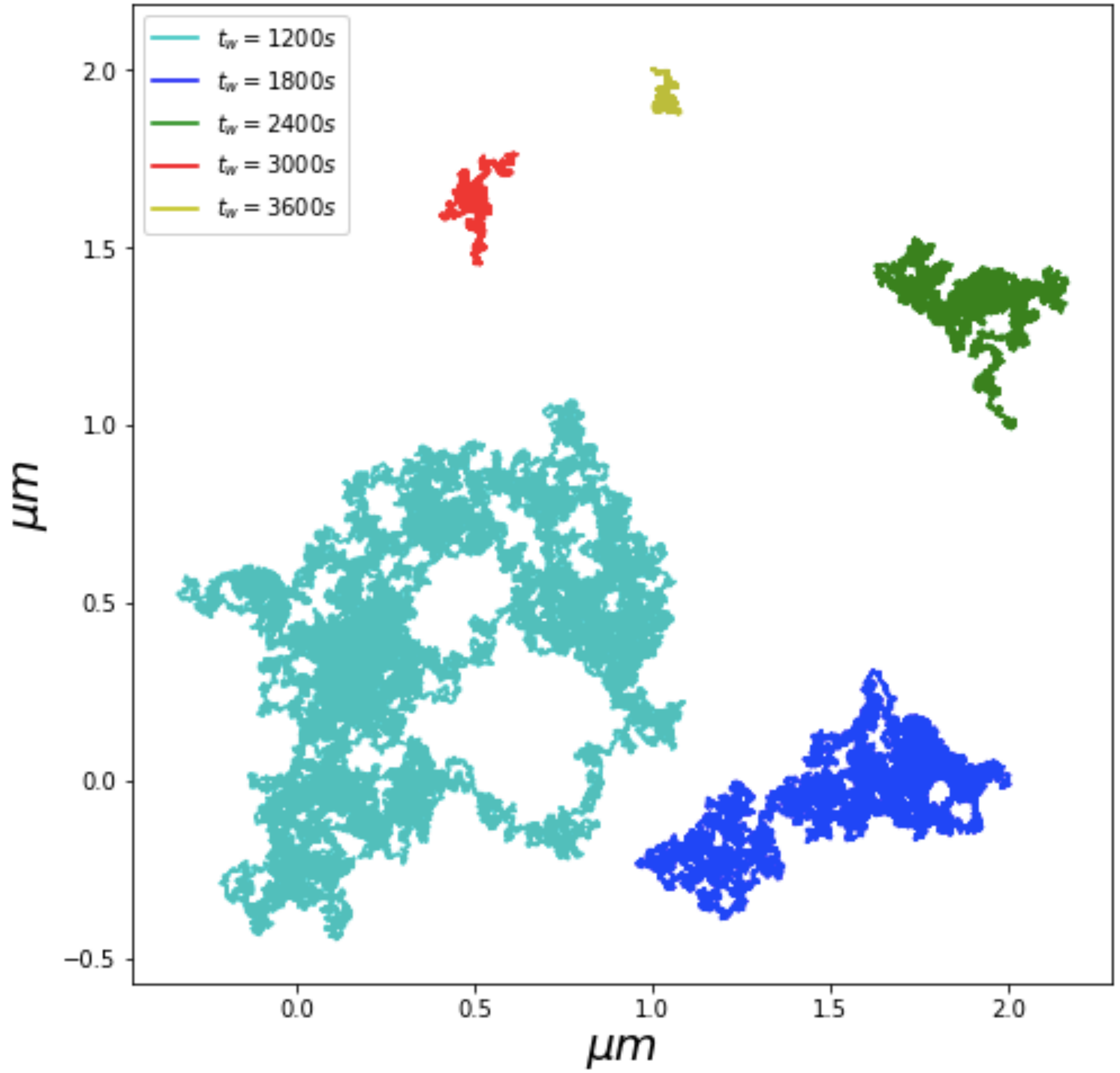


Fig.22 : Trajectories at various waiting Time

- Trajectories are generated for five different ageing times.
- Fixed Time step method used.
- $\Delta t = 10^{-3}s, \quad t_{max} = 60s$
- Since viscosity of medium increases with time hence, spatial extent of diffusion is decreasing with time. Or,
- since, $\eta(t) = \eta_0 \cdot exp(\alpha \cdot t)$ and $D(t) = \dfrac{k_B T}{6\pi a \eta(t)}$

