MATH0488 – Elements of stochastic processes

Molecular dynamics: polymeric fluids

Maarten Arnst, Marco Lucio Cerquaglia, and Adrien Crovato

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Outline

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Molecular dynamics

■ Molecular dynamics is about understanding the **behavior and evolution of molecular systems**.

■ Basically, in molecular dynamics, many-body systems are treated as collections of individual mass points whose motion obeys the **laws of classical mechanics**:

$$
m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = -\boldsymbol{\nabla}_{\boldsymbol{r}_i} \underbrace{\phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n)}_{\substack{\text{potentiel function for intermolecular forces} \\ \text{deduced from experiments} \\ \text{or obtained from quantum mechanical considerations}}} + \underbrace{\boldsymbol{f}_i}_{\text{external force}}, \quad i = 1, 2, \ldots, n.
$$

Depending on the particular context (behavior under pressure, behavior at constant temperature,...), additional terms can be introduced in the equations of motion (friction and random force consistent with thermal agitation,...).

■ Molecular dynamics increasingly finds **many applications** in chemistry, physics, mechanics, biology, material science, medicine,...
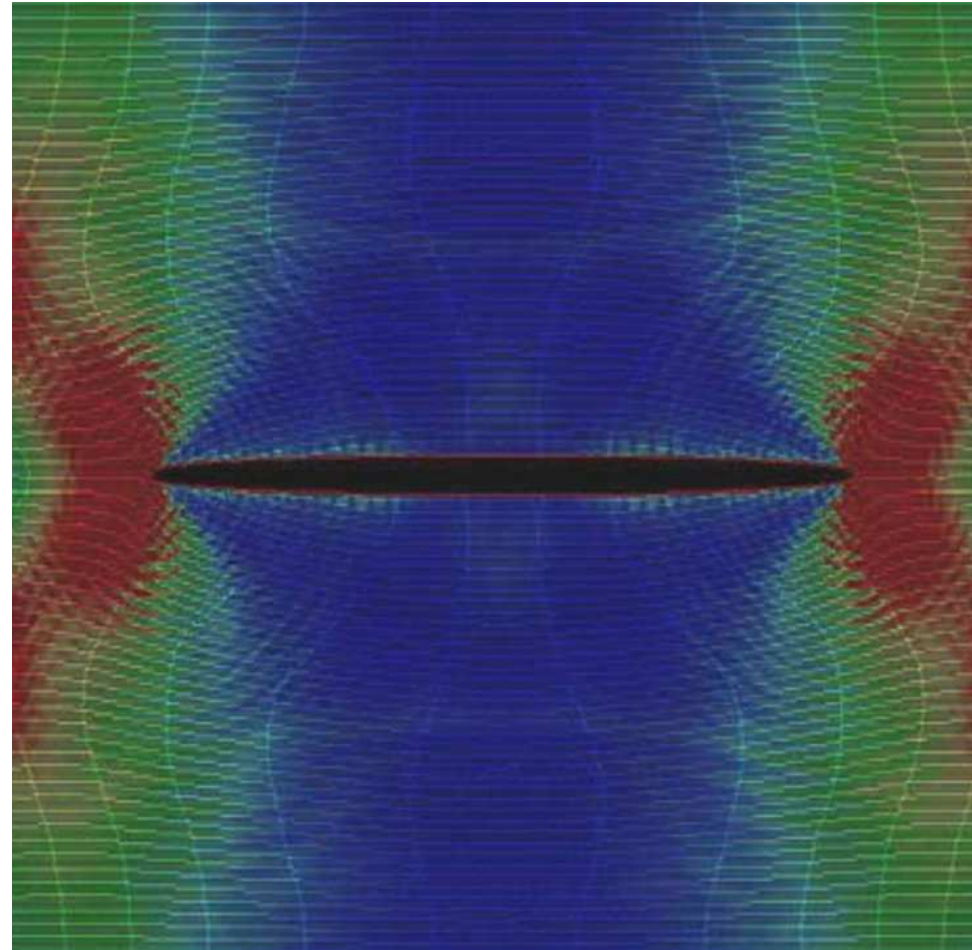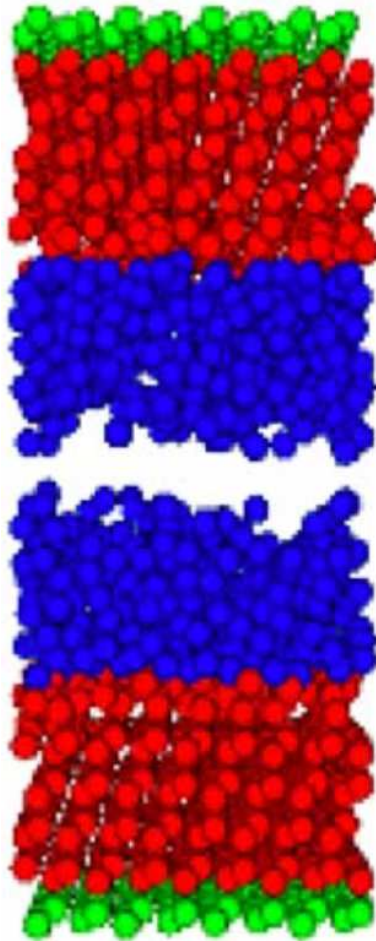
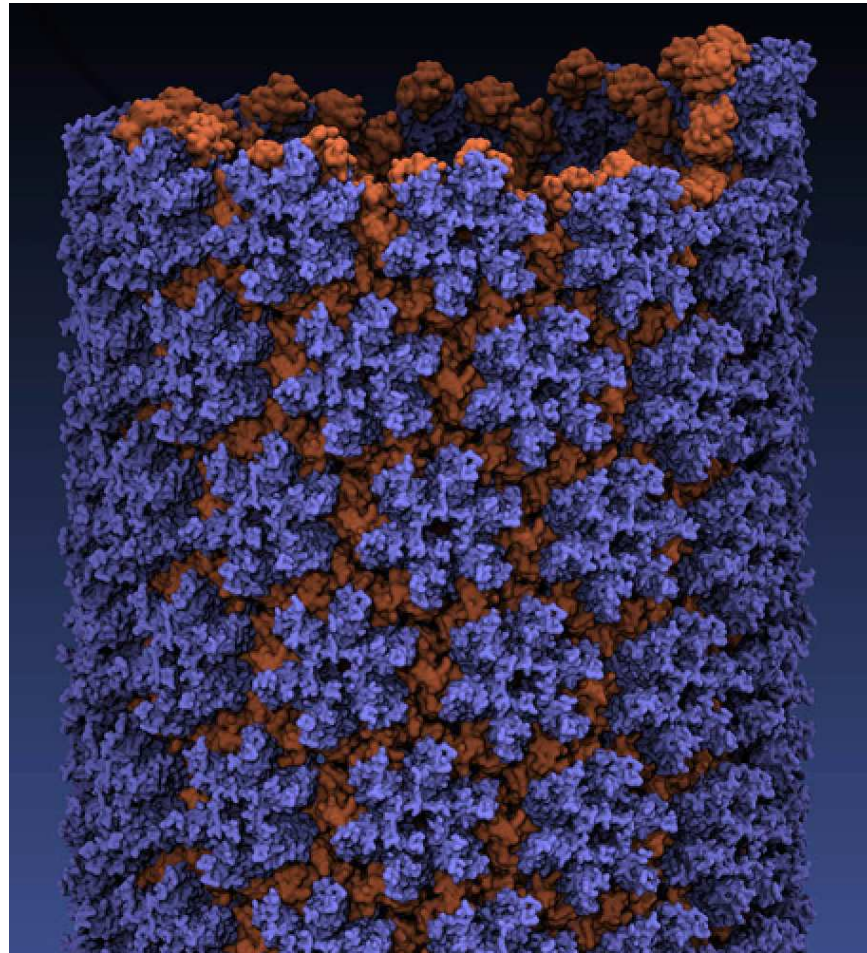Studies of friction and fracture in mechanical engineering.
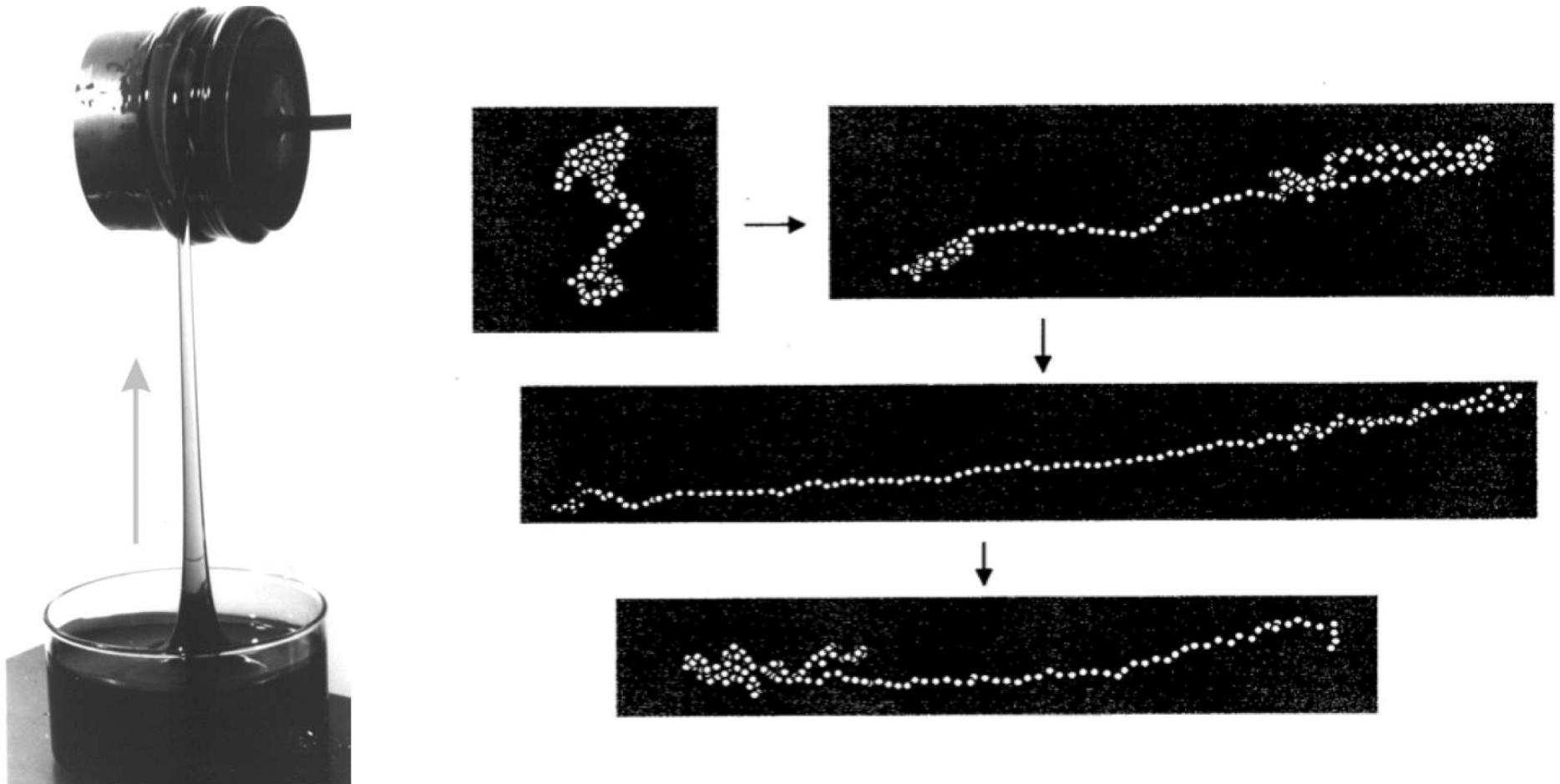From: W. Liu et al, CMAME, 2004.
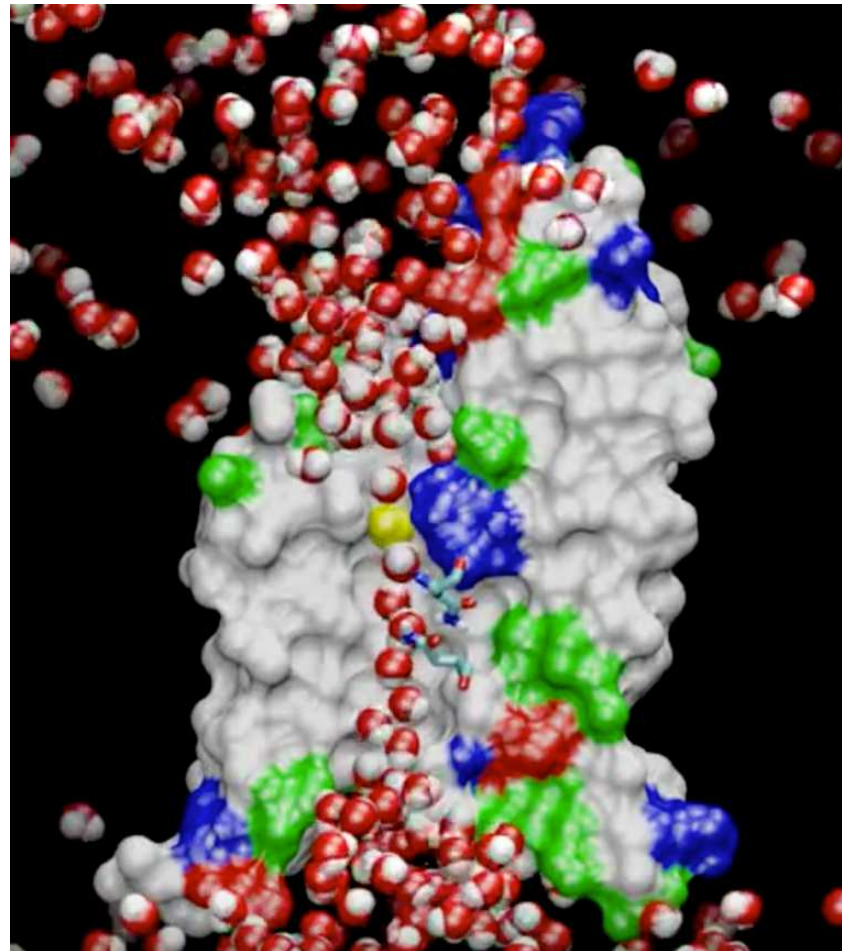
Study of water molecules passing through cell membrane pores in biology.
From: http://www.ks.uiuc.edu.

