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

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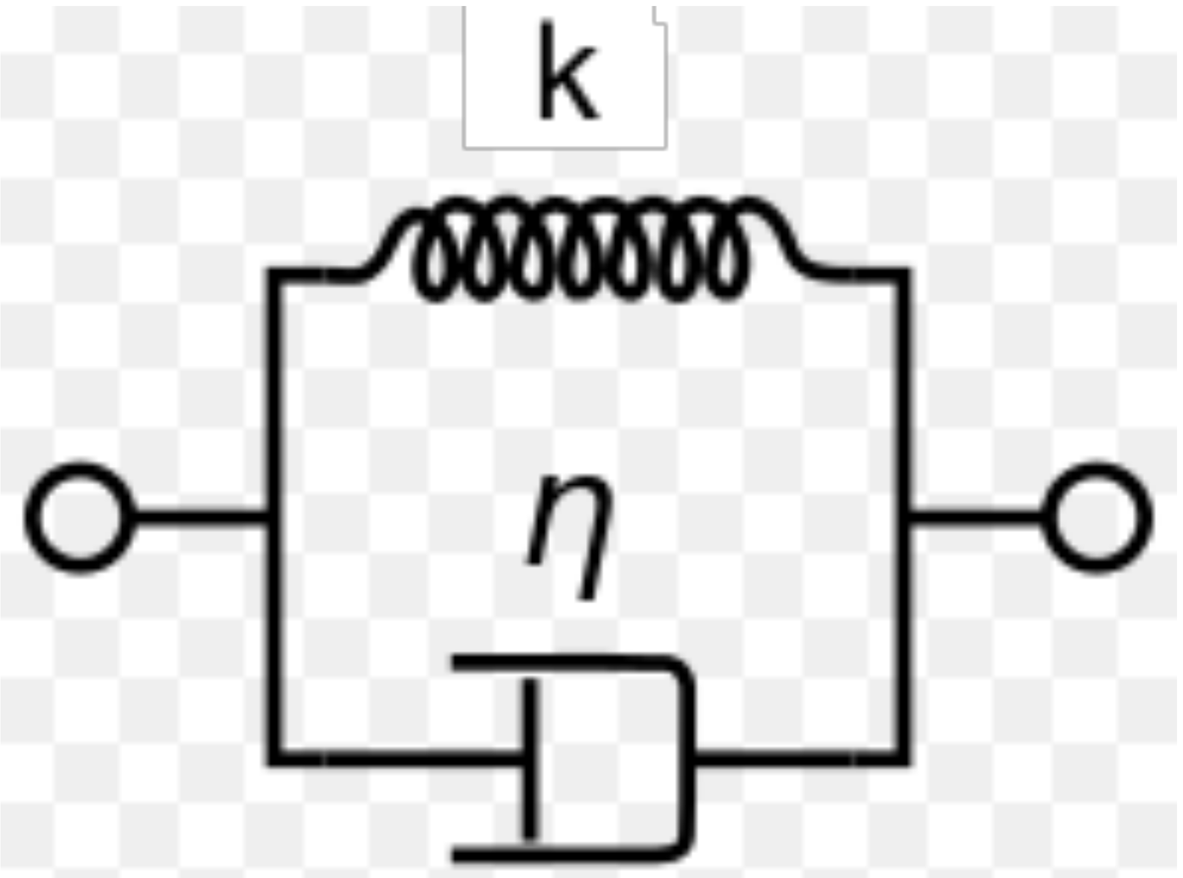
Kelvin-Voigt Model : Description

- 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.
- We will proceed with similar line of thought as Hopkins(1958), who did it for the time dependent Maxwell Material*.

[*Link to Hopkins paper : https://doi.org/10.1002/pol.1958.1202811817](https://doi.org/10.1002/pol.1958.1202811817)

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 form $\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} - G\frac{\epsilon}{\eta}$.]

Where 'ϵ' is strain and 'σ' stress.

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

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

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

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

$$\xi(t) = \int_0^t d\xi(t) = \int_0^t \frac{dt'}{\tau(t')}$$ [Transformation Defined]

Case-I : Ageing Kelvin-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:-

$$G(t) = G_O \cdot exp(\beta \cdot t) \qquad hence,\ \tau(t) = \frac{\eta_0}{k(t)} = \frac{\eta_0}{6\pi a G(t)} = \tau_o \cdot exp(-\beta \cdot t)$$

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

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

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

- We have taken three waiting time :

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

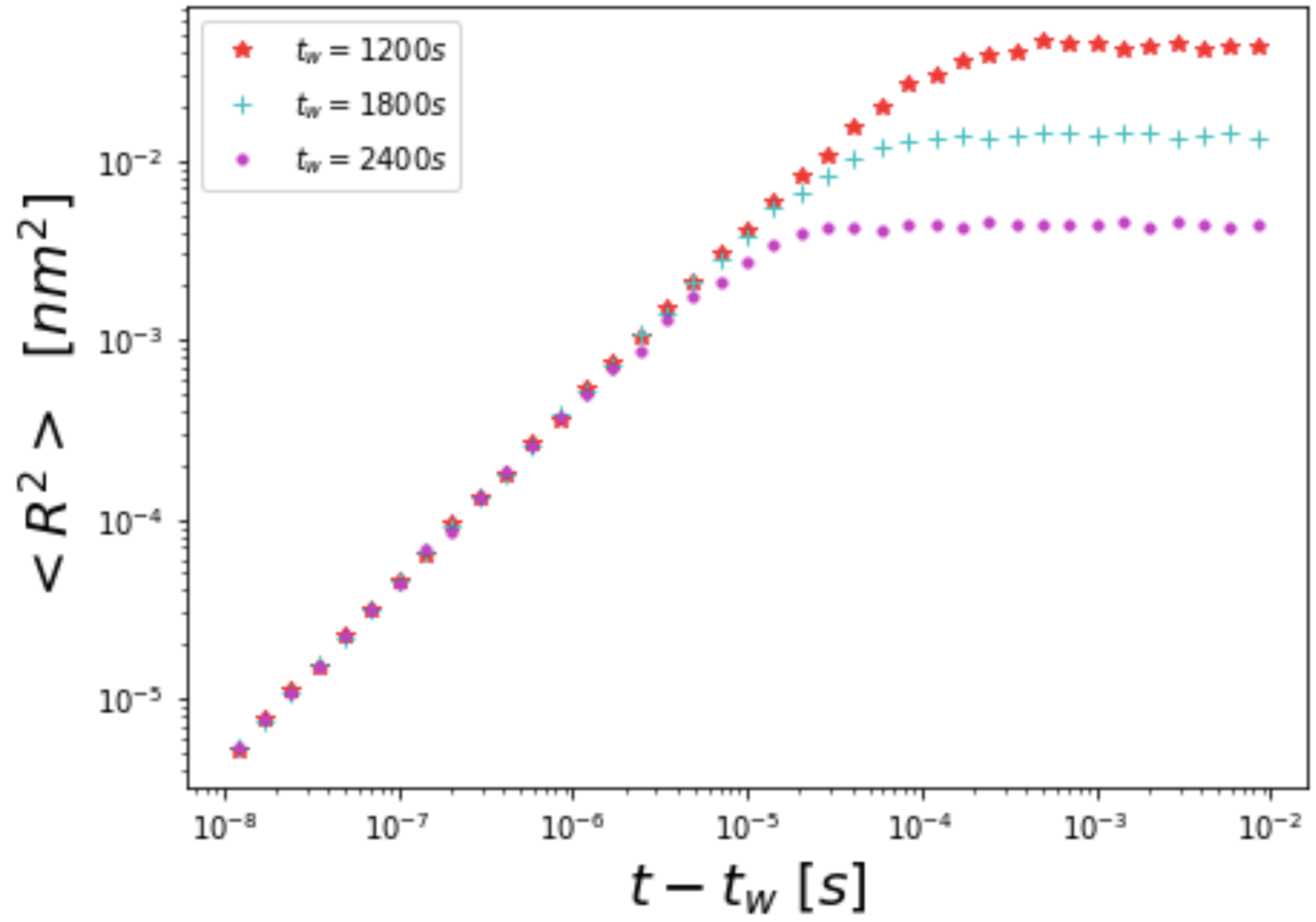
- Each simulation is for **60 second**. For each waiting time, in duration of 60 second, sample has not aged considerable. Or,

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

- Hence, system can be assumed to be temporally stationary for 60 second of simulation time.
- From here we are simulating the system for each waiting time for duration of 60 second like we do for non-ageing cases.

Case-I : Mean square displacement for different waiting time

- UDLT method
- $\Delta t \in [10^{-8}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$

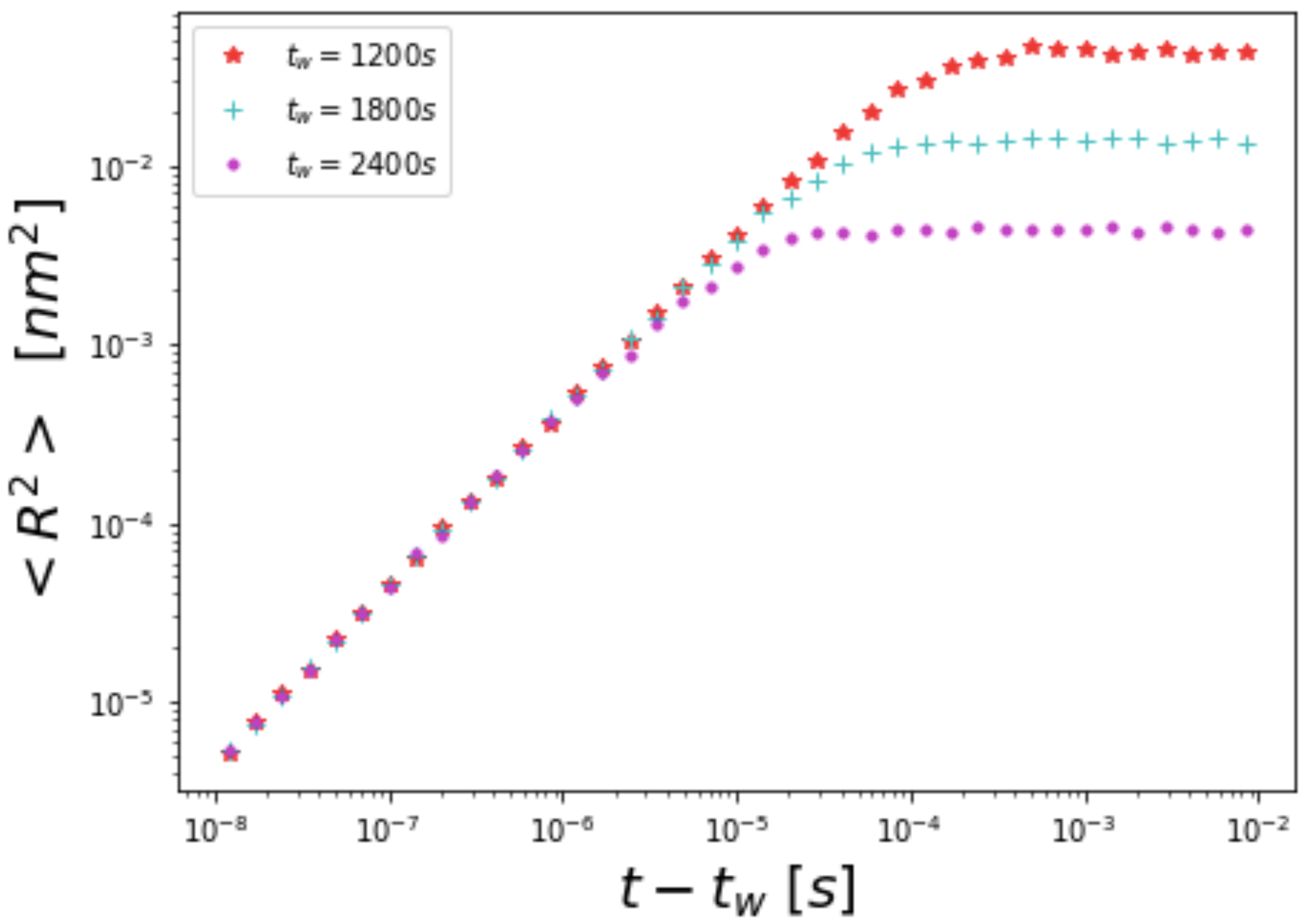


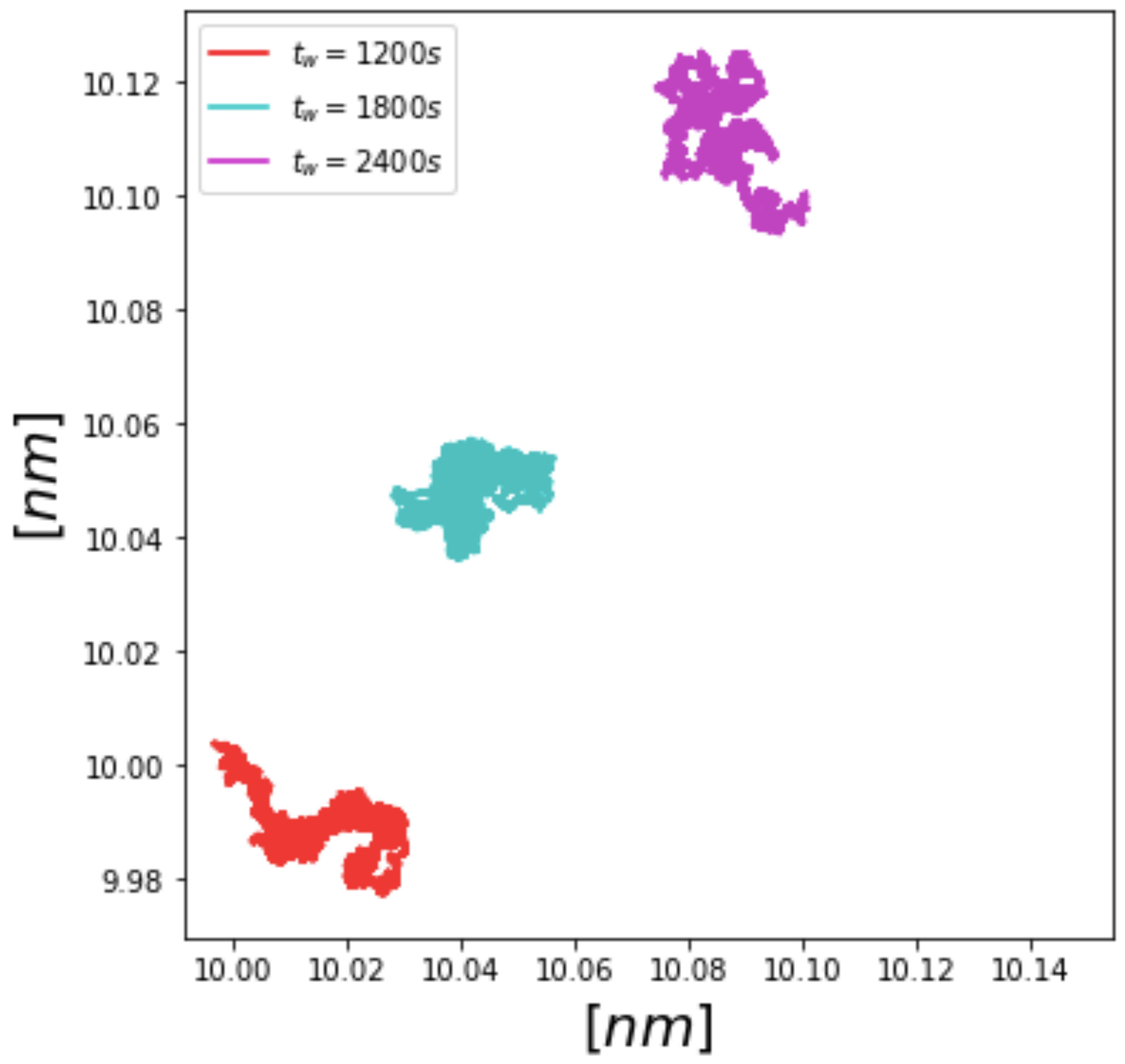
- Here, $t - t_w$ is used with sense of time-lag (τ).
- As material ages, -Plateau value decreases