Hence, $\eta(t)\ [\uparrow] \Rightarrow D(t)\ [\downarrow]$

- We are taking $\eta(t) = \eta_0 \cdot exp(\alpha \cdot t);\ \ \alpha = 1.9 \times 10^{-3}[1/s]; \eta_0 = 10^{-3} Pa \cdot s$

Mean Square Displacement

- Fixed time step: $\Delta t = 10^{-3}s$.
- Total simulation time: $t_{max} = 60s$

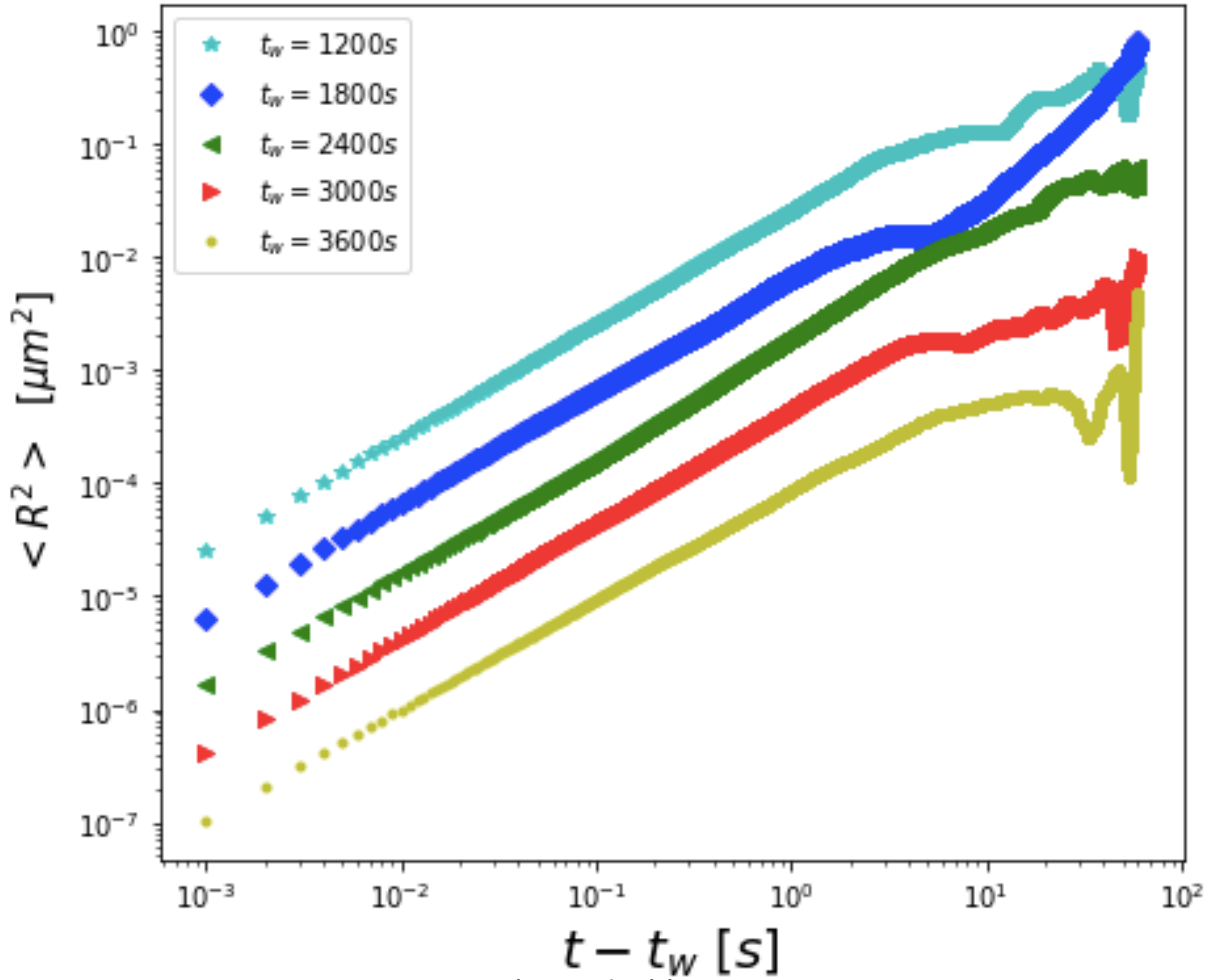


Fig.23 : MSD for different Waiting Time

- UDLT method