Study of molecular structure of packaging of genome of HIV virus in medicine.
From: http://www.ks.uiuc.edu.

Here, we will use molecular dynamics to study how adding polymers to fluids can increase viscosity.

Constitutive modeling

- An **elastic solid** remembers only its initial configuration. For example, concrete and steel. The constitutive model for a linear isotropic elastic solid reads as

$$\boldsymbol{\sigma} = \lambda \mathrm{tr}(\boldsymbol{\epsilon})\boldsymbol{I} + 2\mu\boldsymbol{\epsilon},$$

where $\boldsymbol{\sigma}$, $\boldsymbol{I}$, and $\boldsymbol{\epsilon}$ are the stress, identity, and strain tensors, and λ and μ are Lamé's parameters.

- A **viscous fluid** remembers only the very recent past configuration. Correspondingly, its constitutive model involves only the rate of deformation. For example, classical fluids, such as water, air, and oil. The constitutive model for a Newtonian viscous fluid reads as

$$\boldsymbol{\sigma} = \big(-p + \lambda_{\mathrm{v}}\mathrm{tr}(\boldsymbol{D})\big)\boldsymbol{I} + 2\mu_{\mathrm{v}}\boldsymbol{D},$$

where $\boldsymbol{\sigma}$, $\boldsymbol{I}$, and $\boldsymbol{D}$ are the stress, identity, and rate of deformation tensors, p is the pressure, and λ_{v} and μ_{v} are the volumetric and deviatoric viscosities.

- There are also materials whose behavior is intermediate between elastic and viscous. For example, polymers and various biological meterials, who exhibit **viscoelastic material** behavior.

Constitutive modeling

- One of the prototype viscoelastic materials is the **Maxwell viscoelastic material**.

- The Maxwell viscoelastic material can be represented by a damper and a spring in series:

- In this configuration, the total strain $\epsilon = \epsilon_v + \epsilon_e$ is the sum of the viscous strain ϵ_v in the damper and the elastic strain ϵ_e in the spring. From the differentiation of this relationship with respect to time and from the constitutive models $\sigma = \mu_v \frac{d\epsilon_v}{dt}$ for the damper and $\sigma = E\epsilon_e$ for the spring, we obtain the **differential form** of the constitutive model for the Maxwell viscoelastic material:

$$\frac{d\epsilon}{dt} = \frac{1}{\mu_v}\sigma + \frac{1}{E}\frac{d\sigma}{dt},$$

where σ is the total stress, which is equal to the both the stress in the damper and the stress in the spring, μ_v is the viscosity coefficient of the damper, and E is the elastic modulus of the spring.

- To this differential form corresponds the following **integral form**:

$$\sigma(t) = \exp\left(-\frac{E}{\mu_v}t\right)\sigma(0) + \int_0^t \underbrace{\exp\left(-\frac{E}{\mu_v}(t-s)\right)E}_{\text{relaxation modulus}}\frac{d\epsilon}{ds}(s)ds.$$

Top-left plot: σ vs t, with σ_0 marked. "sudden stress held to σ_0", "release".

Top-right plot: σ vs t. "instantaneous elastic response", "relaxation", "release".

Bottom-left plot: ϵ vs t. "instantaneous elastic response", "viscous deformation at constant rate σ_0/μ_v", "elastic springback", "permanent deformation".