  -Relaxation time decreases

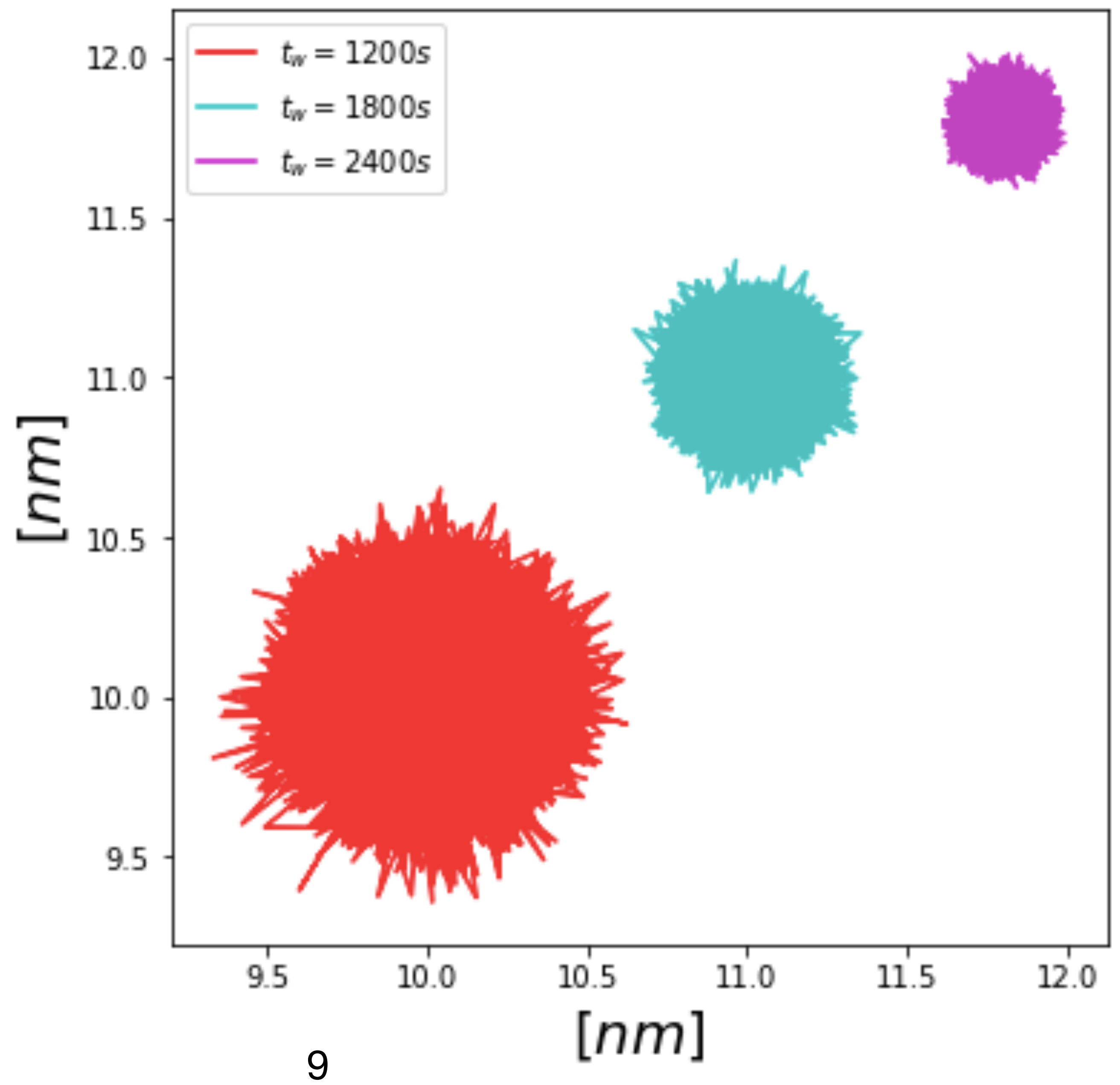
- Plateau value $\propto r_0^2 = \dfrac{k_B T}{6\pi a G(t)}$ (↓) as, $G(t)$ (↑).
- $\tau(t) \propto \dfrac{1}{G(t)}$ hence, $\tau(\downarrow)\ as\ G(t)\ (\uparrow)$.

Case-I : Mean square displacement and sub-trajectories





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

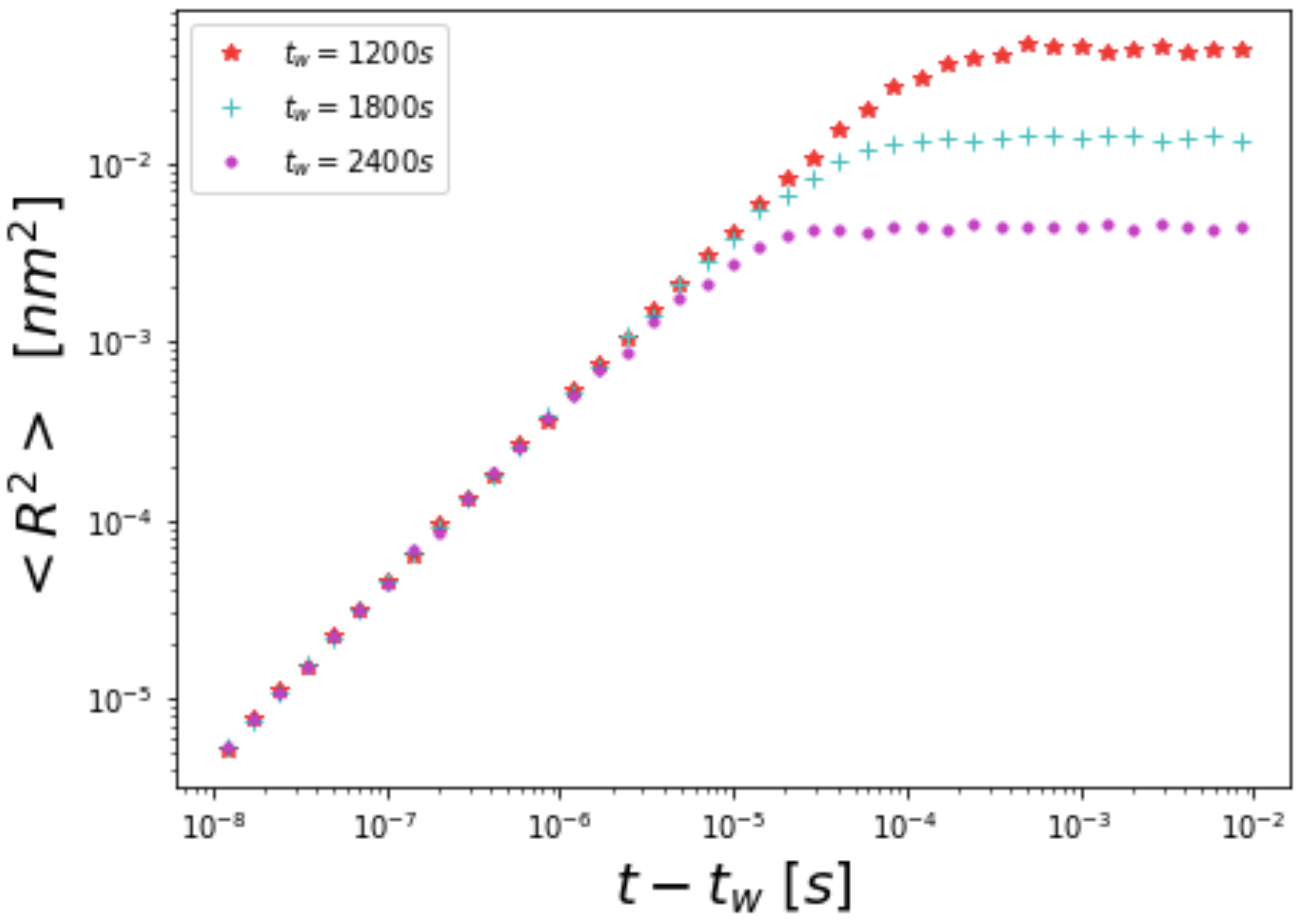


- $t_{max} = 10^{-2}s; No.\ of\ steps = 10^5$
- The extent of spread at each ageing time is different.
- This is due to ageing in elastic component of the material

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



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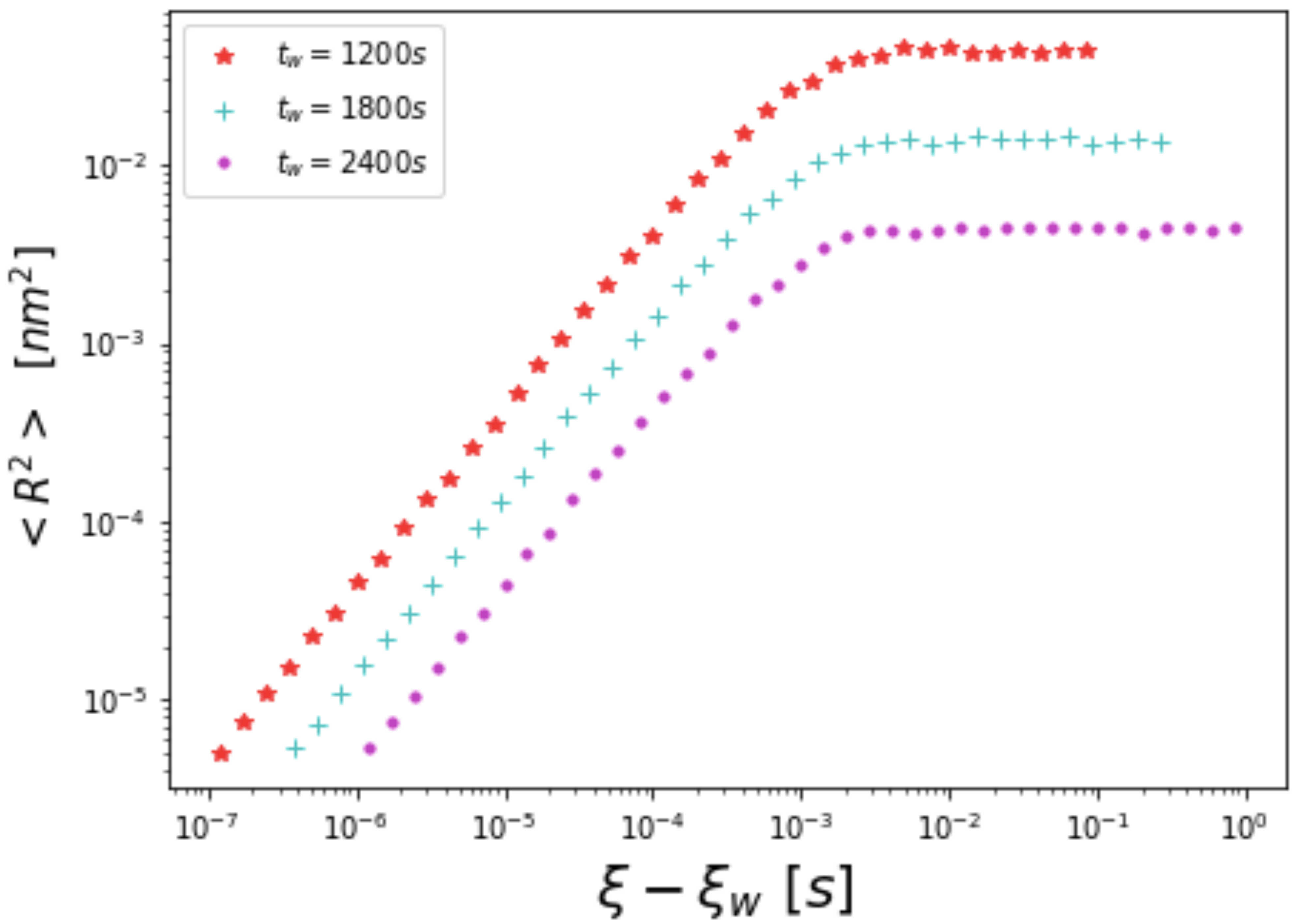


- Comparing both the graphs makes it clear that the time domain transformation horizontally shifts each MSD curve in such a way that in new time domain they have matching relaxation time.

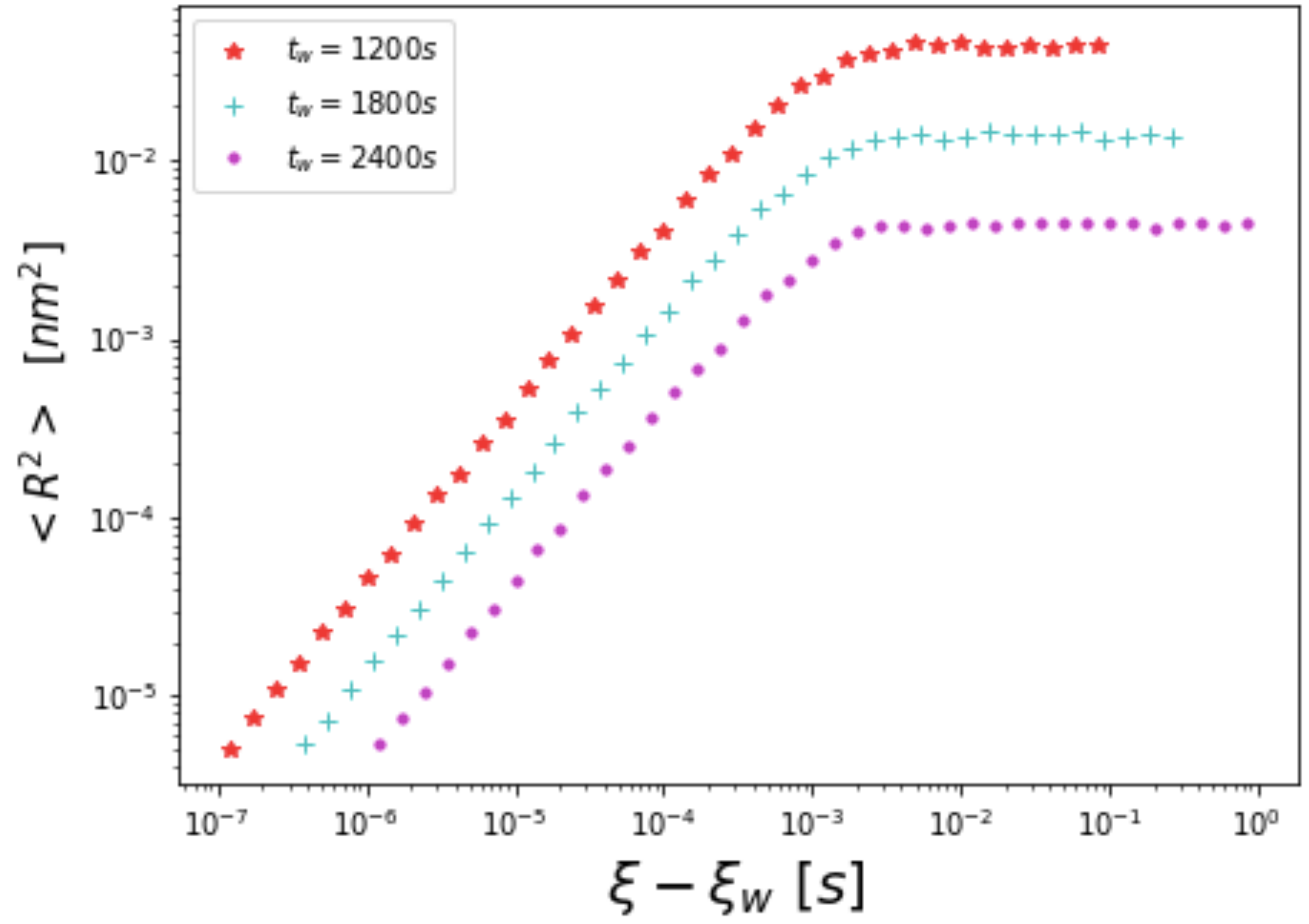
Case-I : Effective Time Translation (Continue…)