- $\Delta t \in [10^{-6}, 10^{-2}]\ sec\ ; t_{max} = 60sec$

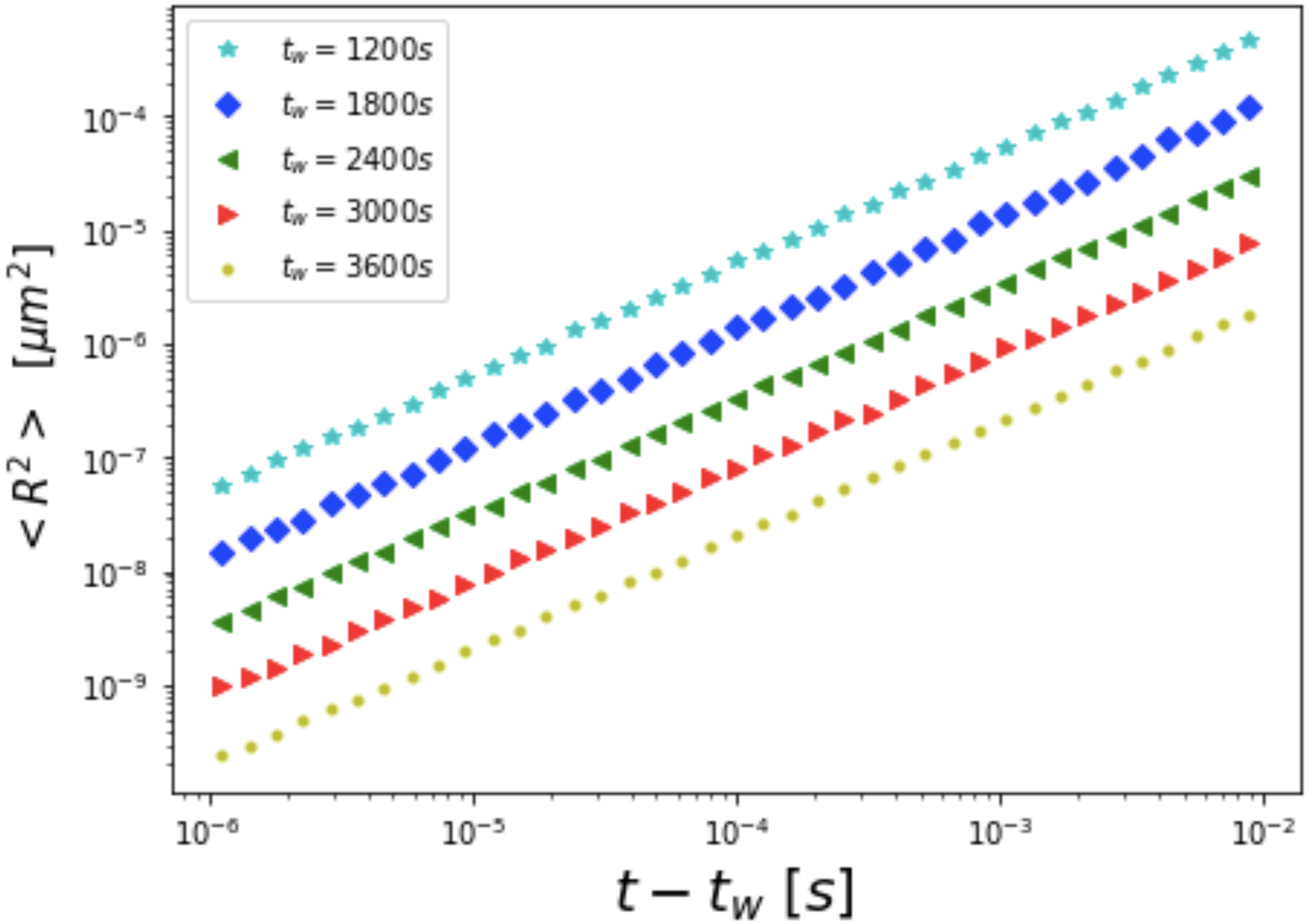


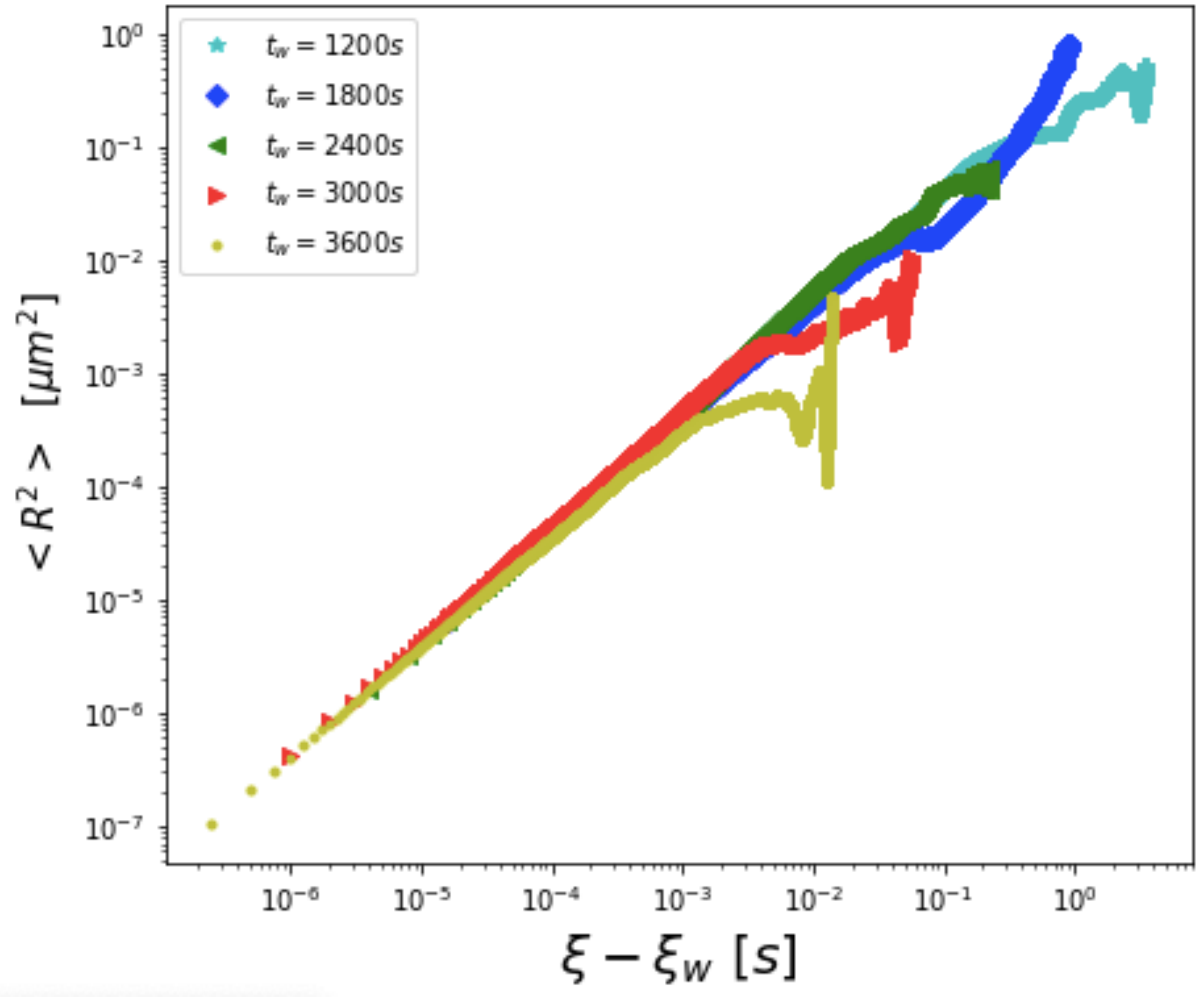
Fig.23 : MSD for different Waiting Time