Bottom-right plot: ϵ vs t, with ϵ_0 marked. "sudden strain held to ϵ_0", "elastic springback", "permanent deformation".
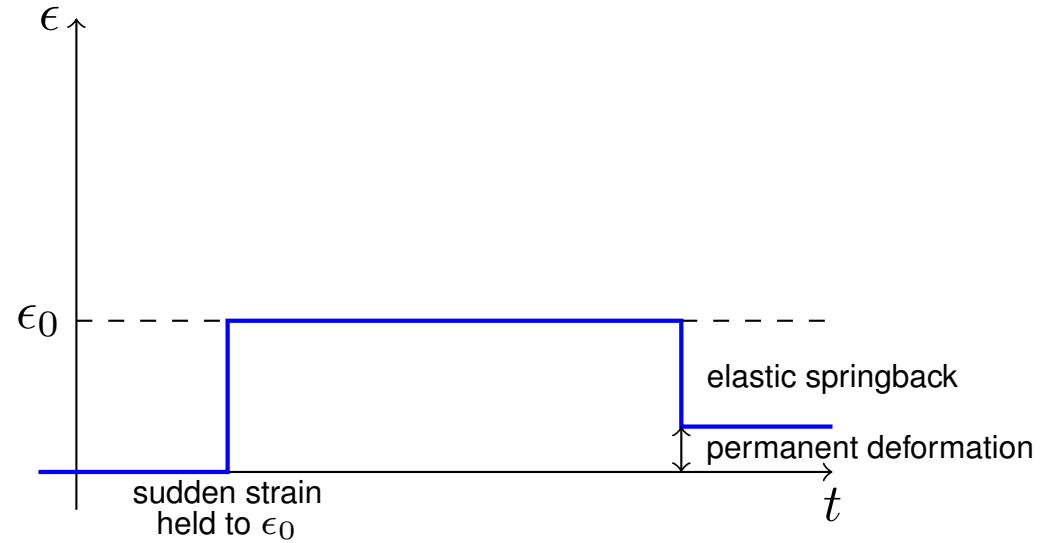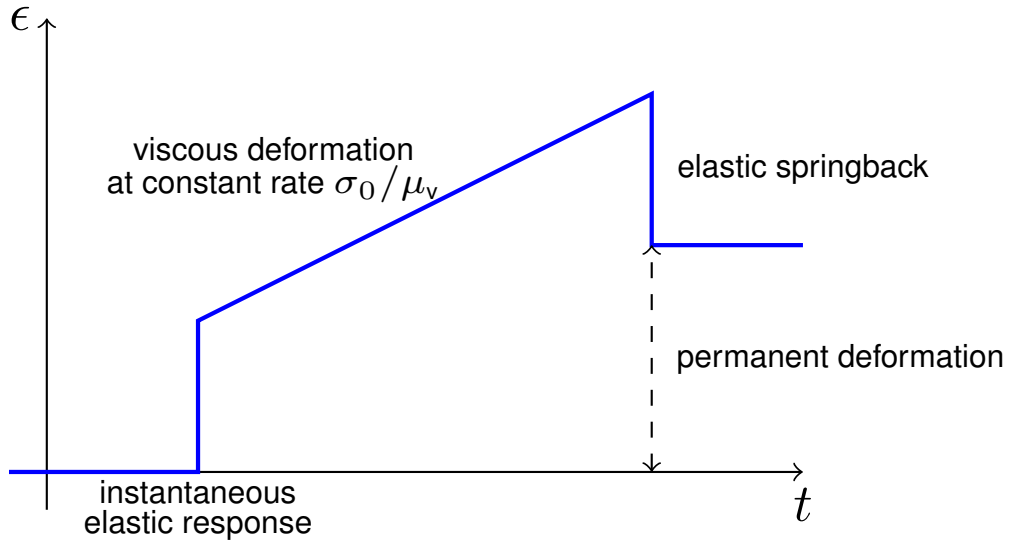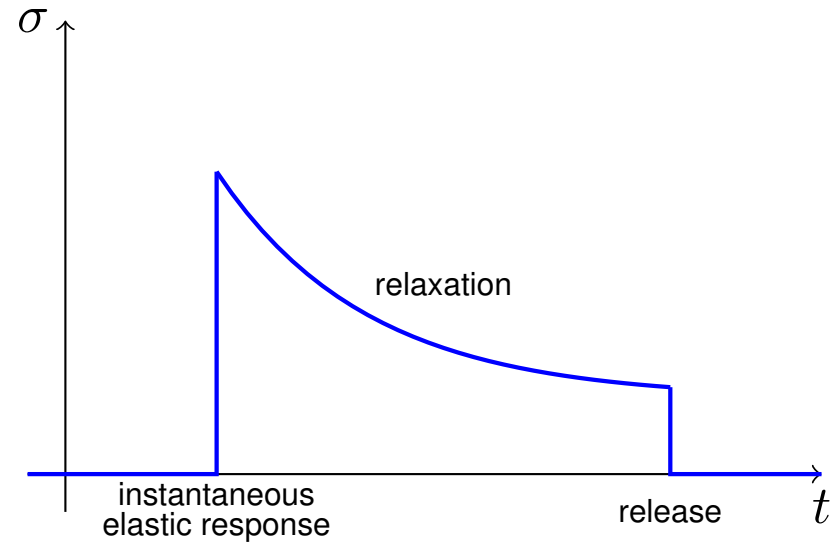
Constitutive modeling