- 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 :-



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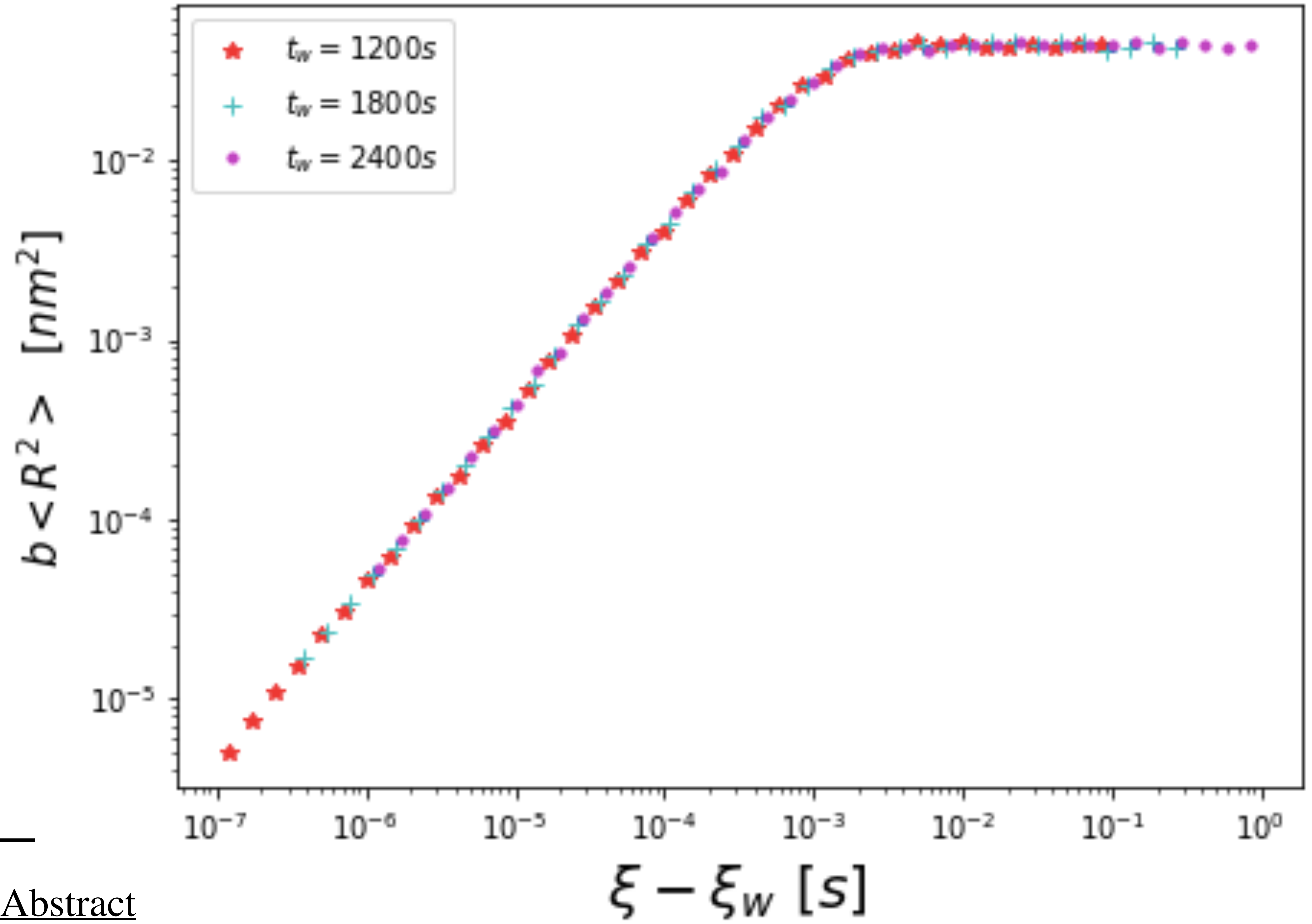


* Soft Matter, 2012, 8, 4171 : https://pubs.rsc.org/en/Content/ArticleLanding/SM/2012/C2SM07071E#!divAbstract

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 $\eta_0 = 10^{-3}Pa \cdot s \quad \Rightarrow \tau_0 = 10^{-6}[s]$

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

- We have taken three waiting time :

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

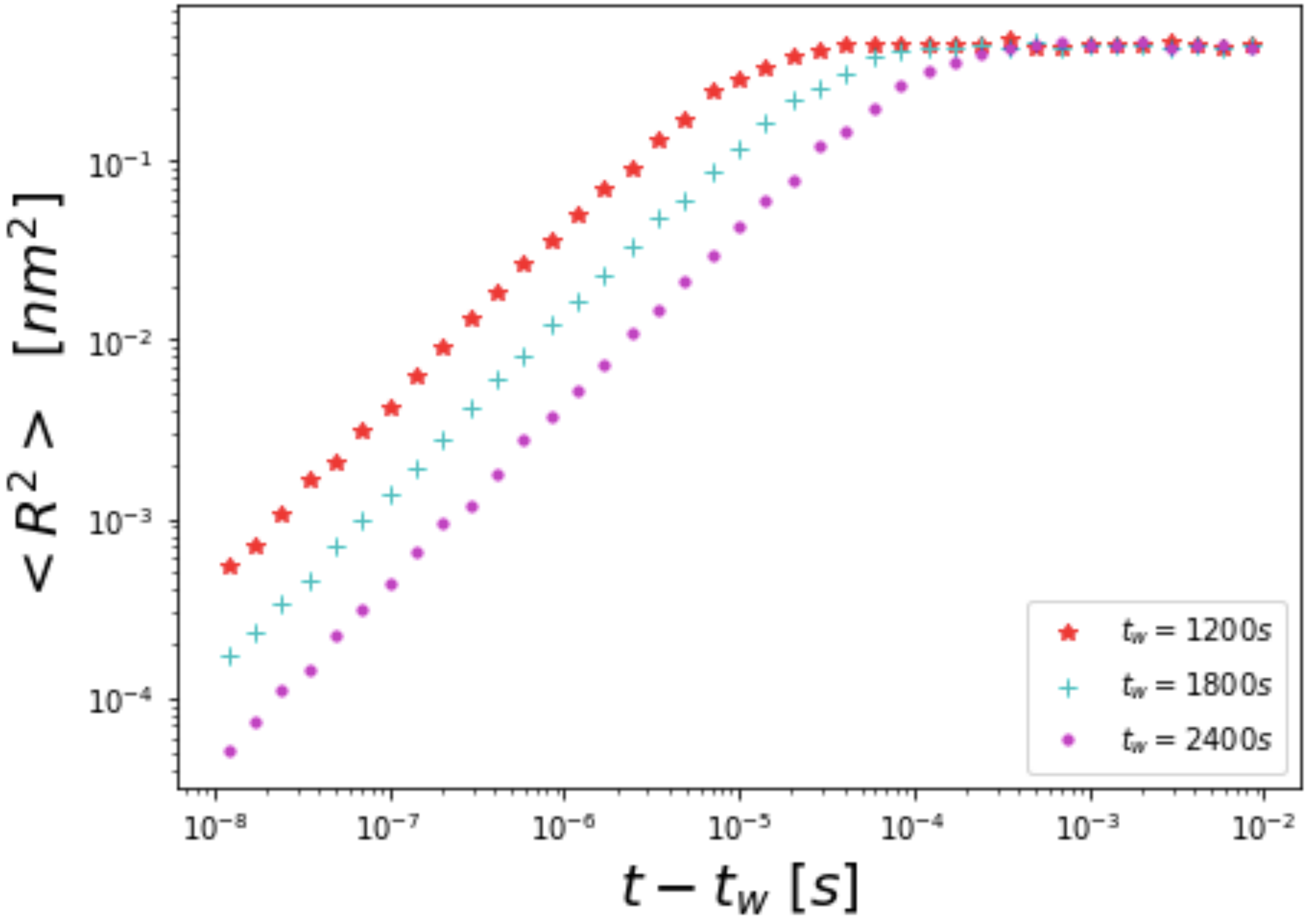
- Each simulation is for **60 second**. For each waiting time, in duration of 60 second, sample has not aged considerable. Or,

$$\frac{\eta(t_w + 60)\ -\ \eta(t_w)}{\eta(t_w)} \sim 0.2 \quad ; for\ all\ t_w$$

- Hence, system can be assumed to be temporally stationary for 60 second of simulation time.
- From here we are simulating the system for each waiting time for duration of 60 second like we do for non-ageing cases.

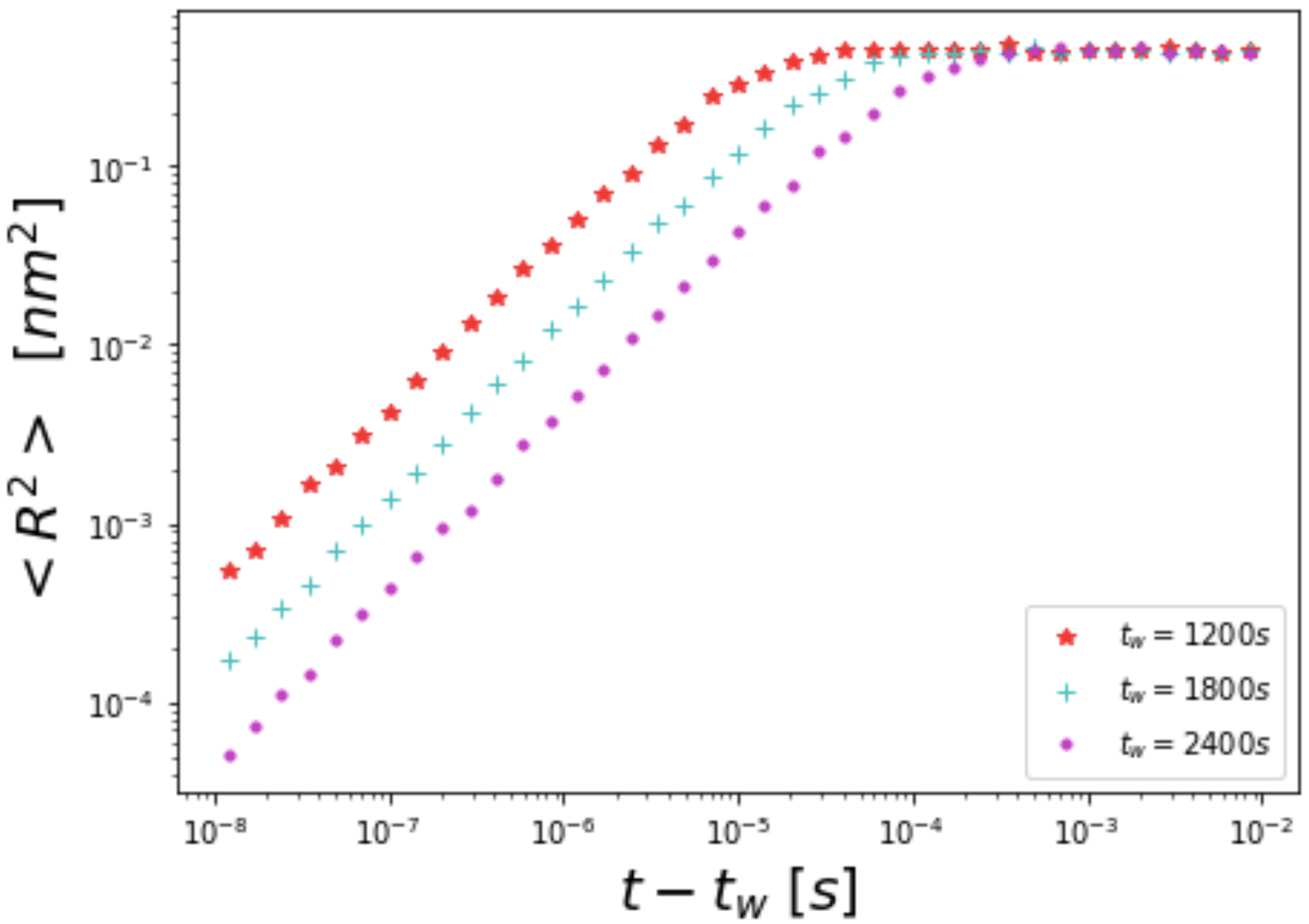
Case-II : Mean square displacement

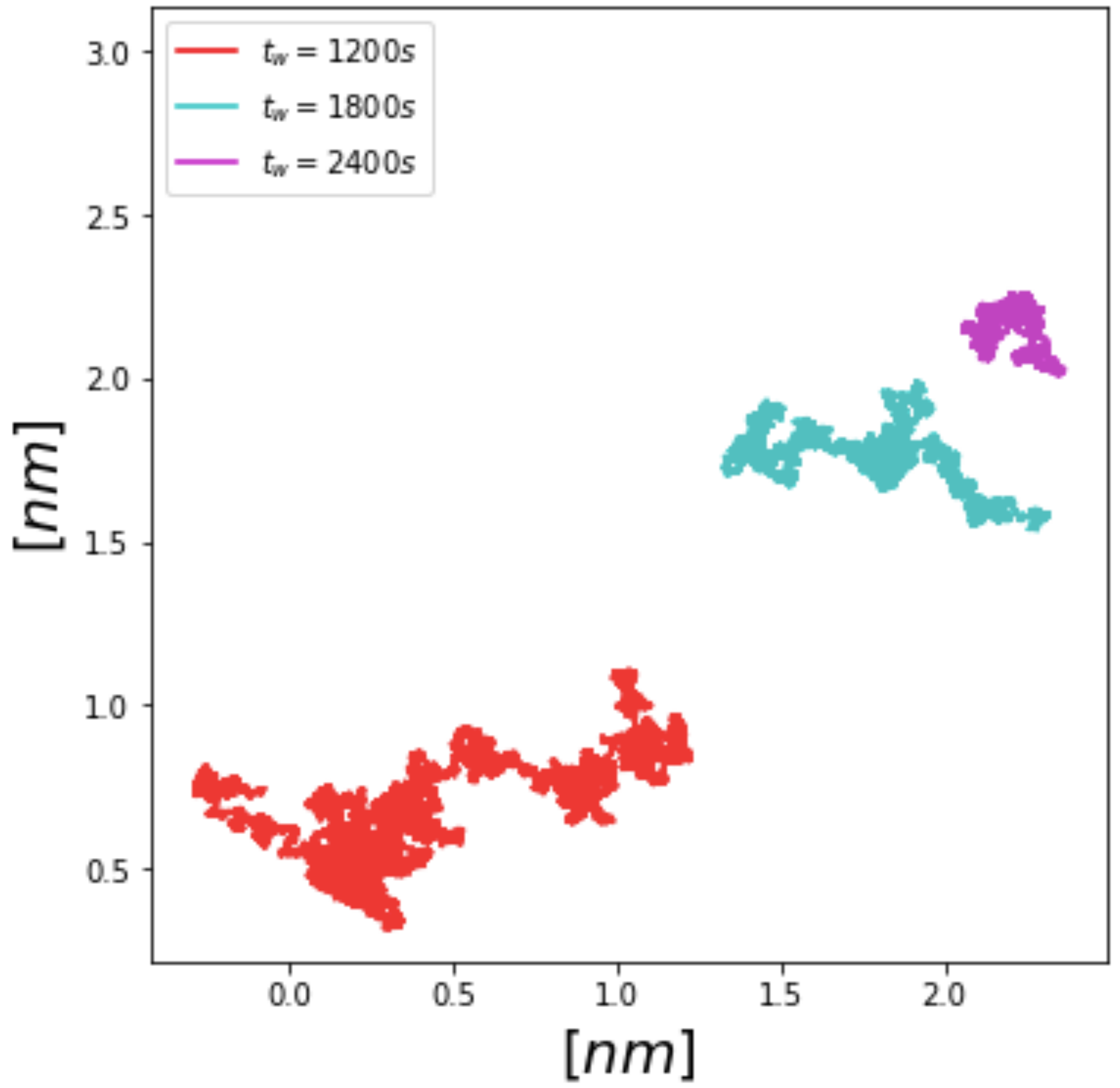
- UDLT method
- $\Delta t \in [10^{-8}, 10^{-2}]$ sec ; $t_{max} = 60sec$