- Due to ageing in the medium its viscosity increases as time progresses. Hence, Diffusion coefficient decreases with progress of time.

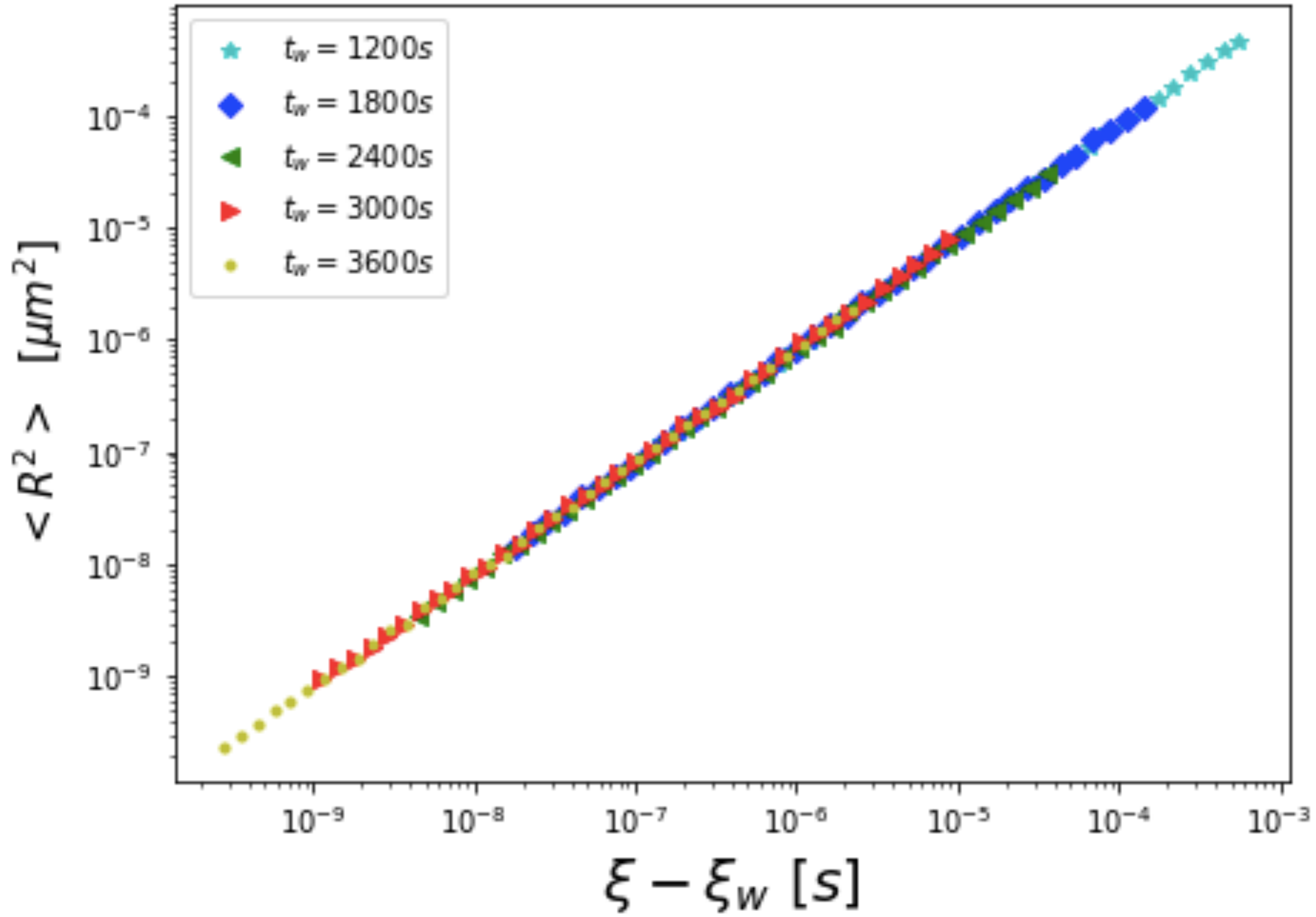
Effective Time Transformation for Viscous medium

