Diffusion of a spherical particle in ageing viscoelastic mediums

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Abstract: We are presenting the Brownian dynamics simulation results for generalised linear viscoelastic (GLVE) mediums. We are modelling GLVE mediums as per the Generalised Maxwell model (GMM). This model takes the multiple relaxation modes of the GLVE medium into account. As per this model, We make physical sense of each relaxation mode of the system is due to the spring and dashpot-like nature of the medium. Hence a diffusing probe particle experiences a harmonic potential well which itself is under the influence of another harmonic well created by the remaining relaxation modes of the system. The trajectory of the diffusing probe particle is created using a random walk algorithm with uniformly distributed logarithmic time (UDLT) steps. The UDLT method helps us to extend the simulation time to cover a wide dynamic range. This completes all required precursors for simulation in an ageing medium. Currently, we are working on the simulation of an ageing viscoelastic medium utilizing the effective time-domain approach.

Introduction:

In the previous semester, we presented the Brownian dynamics simulation for the viscous and viscoelastic medium. We used the Maxwell-Voigt model(MVM) for modelling the viscoelastic medium. MVM is a relatively simple model and works well for some selective viscoelastic mediums. For example, the wormlike micellar solution shows a single stress relaxation time. Stress relaxation time refers to a time scale associated with a gradual decrease in developed stress in the system when strain is applied. The model includes spring and dashpot to explain the relaxation occurring in the system. The Spring component stores the energy when strain is applied, and the dashpot explains why the system finally gets rid of the stored energy as time progresses. But there are plenty of viscoelastic mediums which show multiple relaxation times. That means the relaxation does not occur at a single time, but it gradually occurs at a set of times. Some important examples are-

(a) a polymer system at the gel point,
(b) a concentrated oil-in-water emulsion system, and
(c) some specific polymer blend systems.

The above-mentioned systems come under the category of Generalised linear viscoelastic medium. Hence, its rheological properties can be studied well by modelling them as per the generalised Maxwell model(GMM).

GMM and its physical sense:

In the GMM model, several spring-dashpot units are connected to each other in a parallel arrangement. Each spring-dashpot unit has its own spring constant (k_i), and viscosity coefficient (η_i). Spring constant(k_i) gives rise to relaxation strength (g_i) through $k_i = 6\pi \cdot a \cdot g_i$. The characteristic relaxation time(λ_i) of the particular mode is given by $\lambda_i = \eta_i / g_i$.

Stress ($\sigma(t)$) and shear strain ($\gamma(t)$) in a linear viscoelastic medium are related by stress relaxation modulus ($G_r(t)$) through

$$\sigma(t) = G_r(t) \cdot \gamma(t) \qquad \text{(i)}$$

If we model our viscoelastic medium as per GMM using M number of the spring-dashpot system then we have M set of (g_i, λ_i) $\{i \in (0, M-1)\}$ called relaxation spectrum. Our job is to find the relaxation spectrum for a system such that it matches the experimental stress relaxation modulus ($G_r(t)$) of the system as per below relationship.

$$G_r(t) = \sum_{i=0}^{M-1} g_i \cdot exp(-t/\lambda_i) \qquad \text{(ii)}$$

Once we find a set of $\{(g_i, \lambda_i)\}$ for the system, we feed it into the Brownian dynamics simulation. In the simulation, each of the $\{(g_i, \lambda_i)\}$ is like harmonic potential well, exhibiting long-term diffusion. The logic of the simulation is now to generalise the algorithm used for MVM fluid(where a single (g, λ) exists).

Polymer system at gel point: Polymers form some of the most important viscoelastic mediums. It shows some exotic properties at its gel point, where an abrupt change in the viscosity of the system occurs due to the formation of polymer networks in the system due to cross-linking. In this case, it is known that the relaxation spectrum $\{(g_i, \lambda_i)\}$ has a power-law dependence, i.e., $g_i \sim \lambda_i^{-0.5}$. hence, relaxation modulus of the system comes out to be $G_r(t) \sim t^{-0.5}$. $(Fig. 1)$

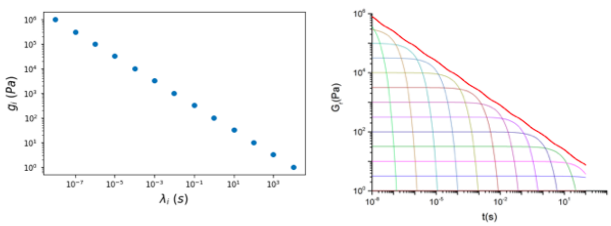

Fig. 1: [Left] selection of (g_i, λ_i)in order to fit stress relaxation modulus $G_r(t)$as per equation(ii). [Right] fitted curve $G_r(t)$ in red after selecting the appropriate selection of g_i *and* λ_i.