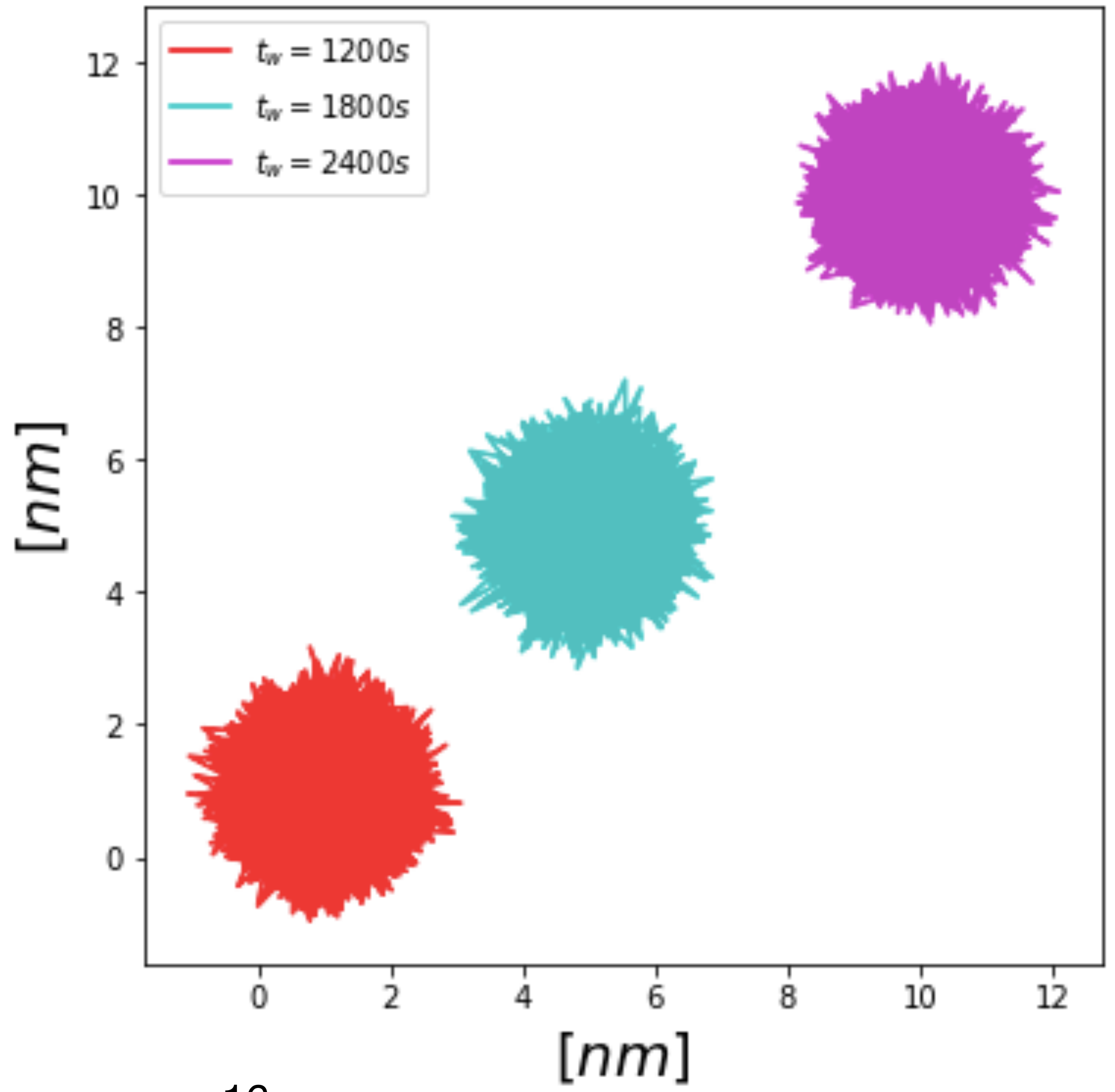
- Here, $t - t_w$ is used in sense of time-lag (τ).
- As material ages, -Plateau value remain same
  -Relaxation time increases
- Plateau value = $r_0^2 = \dfrac{k_B T}{6\pi a G_0}$ $(is\ constant)$ as, G_0 $[is\ constant]$.
- $\tau(t) \propto \eta(t)$ hence, $\tau(\uparrow)\ as\ \eta(t)\ (\uparrow)$.

Case-II : Mean square displacement and sub-trajectories





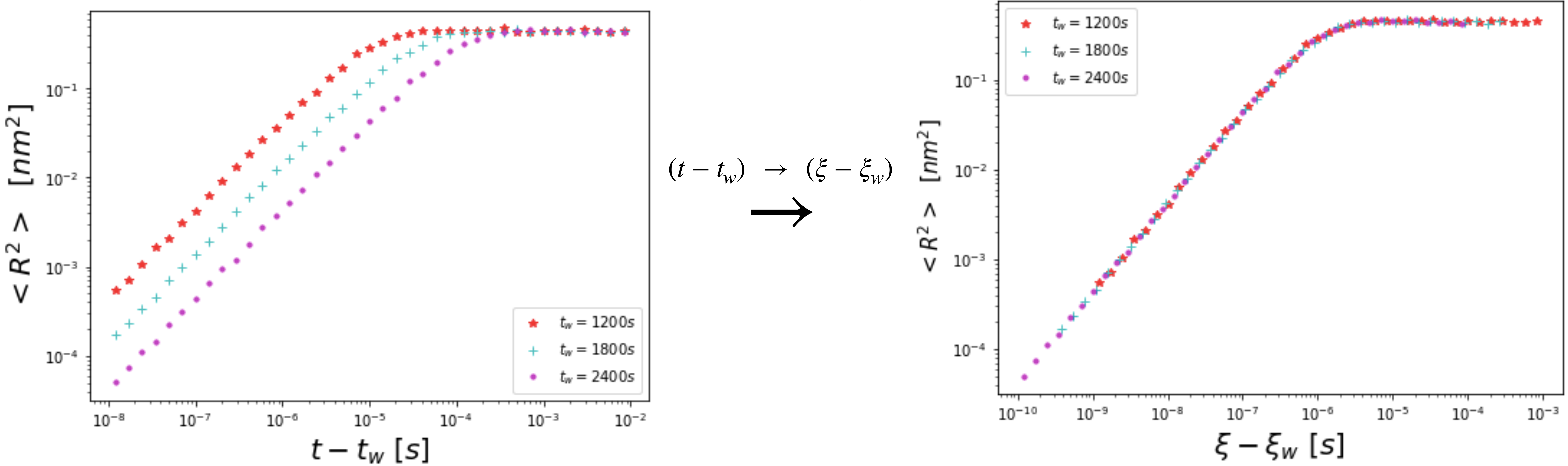
- $t_{max} = 10^{-5}s; No.\ of\ steps = 10^5$
- The extent of spread at each ageing time is different.
- This is due to ageing in viscous component of the material.



- $t_{max} = 10^{-2}s; No.\ of\ steps = 10^5$
- The extent of spread at each ageing time is same.
- 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, $\tau(t) = \tau_0 \cdot exp(\alpha \cdot t) \Rightarrow \xi - \xi_w = \dfrac{exp(-\alpha \cdot t_w) - exp(-\alpha \cdot t)}{\alpha}$



- 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, $b_{t_w=1200s} = b_{t_w=1800s} = b_{t_w=2400s} = 1.$

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 : $G_0 = 1000Pa$ 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,

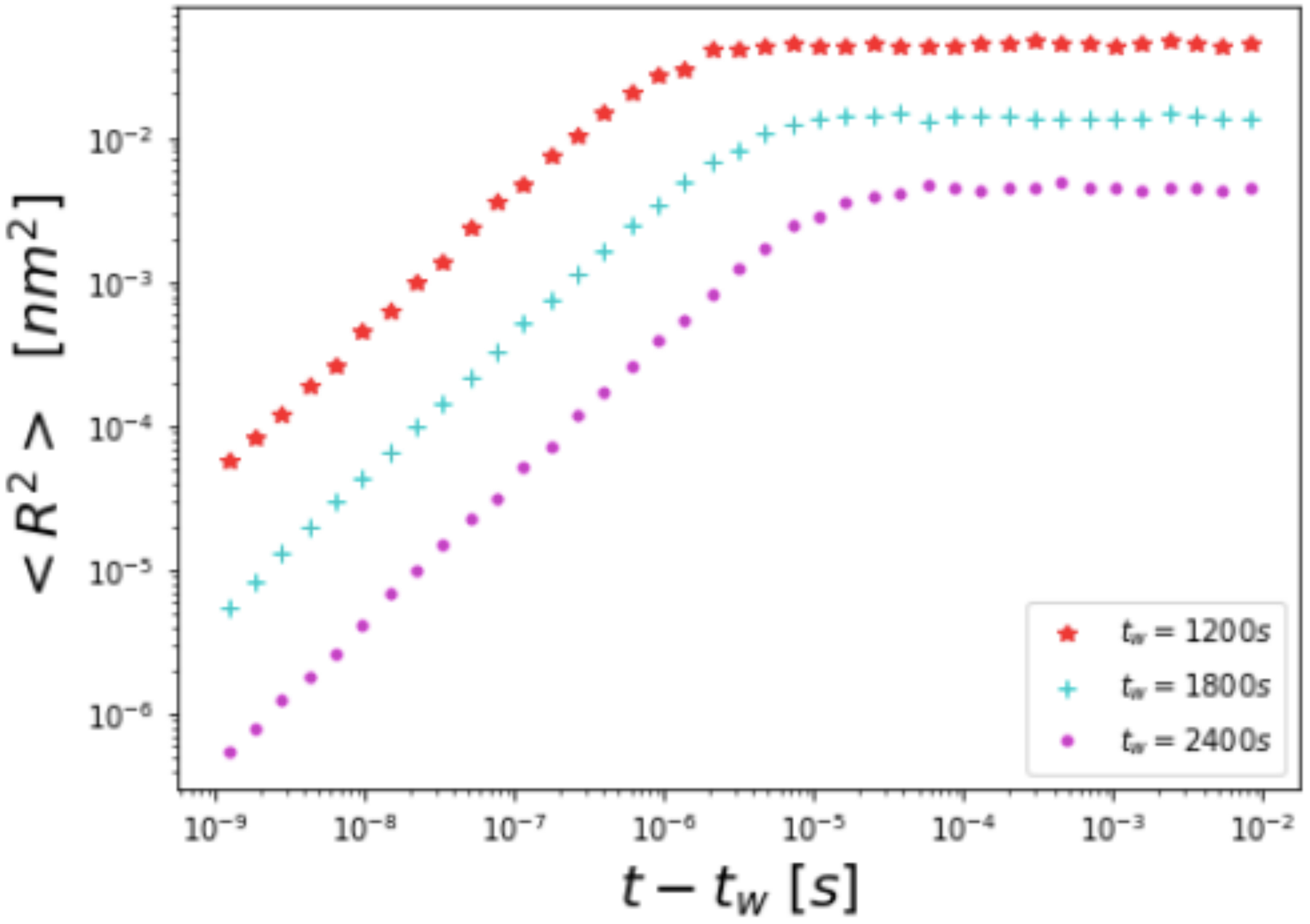
$$\frac{\eta(t_w + 60)\ -\ \eta(t_w)}{\eta(t_w)} \sim 0.1 \quad ; for\ all\ t_w$$

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

- Hence, system can be assumed to be temporally stationary for 60 second of simulation time.
- From here we are simulating the system for each waiting time for duration of 60 second like we do for non-ageing cases.

Case-III : Mean square displacement

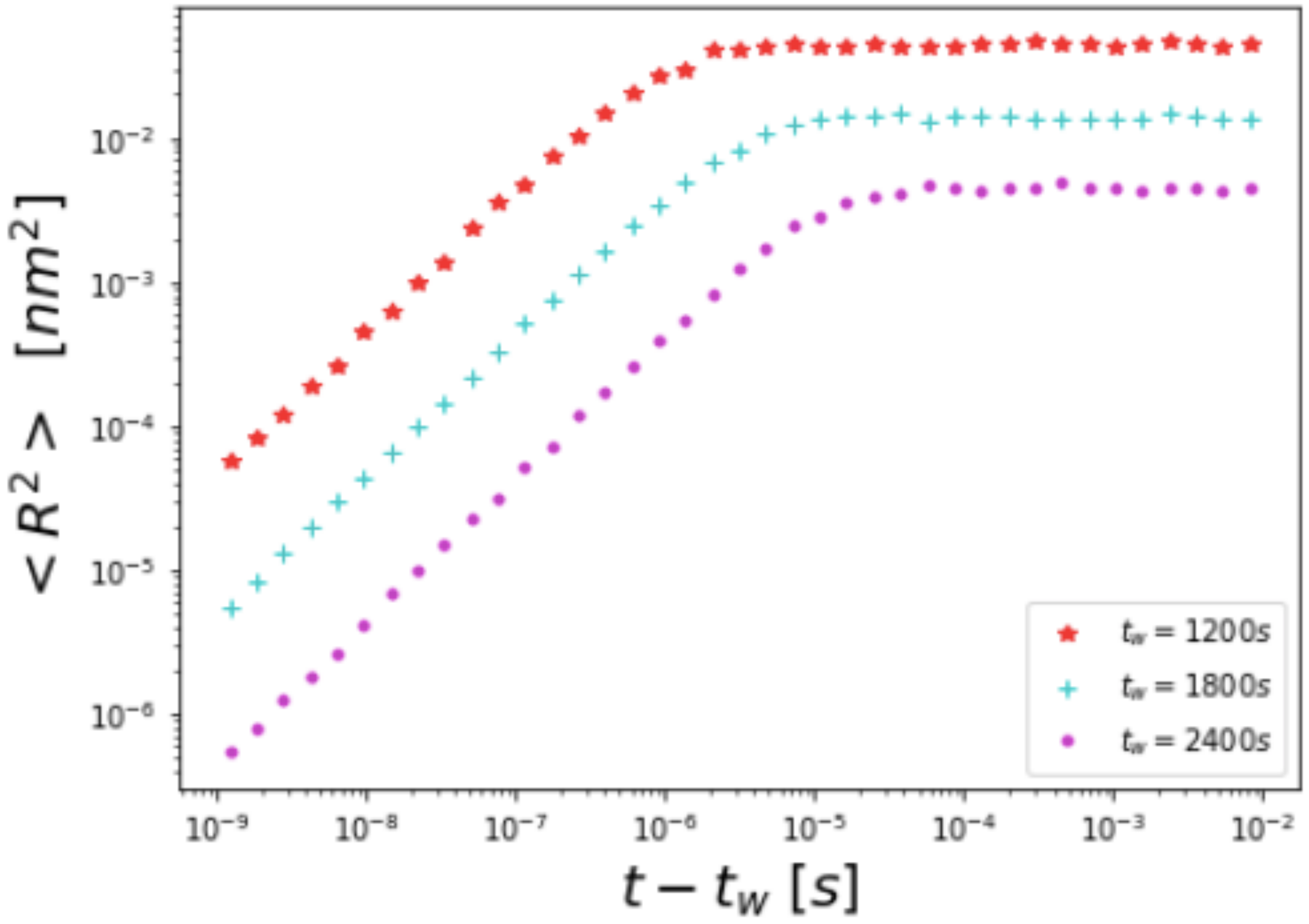
- UDLT method
- $\Delta t \in [10^{-8}, 10^{-2}]\ sec\ ; t_{max} = 60 sec$
-