- We are taking $\eta(t) = \eta_0 \cdot exp(\alpha \cdot t) \Rightarrow \quad \zeta(t) = 6\pi a \eta(t)$
- Since, $\dfrac{dt}{\zeta(t)} = d\xi$ which gives, $\Rightarrow \; \xi - \xi_w = \dfrac{exp(-\alpha \cdot t_w) - exp(-\alpha \cdot t)}{\alpha}$
- If we use this Transformation we get following result.

Fixed Time method



UDLT method



MSD in Effective Time domain for five waiting times. Reference state is $t_w = 1200s$.

⭐ Brief Summary of Ageing in viscous medium

- We are taking a slow ageing viscous medium.
- We selected five waiting times, and all are relatively high when compared to simulation time. Or, $t - t_w \ll t_w$
- A very similar transformation defined as $\dfrac{dt}{\zeta(t)} = d\xi$ works like Effective Time domain for this case too.
- 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
in reference state.

Vertical shift Factor ('b') not required.

Then is nothing like elastic modulus for this case system

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).

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

Where 'ϵ' is strain and 'σ' stress.

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

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

- $taking, \; \tau = \frac{\eta}{G} \quad \Rightarrow \quad \tau\frac{dx}{dt} = \frac{F}{G} - x \quad \Rightarrow \quad \frac{dx}{dt/\tau} = \frac{F}{G} - x$

- Defining $\quad dt/\tau(t) = d\xi(t)$
- Hence,

$$\int_{t_w}^{t} d\xi(t) = \int_{t_w}^{t} \frac{dt'}{\tau(t')} = \xi(t) - \xi(t_w) \qquad \text{[Transformation Defined]}$$

- This identical to what we get for Maxwell Material.

⭐Functional form of relaxation time of ageing medium

- In literature we mostly encounter following two different time dependence for an ageing medium-

(i) Exponential time dependence: $\tau(t) = \tau_0 \cdot exp(\alpha \cdot t)$

- this dependency is experimentally observed in aqueous LAPONITE suspension.
- value of constant α depends on sample preparation i.e, the amount of Laponite added, and what is used as solvent for sample preparation. (Laponite is commercially available in powder form. It is mixed in an appropriate solvent to make a suspension)
- references :

(A. Shahin and Y. M. Joshi, Phys. Rev. Lett., 2011, 106, 038302: http://home.iitk.ac.in/~joshi/PhysRevLett.106.038302.pdf)
(B. M. Vyas and Y.M. Joshi et.al, *Soft Matter,* 2016, 12, 8167:
https://drive.google.com/file/d/1xlSteeuLQM54WCmYiswC7cddYV_I2Kmf/view?usp=sharing)

(ii) Power Law time dependence: $\tau(t) = \tau_0 \cdot (\dfrac{t}{\tau_0})^{\mu} = \tau_0^{1-\mu} \cdot t^{\mu}$

- If $\mu > 1$; it is named hyper-aging. (example : Hair gel[†] etc.)
- If $\mu < 1$; it is named sub-aging. (example : emulsion paint[†] etc.)