The Mean square displacement(MSD) plot with time-lag shows $< \Delta R^2 > \sim \sqrt{\tau}$. This implies uniform sub-diffusion of probe particles in the whole time domain.

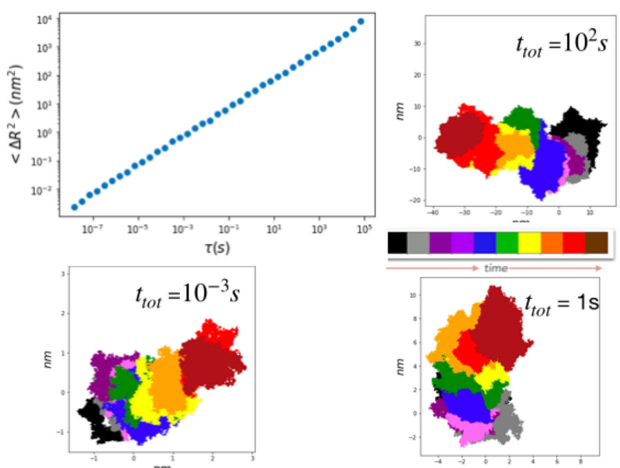

Fig. 2: [Top Left] MSD vs Time-lag shows sub-diffusion of particles all over the simulation time. The remaining graphs are Brownian trajectories captured for different total simulation times (t_{tot}). Different colour within a trajectory is to show the time evolution of the trajectory.

A concentrated oil-in-water emulsion system: For this viscoelastic system, the relaxation modulus is given as $G_r(t) = 6.5 + 1.1 \cdot t^{-0.3} - 0.03 \cdot t^{-0.55} + 4.7 \cdot t^{-0.5} + 0.5 \cdot \delta(t)$. Hence we are fitting the $G_r(t)$ using thirteen sets of $\{(g_i, \lambda_i)\}$ as plotted in Fig-3.

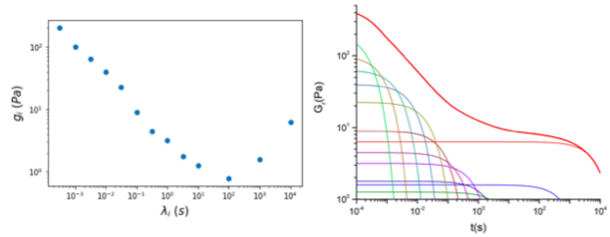

Fig. 3: [Left] selection of (g_i, λ_i)in order to fit stress relaxation modulus $G_r(t)$as per equation (4). [Right] fitted curve $G_r(t)$ in red after selection of appropriate selection of g_i *and* λ_i.

MSD plot of the probe particle shows that at shorter time-lag value there is linear diffusion. But as time progresses, the MSD shows a plateau shape which means the probe particle is undergoing bounded diffusion.

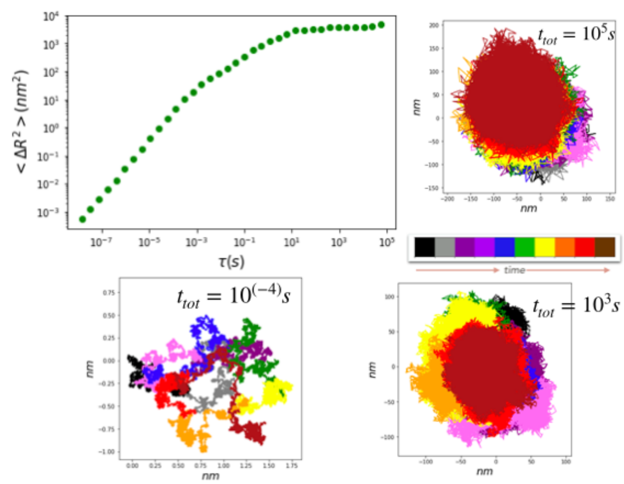

Fig. 4: [Top Left] MSD vs Time-lag shows sub-diffusion at lower time-lag, and then at the higher time-lag, it shows bounded diffusion(plateau in the graph). The remaining graphs are Brownian trajectories captured for different total simulation times (t_{tot}). We can see unbounded trajectories at shorter time-lag and bounded trajectories as time progresses.

Ageing Mediums: In an ageing medium, viscous and elastic properties changes with time. Hence, the relaxation time(λ) of a medium is not constant. It has a time dependence $\lambda(t)$.Hence, we are applying the effective time theory, which is a time-domain transformation theory. This transformation works in such a manner that the new time domain is free from the effect of ageing.

References:

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