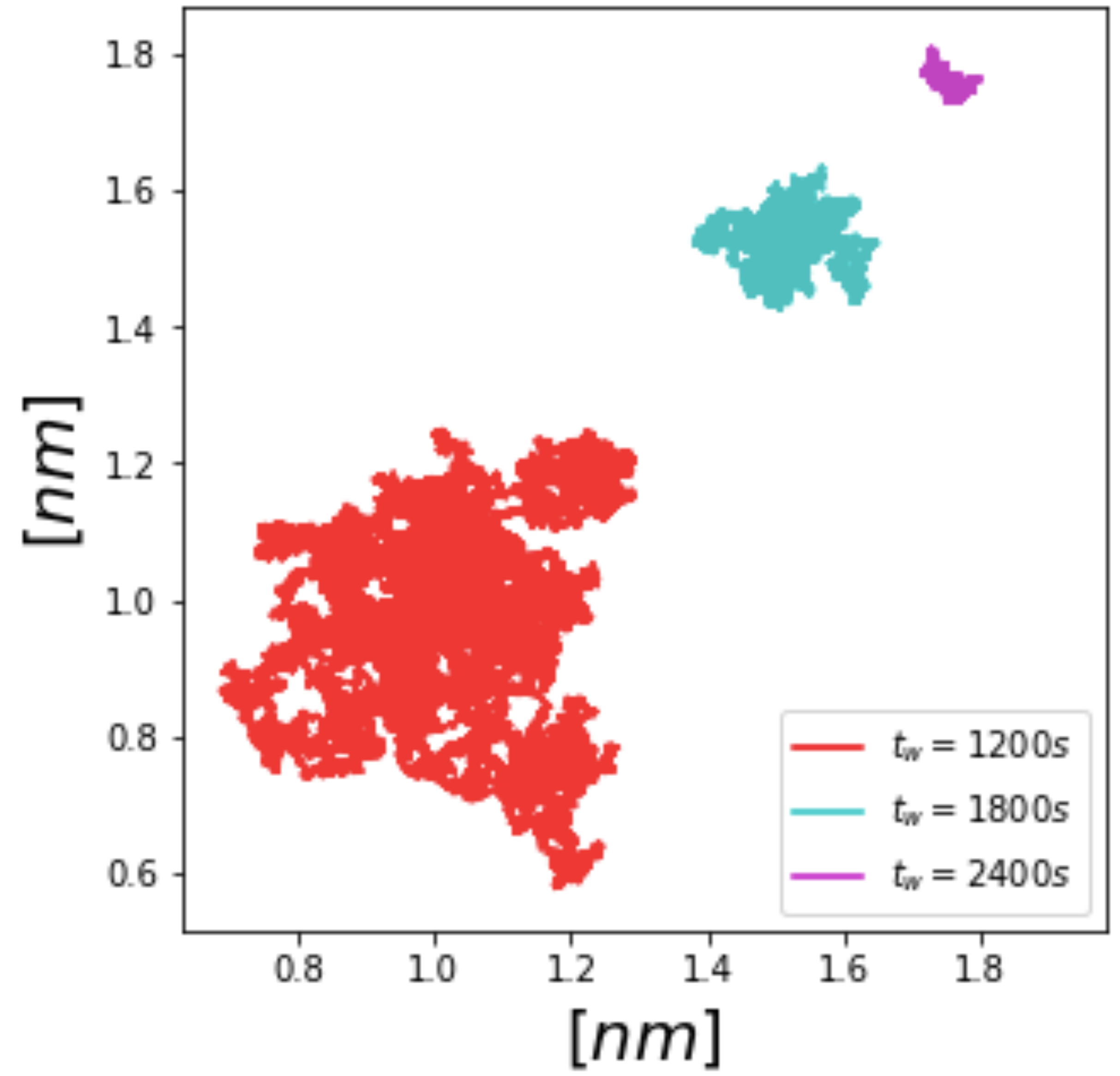


- Here, $t - t_w$ is used in sense of time-lag (τ).
- As material ages, -Plateau value decreases

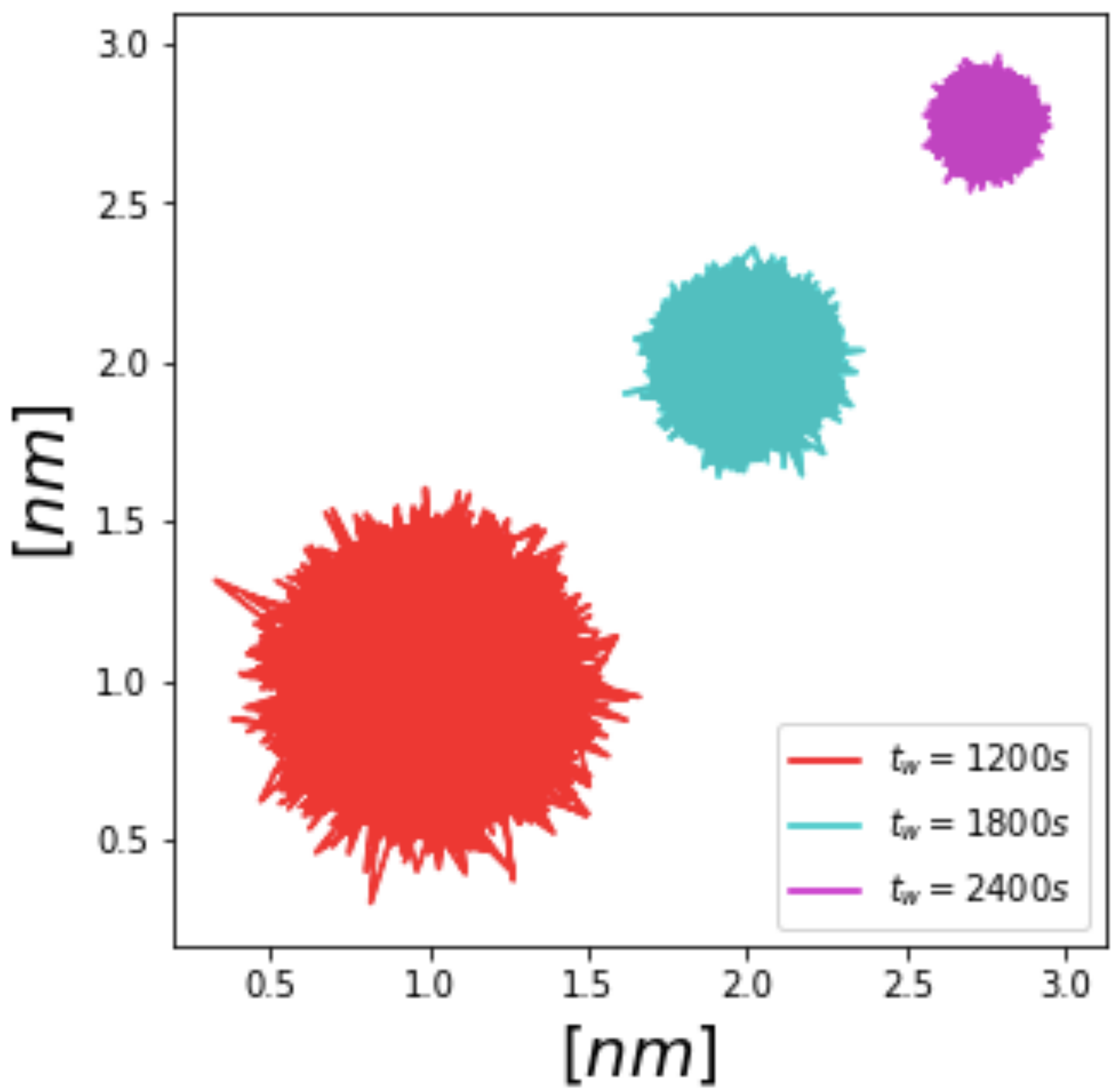
  -Relaxation time increases
- Plateau value $\propto r_0^2 = \dfrac{k_B T}{6\pi a G(t)}$ (↓) as, $G(t)$ (↑).
- $\tau(t) \propto \eta(t)$ hence, $\tau($ ↑ $)\ as\ \eta(t)$ (↑).

Case-III : Mean square displacement and sub-trajectory





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

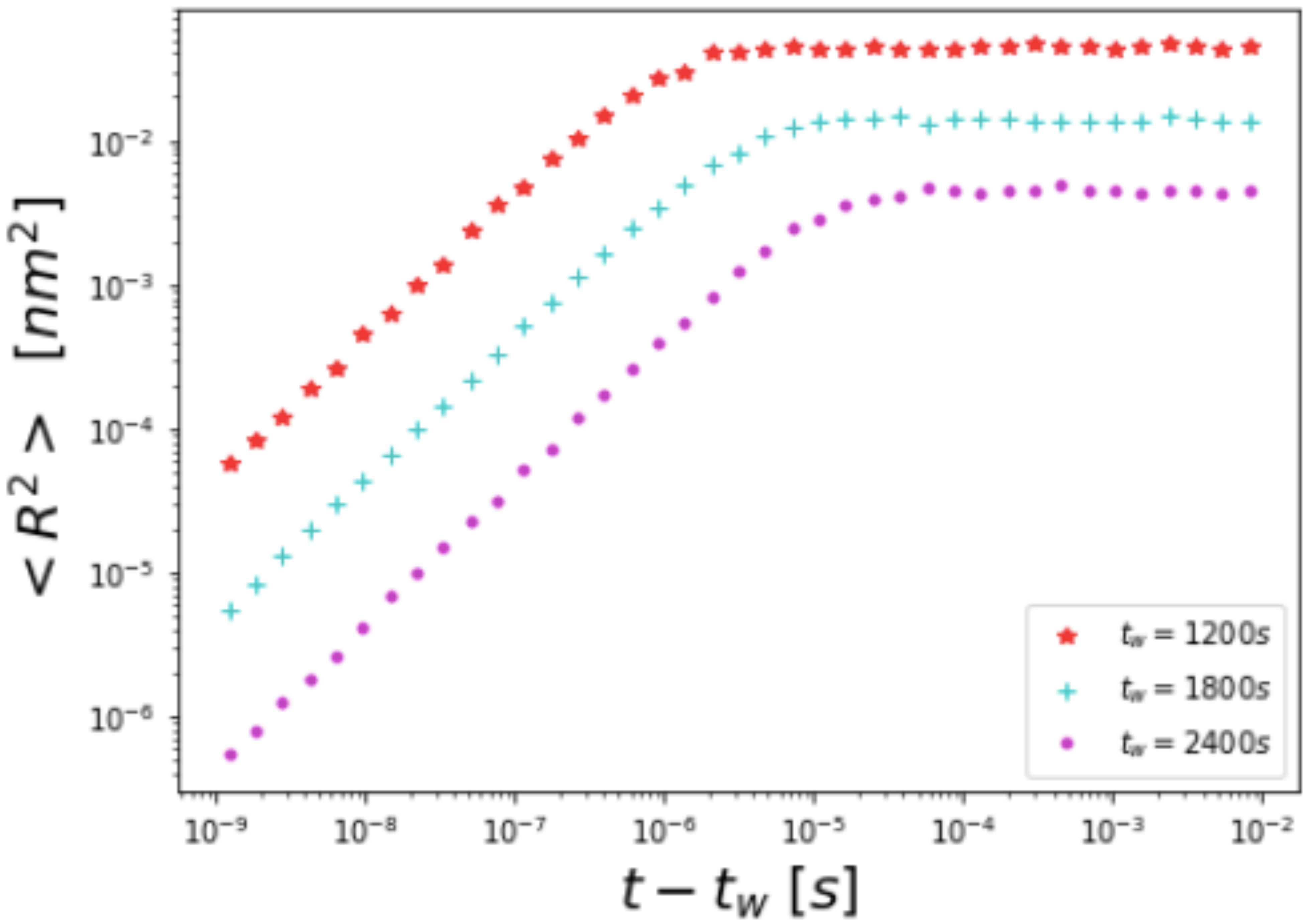


- $t_{max} = 10^{-2}s; No.\ of\ steps = 10^5$
- The extent of confinement at each ageing time is decreasing with time.
- This is due to ageing in elastic component of the material.

Case-III : Effective Time Tranformation(ETT)

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

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



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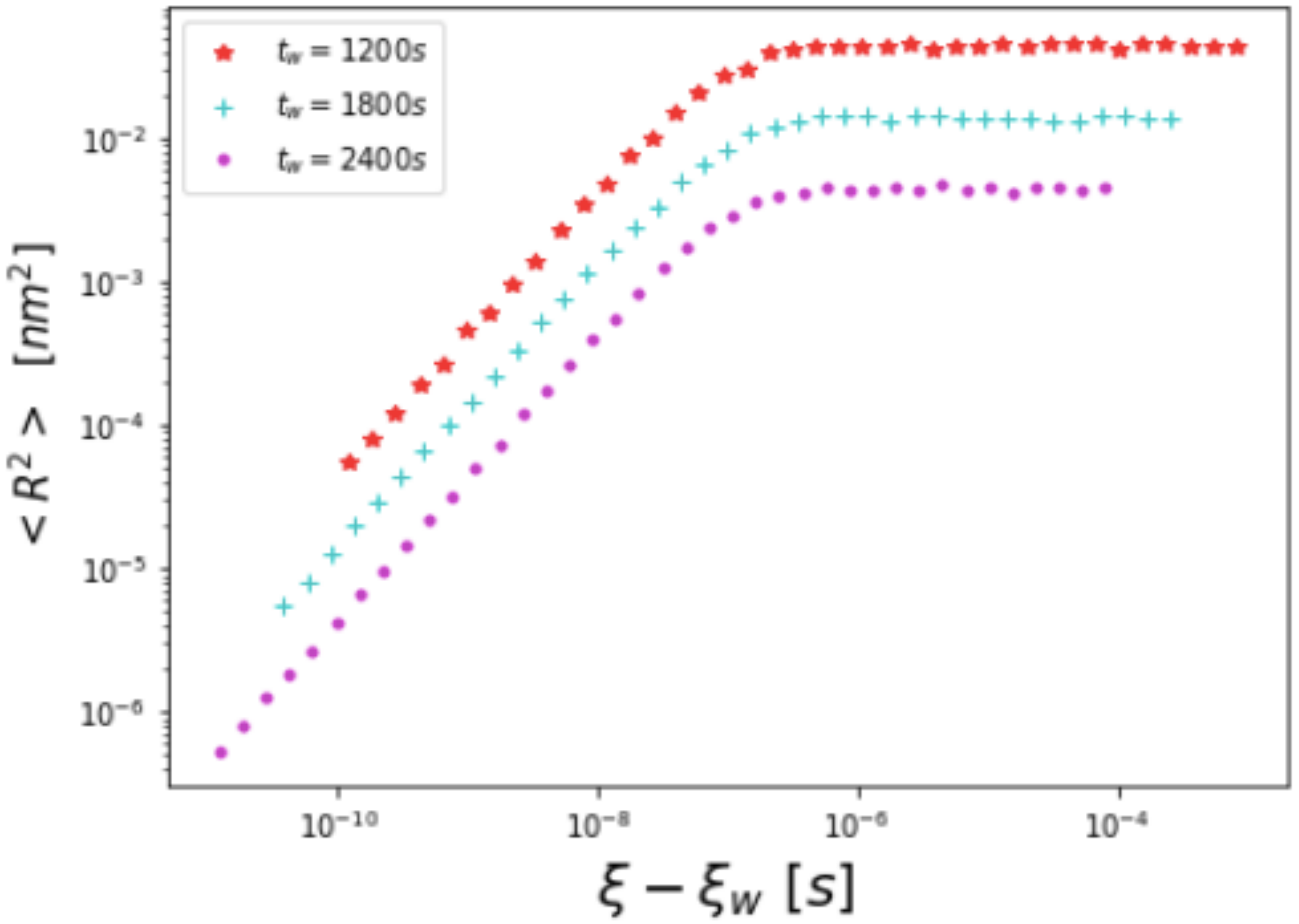


- Comparing both the graphs makes it clear that the time domain transformation horizontally shifts each MSD curve in such a way that in new time domain they have matching relaxation time.