  - value of constant μ depends on sample composition i.e, the relative amount of constituents added in sample. (It is reported that two samples prepared by adding different percentage of species 'A' and 'B' age differently or, they will have different μ[‡])

  - references :

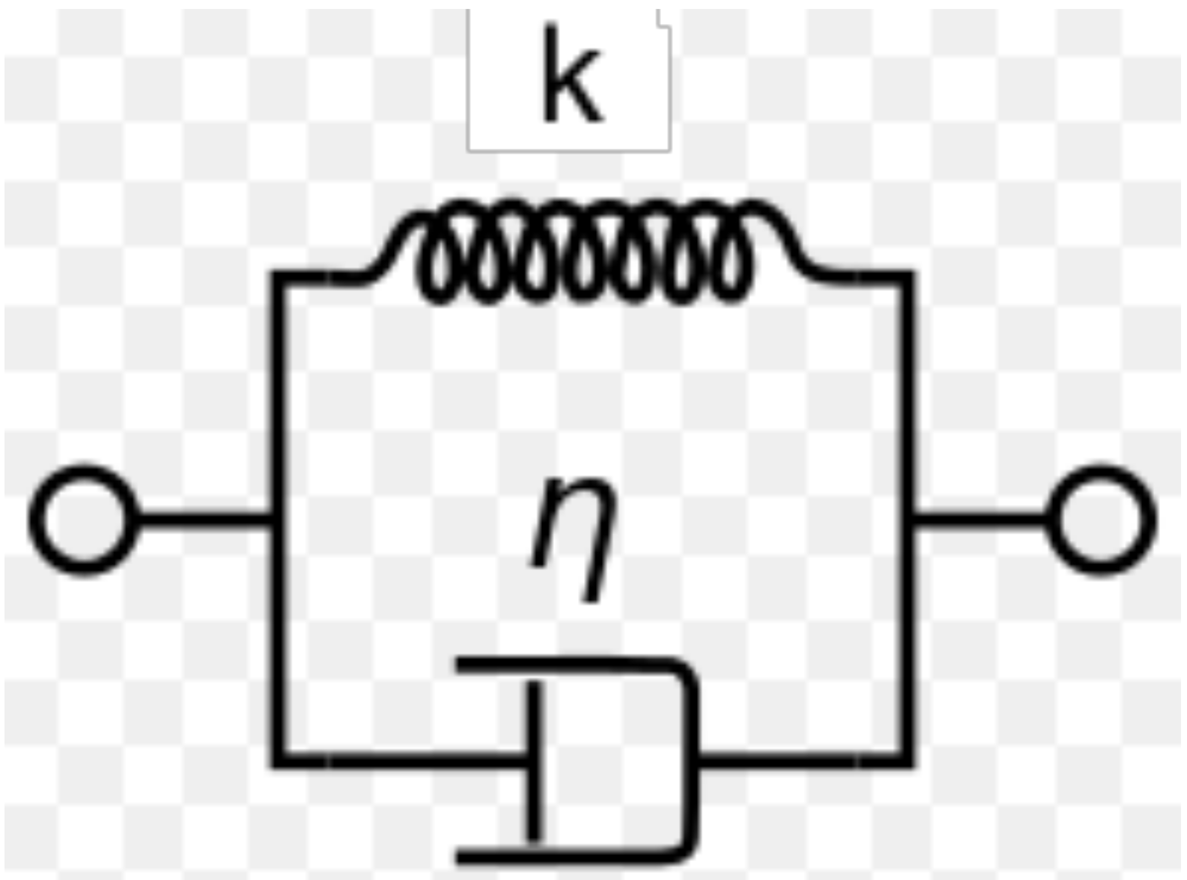
(†A. Shahin and Y. M. Joshi, Phys. Rev. Lett., 2011, 106, 038302: http://home.iitk.ac.in/~joshi/PhysRevLett.106.038302.pdf)