- The integral form of the constitutive model for the **Maxwell viscoelastic material** indicates that the stress at the present time depe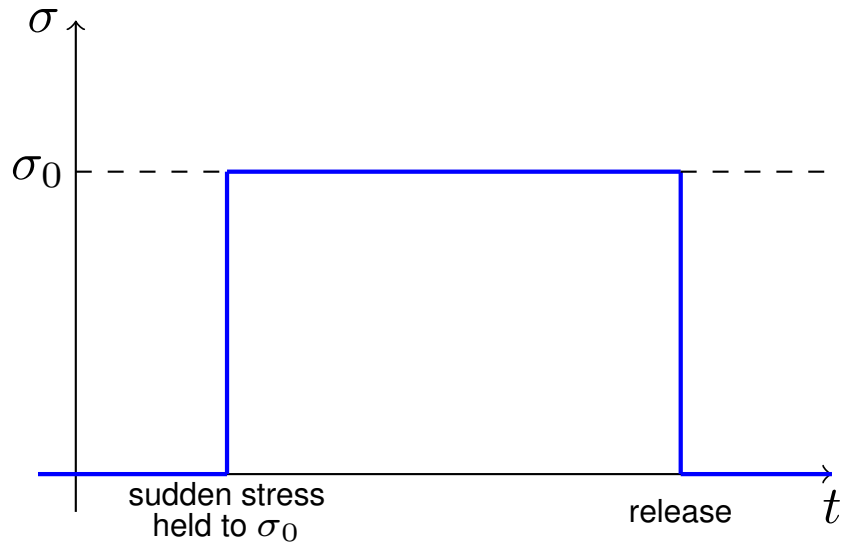nds on the rate of strain at past times with a weighting factor that decays exponentially as one goes backwards in time. This represents a "**fading memory**", with a **characteristic time scale** of $\frac{\mu_v}{E}$. The Maxwell viscoelastic material remembers well what it has recently experienced, but it has only a hazy recollection of events in the more distant past.

- There exist many other viscoelastic constitutive models, such as the Kelvin–Voigt viscoelastic material (damper and spring in parallel), the generalized Maxwell viscoelastic material,...

- In the following, we will see that when polymers are added to a (viscous) fluid, these polymers will contribute to the constitutive behavior of the polymeric fluid thus obtained.

Specifically, we will see that **adding polymers to a (viscous) fluid leads to viscoelastic behavior**. Although the constitutive model that we will find does not have the exact same form as that of the Maxwell viscoelastic material described above, we will find that adding polymers to a (viscous) fluid leads to **increased viscosity**, as well as to a "**fading memory**" whereby the stress depends on the "history" of the rate of strain for all past times, with a certain **characteristic time scale**.

Polymeric fluids

Bead-spring model

- We will consider a simple model, wherein the polymers are represented by **bead-spring chains**:
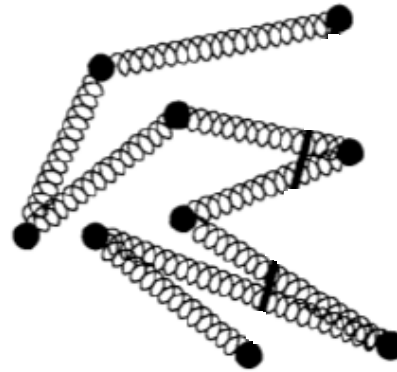
  - ◆ the **springs** will represent the **chemical bonds** of the polymers,
  - ◆ **friction forces** applied to the beads will represent the polymers/fluid **drag**,
  - ◆ **white noise** applied to the beads will represent the effects of **molecular collisions**.

- As in the case of the Langevin equation for the Brownian motion in the previous lecture, this bead-spring model is a rather **phenomenological model**. The intermolecular interactions between the polymers and the fluid molecules are not modeled explicitly; instead, their entire complexity is lumped into spring stiffnesses, friction coefficients, and the white-noise assumption.

- Comparisons with experiments and physical insight have shown that this bead-spring model is rather crude. Many aspects of the physical behavior are neglected, such as distributed drag along the polymer, intramolecular interactions along the polymer, finite strength of chemical bonds,. . .

- To simplify things even further, we will consider the case wherein there are only two beads linked by a single spring, a case that is also called that of "**Hookean dumbbells**."

Shear flow

■ Using the bead-spring model, we will investigate constitutive behavior in **shear flow**:

$$v_1 = \dot{\gamma} r_2, \qquad v_2 = 0, \qquad v_3 = 0.$$
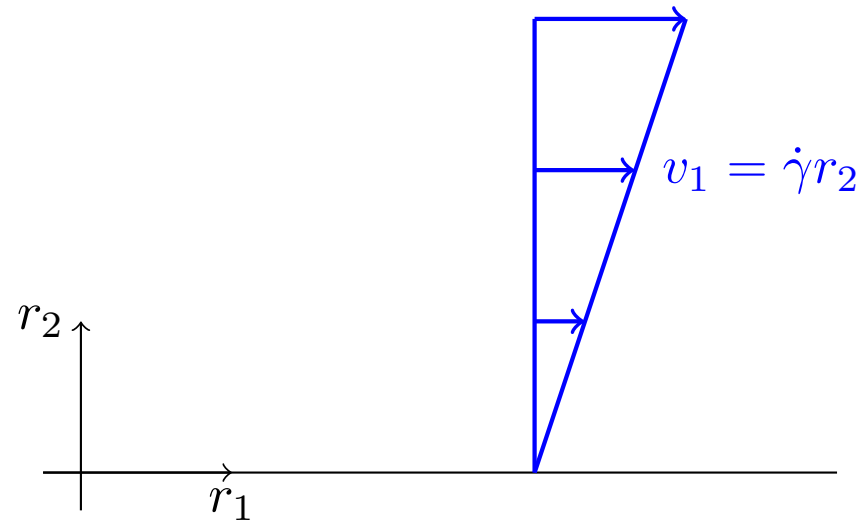
$$[L] = \mathbf{D}_{\boldsymbol{r}} \boldsymbol{v} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

■ If there were no polymers, the shear stress developed in the fluid would read as $\sigma_{12} = \mu_{\mathsf{v}} \dot{\gamma}$.

Molecular mechanisms

$$
\begin{cases}
\text{uncoiling} \\
\text{extending} \\
\quad \text{in flow} \\
\\
\text{thermal} \\
\text{agitation}
\end{cases}
\rightarrow
\begin{cases}
\text{positioning} \\
\\
\text{orientation} \\
\\
\text{conformation}
\end{cases}
\rightarrow
\begin{cases}
\text{chemical} \\
\text{bonds} \\
\text{distortions} \\
\text{in flow}
\end{cases}
\rightarrow
\begin{cases}
\text{internal} \\
\text{forces} \\
\text{in flow}
\end{cases}
$$
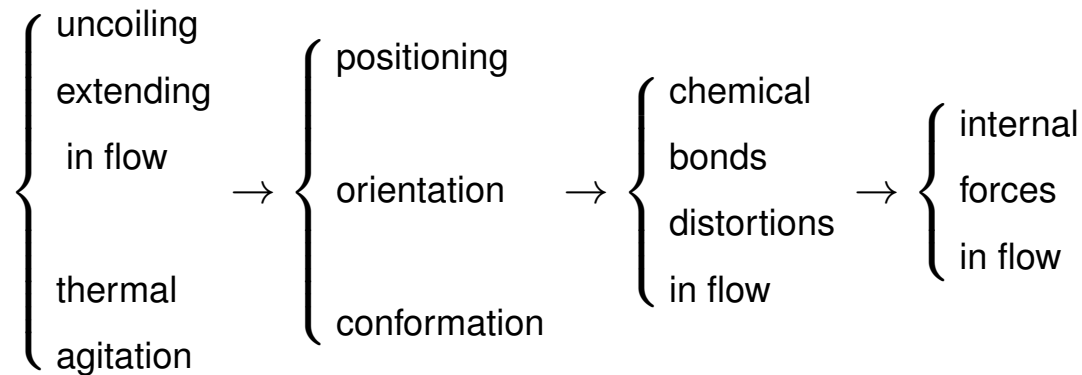
■ **Lengths and angles of chemical bonds of polymers distort** in flow, so that **internal forces** corresponding to these distortions will add to the stress state that develops in this flow.

■ The **geometrical positioning, orientation, and conformation of the polymers** (for example, homogeneous vs. heterogeneous concentration, random vs. preferred orientation, coiled vs. extended,...) will greatly determine how lengths and angles of chemical bonds may distort in flow.

■ Polymers can be expected to **uncoil and extend in the direction of flow**. Such changes in orientation and conformation can be expected to occur with (a) characteristic time scale(s) that depend(s) on inertia, friction between polymers and fluid molecules, stiffness of chemical bonds of polymers,..., thus leading to (a) **characteristic time scale(s) in the constitutive behavior**.

■ Although polymers will tend to uncoil and extend in the direction of flow, intermolecular collisions due to **thermal agitation** will tend to **restore random orientation and random conformation** consistent with the equilibrium conformational distribution. Increased temperature will make the intermolecular collisions more vigorous in their attempts to restore randomness, thus leading to **temperature dependence of the constitutive behavior**.