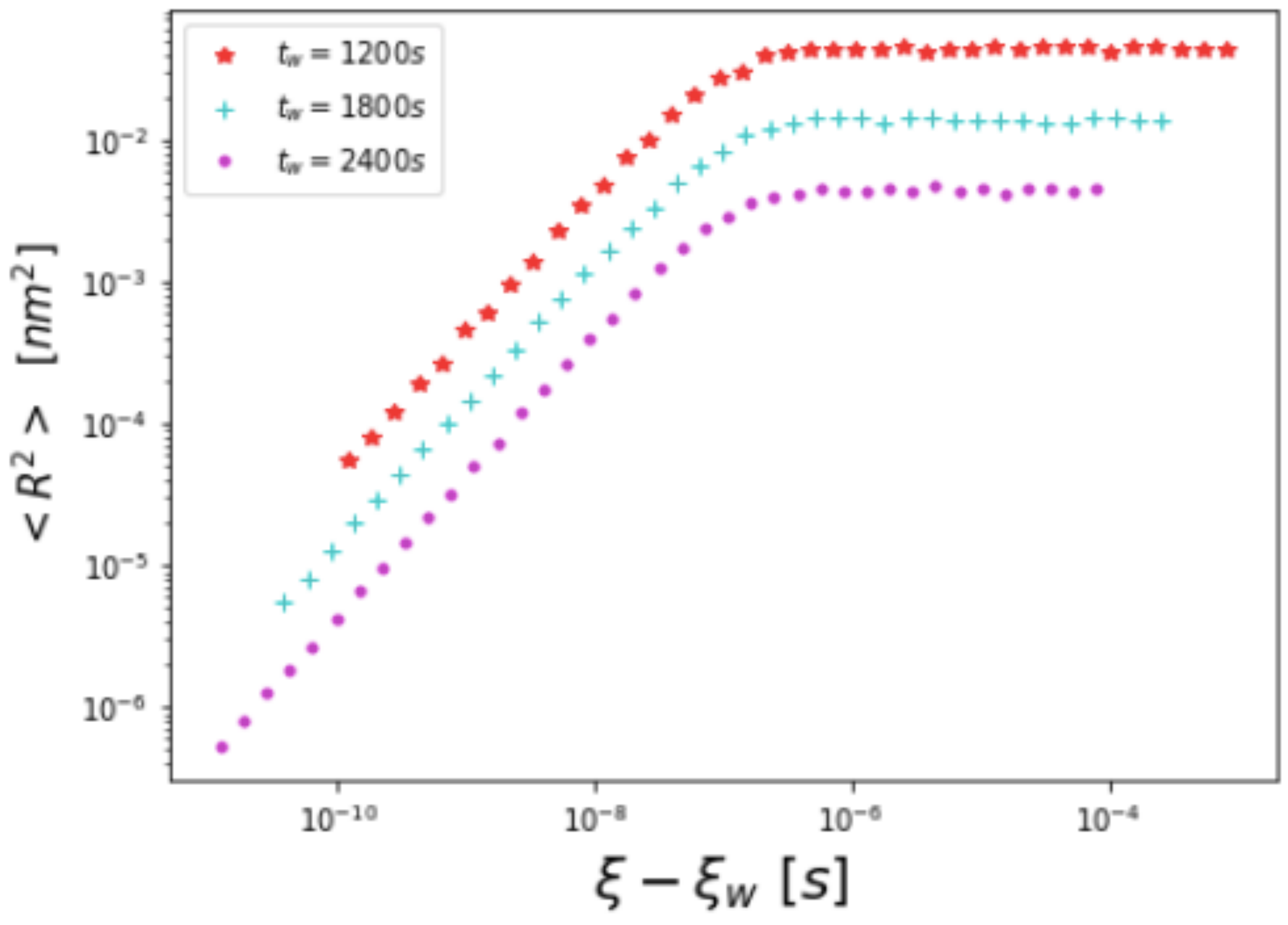
Case-III : Effective Time Translation (Continue…)

- 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 :-



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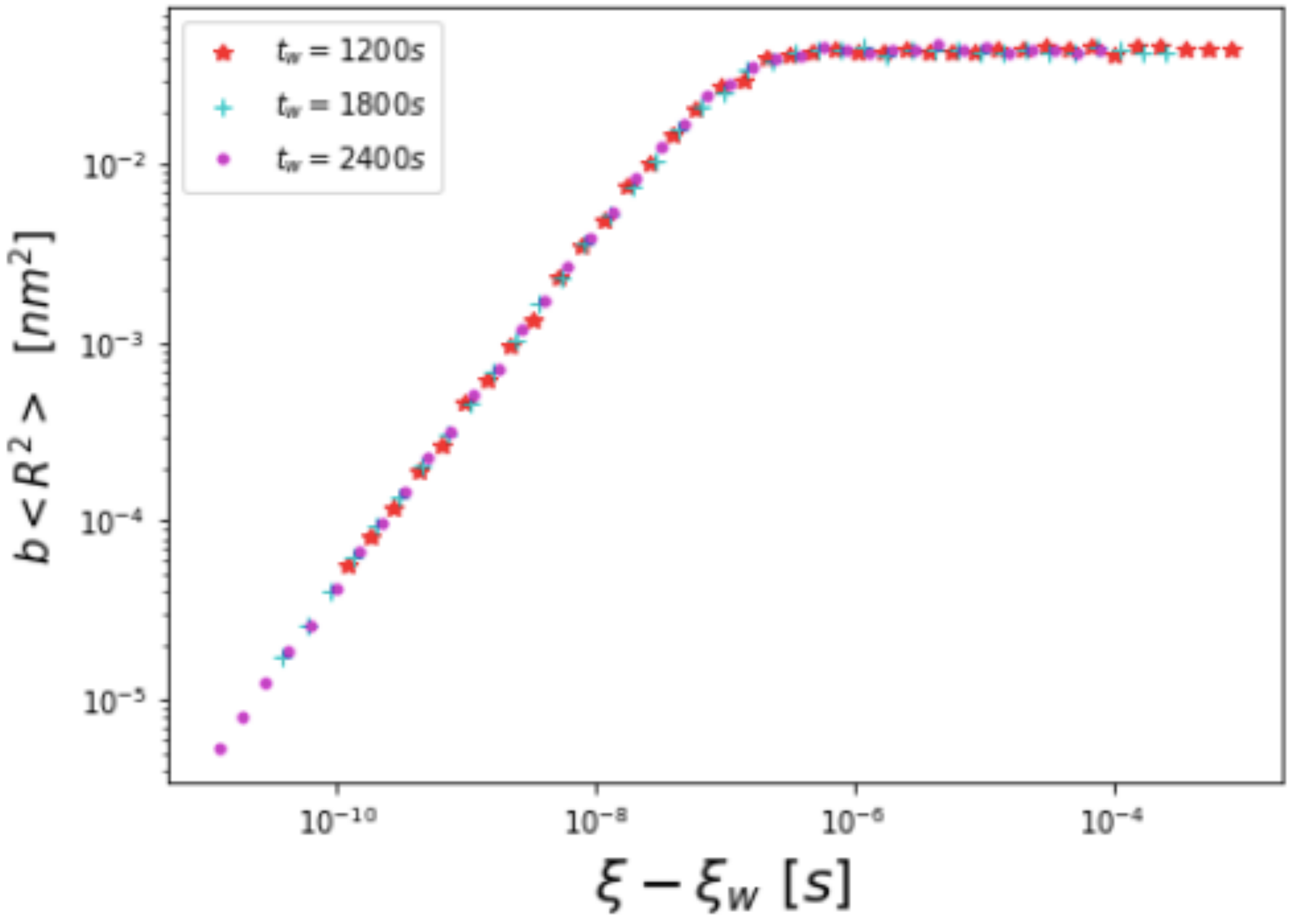
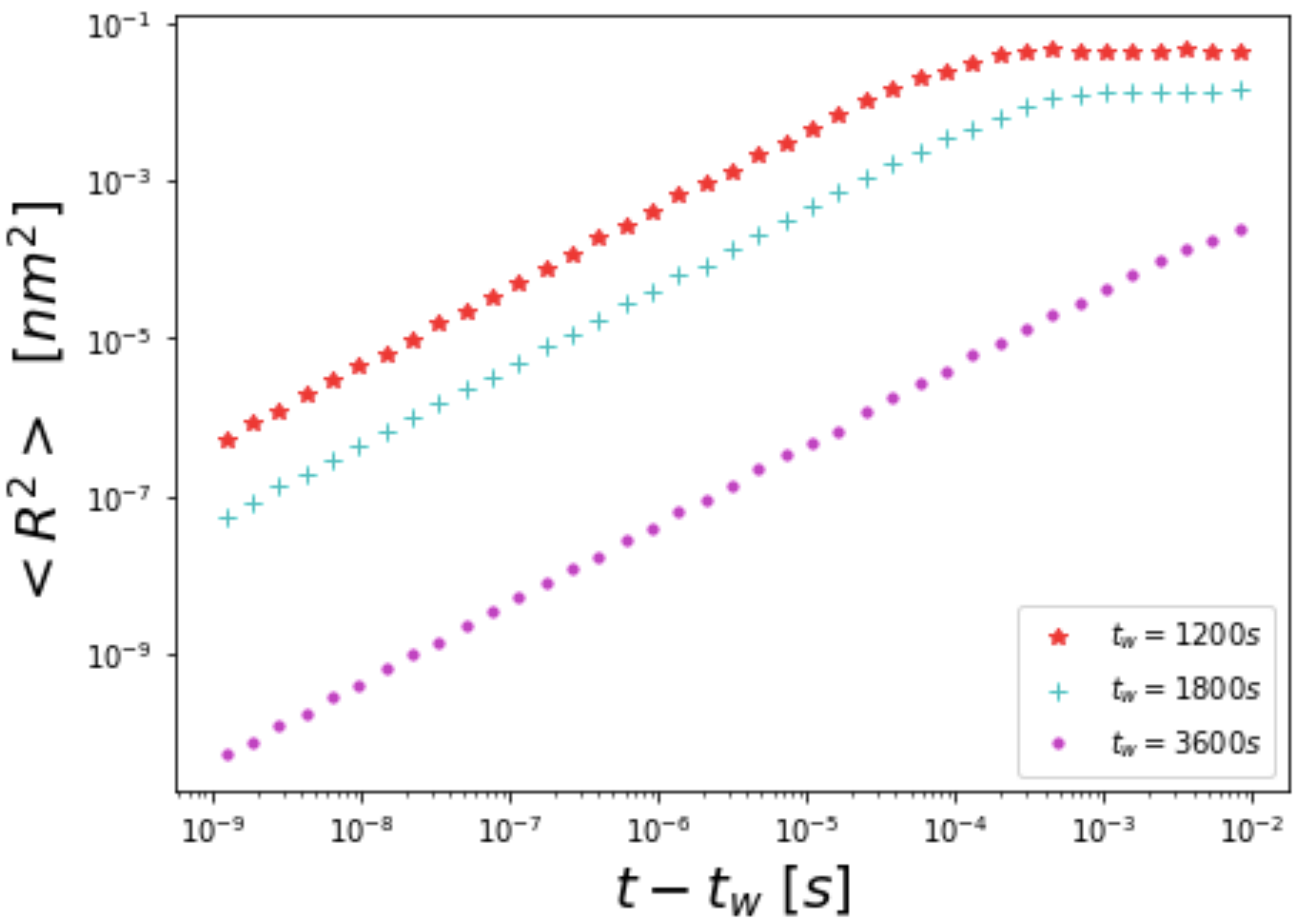


Prediction of long term MSD behaviour using ETT

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

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

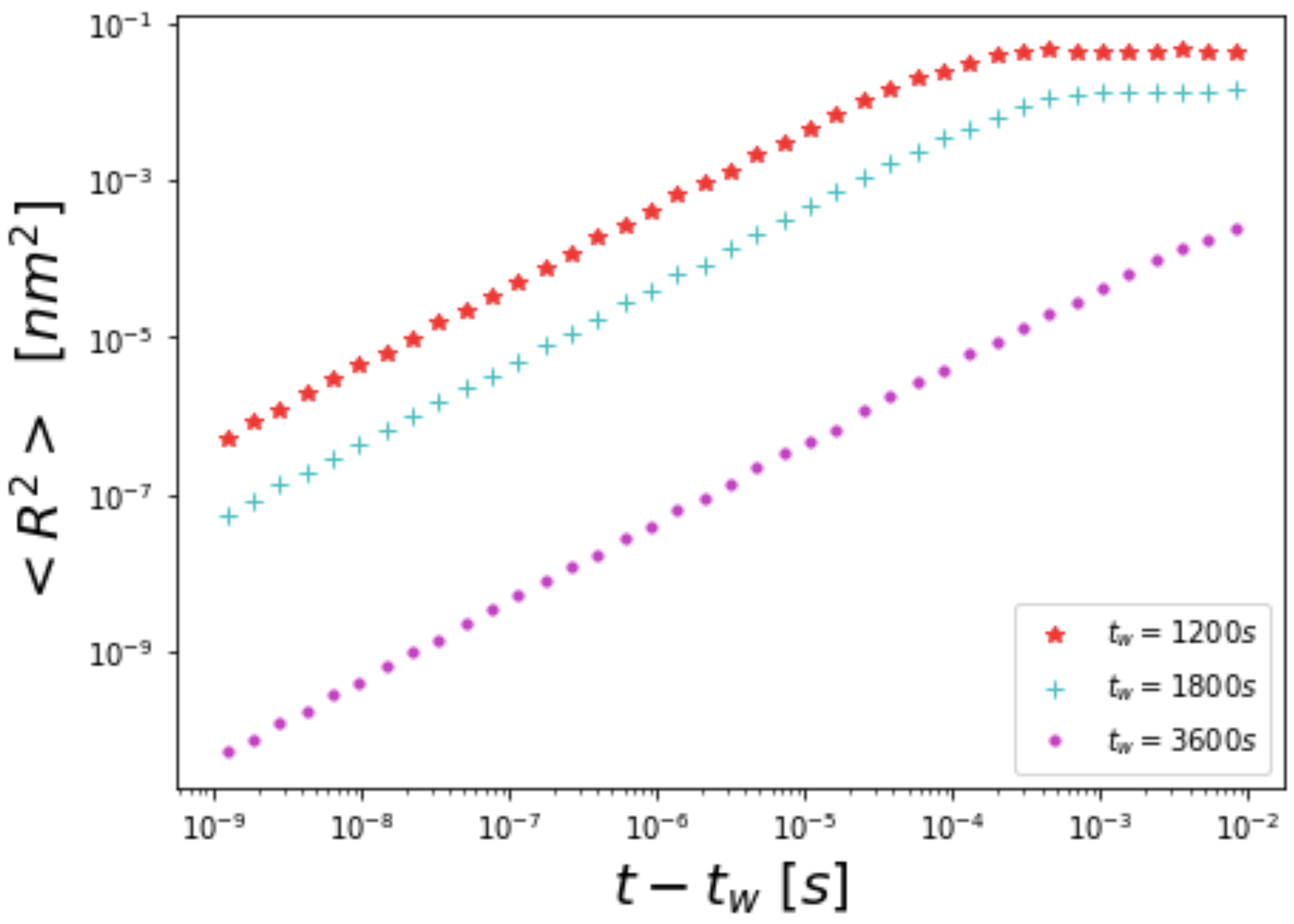
- For above scenario we get following MSD in real time domain:



- 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 slide.