(several examples for an ageing system with power law dependence is mentioned in 'M. Kaushal and Y.M. Joshi: Soft Matter, 2014, 10, 1891' : https://drive.google.com/file/d/1tWZVUkTefddQFRaKuDK09DBZ-0uIHsrX/view?usp=sharing)

(‡B. M. Vyas and Y.M. Joshi et.al, *Soft Matter,* 2016, 12, 8167: https://drive.google.com/file/d/1xlSteeuLQM54WCmYiswC7cddYV_I2Kmf/view?usp=sharing)

Kelvin-Voigt Model : Description

- Short description of Kelvin-Voigt Model:



Source: Wikipedia

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

- Strain in both component is identical: $\epsilon = \epsilon_1 = \epsilon_2$.
- Stress in both components add: $\sigma = \sigma_1 + \sigma_2$.
- Governing equation of the model is : $\dfrac{d\epsilon}{dt} = \dfrac{\sigma}{\eta} - G\dfrac{\epsilon}{\eta}$
- Now we will define Effective time transformation for this Model in next slide.
- We will proceed with similar line of thinking as of Hopkins(1958), who did it for the time dependent Maxwell Material*.

[Link to Hopkins(1958): https://drive.google.com/file/d/1WGEa5M_Utt9qVoSCKLrzoOMdmmJk9oMF/view?usp=sharing](https://drive.google.com/file/d/1WGEa5M_Utt9qVoSCKLrzoOMdmmJk9oMF/view?usp=sharing)

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).

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

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 , $\dfrac{dt}{a(t)} = d\xi(t)$ (*This definition will resolve the problem.*)
- makes, Equation(ii). as $\tau_0 \cdot \dfrac{dx}{d\xi(t)} = \dfrac{F}{G} - x$ .... Equation(iii)
- Equation(i) and Equation(iii) is similar in form. The difference is that $'dt'$ *is replaced by* $d\xi(t)$.
- $\dfrac{dt}{a(t)} = d\xi(t)$ can be written as $\dfrac{dt}{a(t)} = \tau_0 \cdot \dfrac{dt}{\tau(t)}$
- 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.
- https://drive.google.com/file/d/1WGEa5M_Utt9qVoSCKLrzoOMdmmJk9oMF/view?usp=sharing

Let us take Equation(iv), $\int_{t_w}^{t} d\xi(t) = \xi(t) - \xi(t_w) = \tau_0 \cdot \int_{t_w}^{t} \frac{dt'}{\tau(t')}$ and apply it to two know functional form

(i) Exponential time dependence: $\tau(t) = \tau_0 \cdot exp(\alpha \cdot t)$

it gives, $\Rightarrow \ \xi(t) - \xi(t_w) = \dfrac{exp(-\alpha \cdot t_w) - exp(-\alpha \cdot t)}{\alpha}$

(ii) Power Law time dependence: $\tau(t) = \tau_0 \cdot (\dfrac{t}{\tau_0})^{\mu} = \tau_0^{1-\mu} \cdot t^{\mu}$

It gives, $\Rightarrow \ \xi(t) - \xi(t_w) = \tau_0^{\mu}[\dfrac{t^{1-\mu} - t_w^{1-\mu}}{1 - \mu}]$

https://drive.google.com/file/d/1sSnIvnw3jDTaf9E-b_PwIAvpVJZoJGC_/view?usp=sharing

https://drive.google.com/file/d/1xlSteeuLQM54WCmYiswC7cddYV_I2Kmf/view?usp=sharing

https://drive.google.com/file/d/1tWZVUkTefddQFRaKuDK09DBZ-0uIHsrX/view?usp=sharing