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.*



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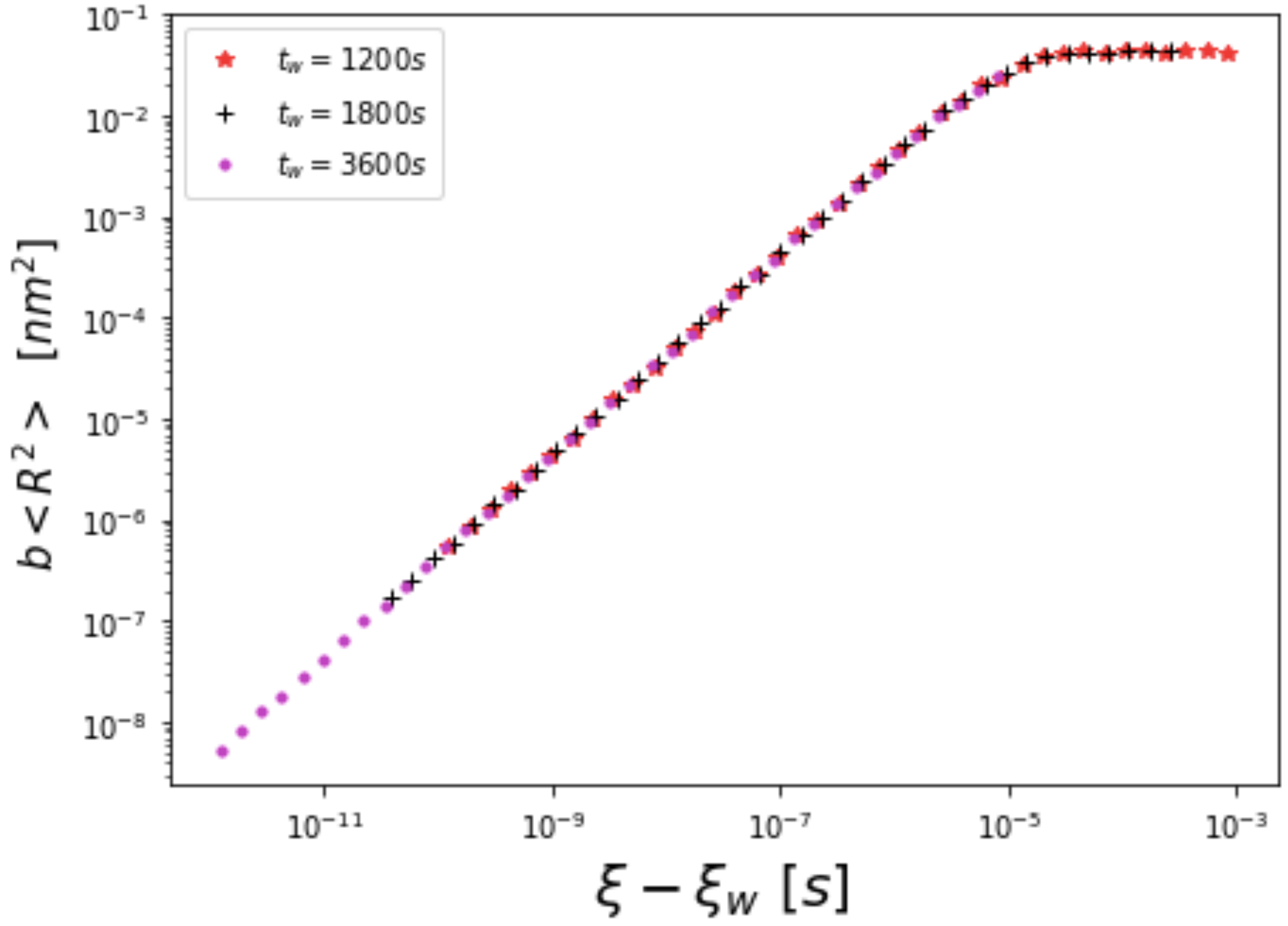
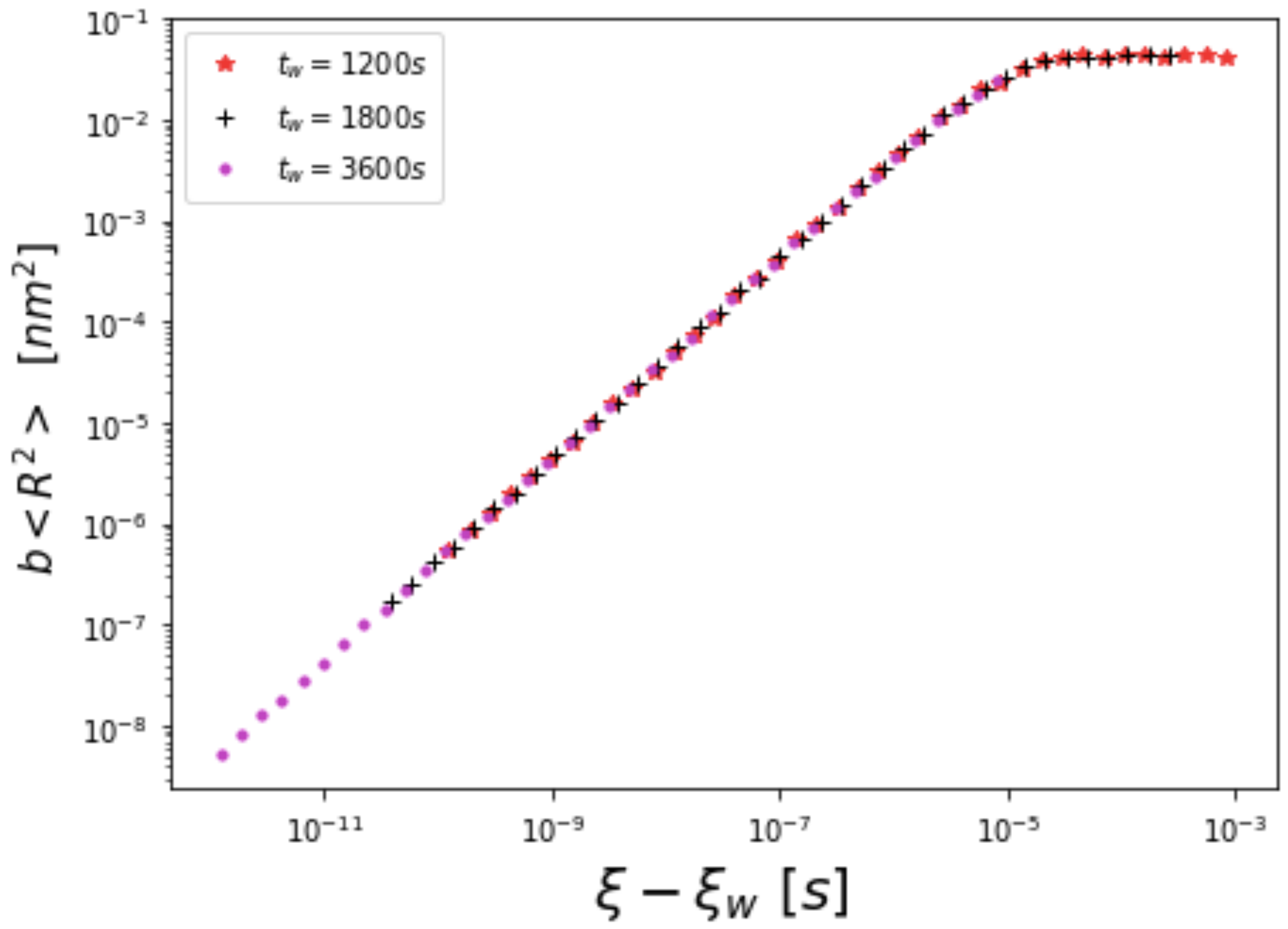


Inverse Transformation from Effective Time Domain of MSD data

- 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 :

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



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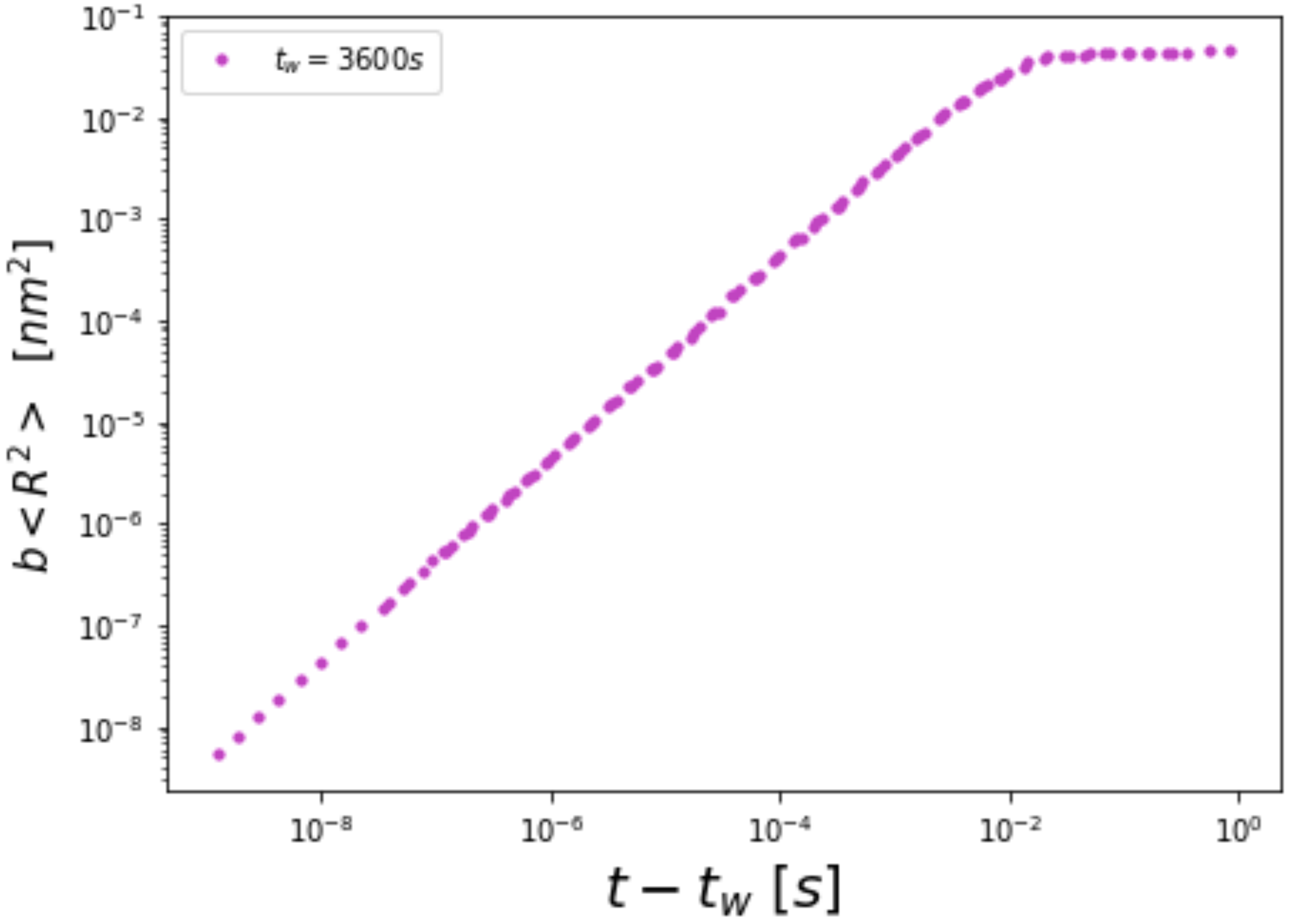
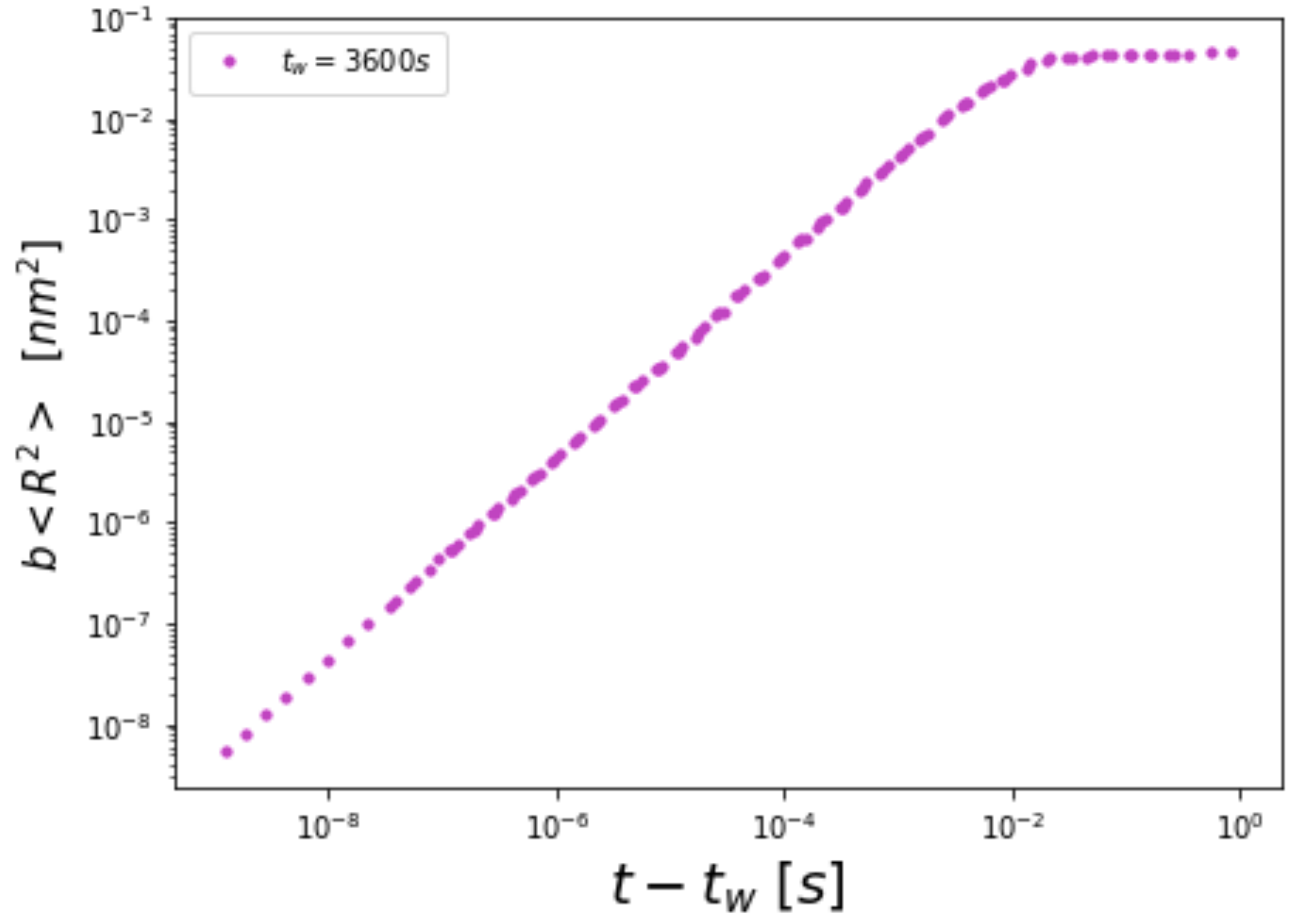


Adjustment using Vertical Shift factor to retrieve the MSD curve

- 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 $t_w = 3600s$.



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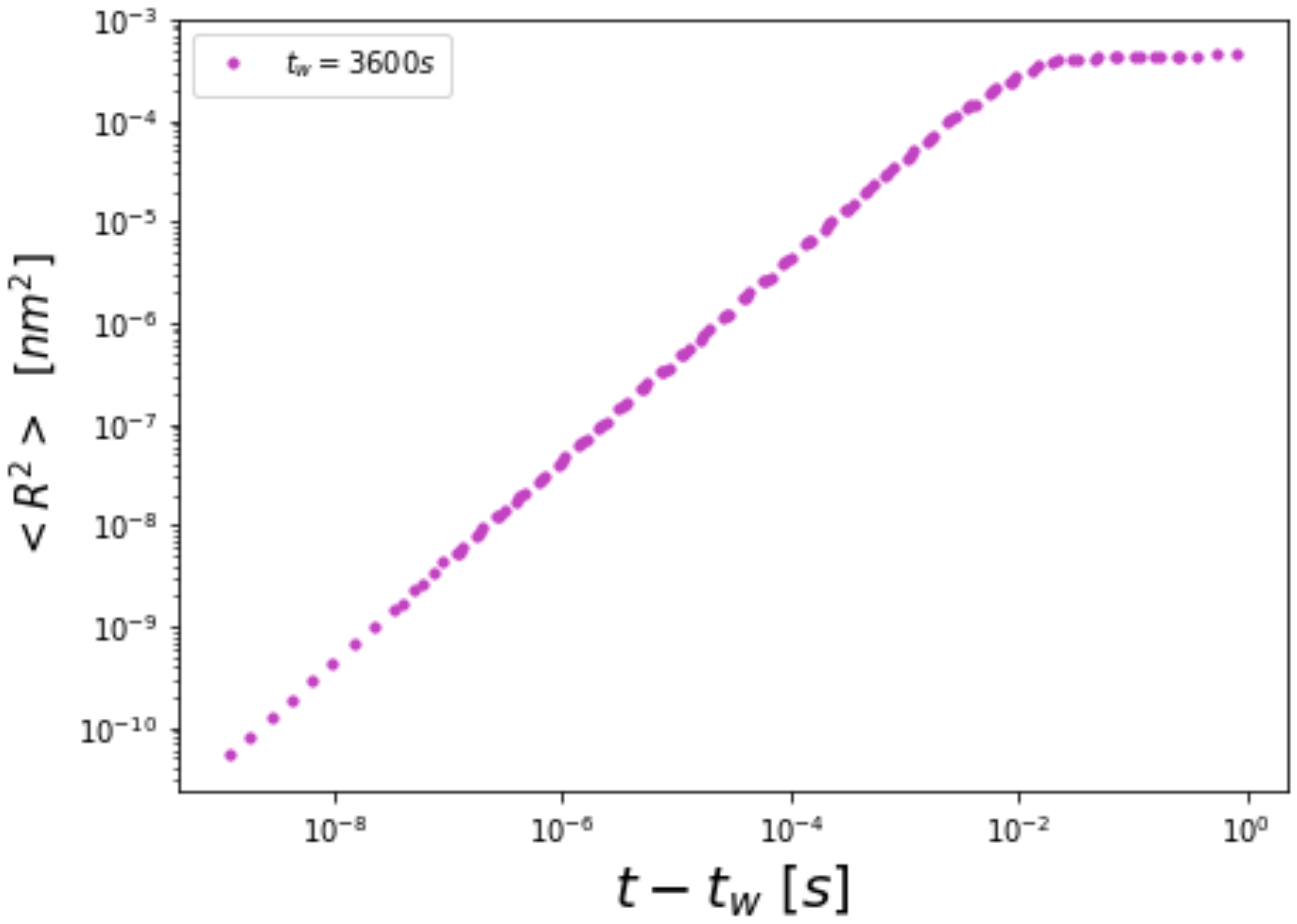
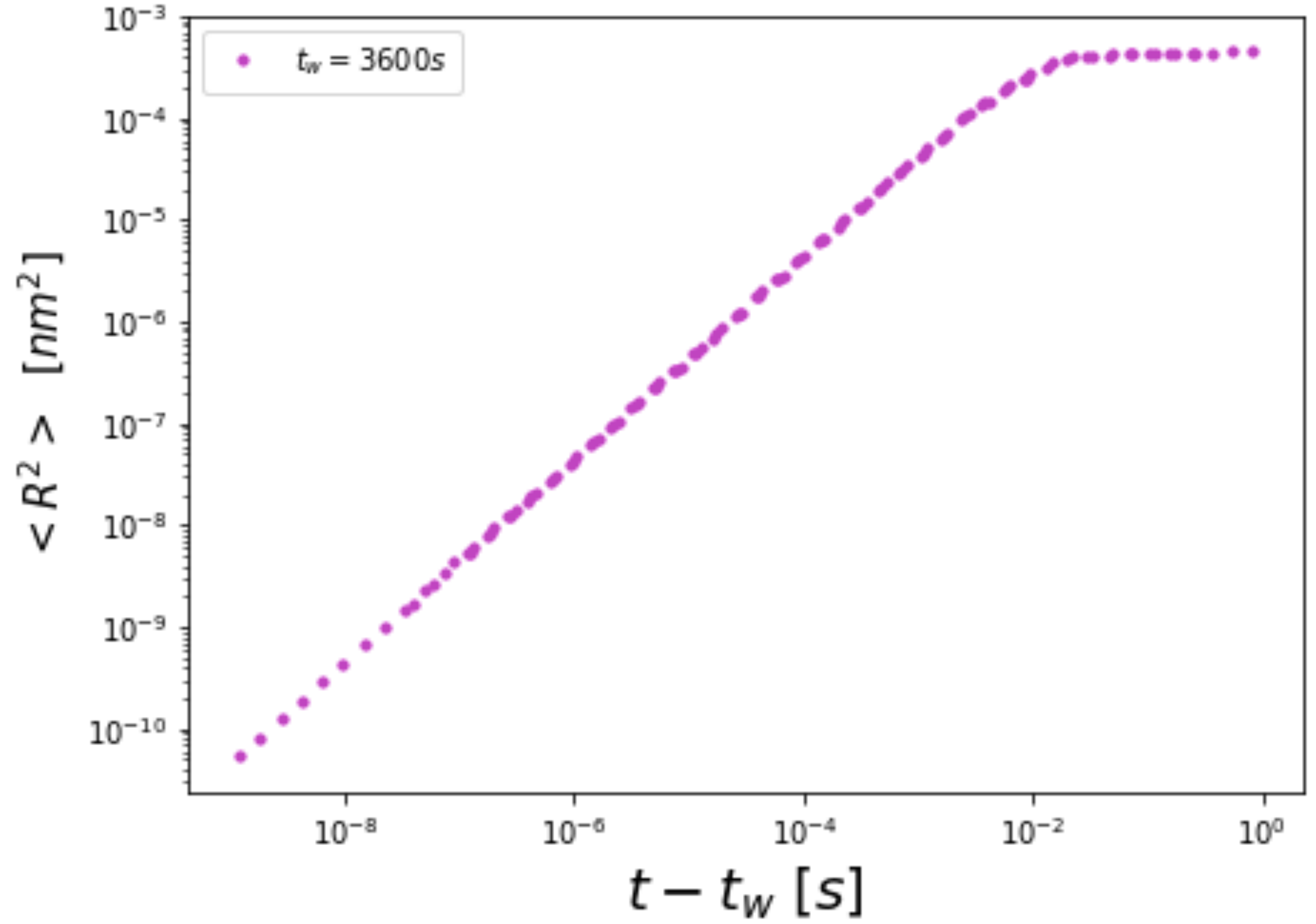


Verifying the MSD graph features for predicted MSD

- 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, $\tau(t = t_w = 3600s) = 10^{-2} s$.
- Plateau Value = $r_0^2 = \dfrac{k_B T}{6\pi a G(t)}$.
- $G(t) = G_O \cdot exp(\beta \cdot t) \ \Rightarrow G(t = t_w = 3600s) = 2.2 \times 10^{-4} [nm]^2$
- 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.



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 material with shows **slow** time dependent change in viscosity.
- We have taken six 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 six 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 six 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

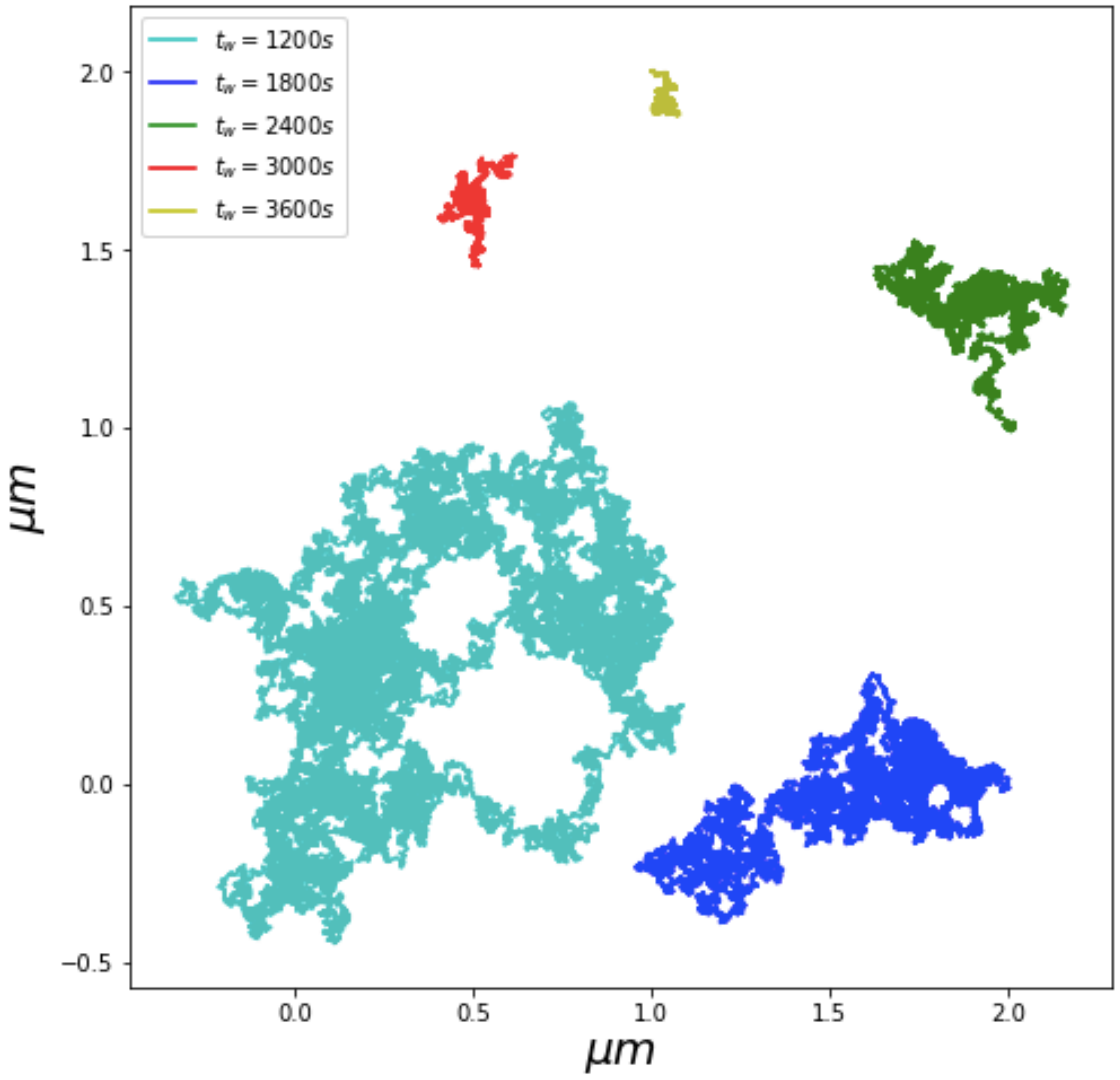
- For a viscous medium we define Friction coefficient $\zeta(t) = 6\pi \cdot a \cdot \eta(t)$.
- We define, $\dfrac{dt'}{\zeta(t')} = d\xi \quad \Rightarrow \quad \displaystyle\int_{t_w}^{t} \frac{dt'}{\zeta(t')} = \int_{\xi_w}^{\xi} d\xi$.
- The motivation for this transformation is coming from Langevin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

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

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

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

Ageing Viscous medium : Trajectory

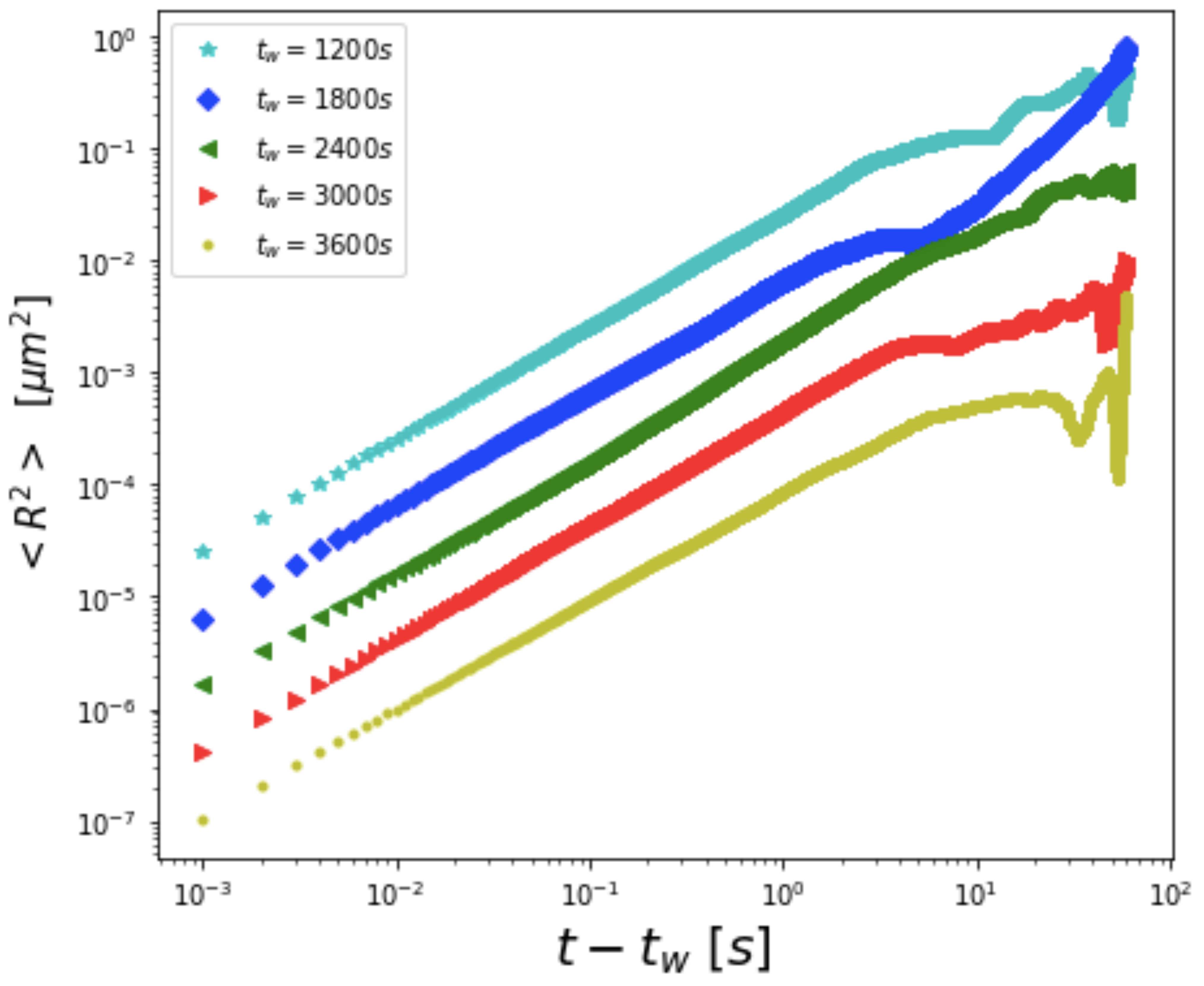


- Trajectories are generated for five different ageing times.
- Fixed Time step method used.
- $\Delta t = 10^{-3}s, \quad t_{max} = 60s$
- Since viscosity of medium increases with time hence, spatial extent of diffusion is decreasing with time. Or,
- since, $\eta(t) = \eta_0 \cdot exp(\alpha \cdot t)$ and $D(t) \propto \dfrac{1}{\eta(t)}$

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

Mean Square Displacement (Fixed time method)

- Fixed time step: $\Delta t = 10^{-3} s$.
- Total simulation time: $t_{max} = 60s$
- We are taking $\eta(t) = \eta_0 \cdot exp(\alpha \cdot t)$; $\alpha = 1.9 \times 10^{-3}[1/s]; \eta_0 = 10^{-3} Pa \cdot s$



Ageing Viscous medium : MSD (Variable time method)