- Within our simple model, the behavior of the Hookean dumbbell in the shear flow is governed by

$$\boldsymbol{Q} = \boldsymbol{R}^{(2)} - \boldsymbol{R}^{(1)}$$
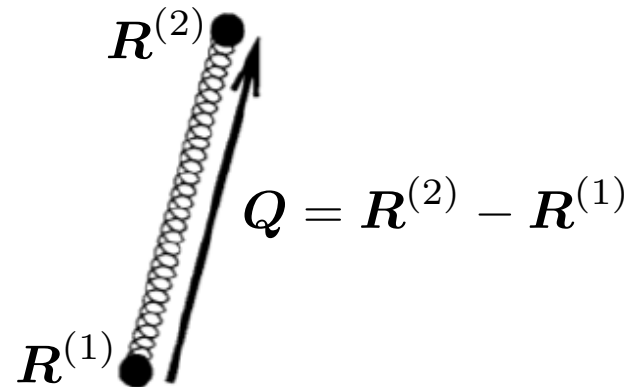
$$\begin{cases} \underbrace{\zeta\left(\dfrac{d\boldsymbol{R}^{(1)}}{dt} - [L]\boldsymbol{R}^{(1)}\right)}_{\text{polymer/fluid drag}} = \underbrace{h(\boldsymbol{R}^{(2)} - \boldsymbol{R}^{(1)})}_{\substack{\text{chemical bonds}\\\text{stiffness}}} + \underbrace{\sqrt{2k_{\mathrm{B}}T\zeta}\dfrac{d\boldsymbol{W}^{(1)}}{dt}}_{\substack{\text{molecular}\\\text{collisions}}} , \\[2em] \zeta\left(\dfrac{d\boldsymbol{R}^{(2)}}{dt} - [L]\boldsymbol{R}^{(2)}\right) = h(\boldsymbol{R}^{(1)} - \boldsymbol{R}^{(2)}) + \sqrt{2k_{\mathrm{B}}T\zeta}\dfrac{d\boldsymbol{W}^{(2)}}{dt} , \end{cases}$$

where ζ is the friction coefficient representing the polymer/fluid drag, h is the Hookean spring stiffness representing the chemical bonds, $\sqrt{2k_{\mathrm{B}}T\zeta}$ is the magnitude of the white noise representing the molecular collisions, and $\{\boldsymbol{W}^{(1)}(t),\ t \in \mathbb{R}^{+}\}$ and $\{\boldsymbol{W}^{(2)}(t),\ t \in \mathbb{R}^{+}\}$ are statistically independent Wiener processes. Inertia is neglected.

- We can write this coupled system of SDEs equivalently as an uncoupled system of SDEs by carrying out a change of variables to the centre of mass and the connector vector:

$$
\begin{cases}
\zeta \left(\dfrac{d\boldsymbol{R}_{\mathrm{G}}}{dt} - [L]\boldsymbol{R}_{\mathrm{G}} \right) = \sqrt{2k_{\mathrm{B}}T\zeta}\, \dfrac{1}{\sqrt{2}}\, \dfrac{d\boldsymbol{V}^{(1)}}{dt}, \\[2ex]
\zeta \left(\dfrac{d\boldsymbol{Q}}{dt} - [L]\boldsymbol{Q} \right) = -2h\boldsymbol{Q} + \sqrt{2k_{\mathrm{B}}T\zeta}\, \sqrt{2}\, \dfrac{d\boldsymbol{V}^{(2)}}{dt},
\end{cases}
$$

where $\boldsymbol{R}_{\mathrm{G}} = \frac{1}{2}(\boldsymbol{R}^{(1)} + \boldsymbol{R}^{(2)})$ is the centre of mass, $\boldsymbol{Q} = \boldsymbol{R}^{(2)} - \boldsymbol{R}^{(1)}$ the connector vector, and $\boldsymbol{V}^{(1)} = \frac{1}{\sqrt{2}}(\boldsymbol{W}^{(1)} + \boldsymbol{W}^{(2)})$ and $\boldsymbol{V}^{(2)} = \frac{1}{\sqrt{2}}(\boldsymbol{W}^{(2)} - \boldsymbol{W}^{(1)})$. It can be readily verified that $\{\boldsymbol{V}^{(1)}(t),\ t \in \mathbb{R}^+\}$ and $\{\boldsymbol{V}^{(2)}(t),\ t \in \mathbb{R}^+\}$ are statistically independent Wiener processes.

- As we saw in the previous lecture, the solution to this uncoupled system of SDEs reads as

$$
\begin{cases}
\boldsymbol{R}_{\mathrm{G}}(t) = \exp([L]t)\boldsymbol{R}_{\mathrm{G}}(0) + \displaystyle\int_0^t \exp\left([L](t-s)\right) \dfrac{1}{\zeta}\sqrt{2k_{\mathrm{B}}T\zeta}\, \dfrac{1}{\sqrt{2}}\, d\boldsymbol{V}^{(1)}(s), \\[2ex]
\boldsymbol{Q}(t) = \exp\left(\left([L] - \dfrac{2h}{\zeta}[I]\right)t\right)\boldsymbol{Q}(0) + \displaystyle\int_0^t \exp\left(\left([L] - \dfrac{2h}{\zeta}[I]\right)(t-s)\right) \dfrac{1}{\zeta}\sqrt{2k_{\mathrm{B}}T\zeta}\, \sqrt{2}\, d\boldsymbol{V}^{(2)}(s),
\end{cases}
$$

where $[I]$ denotes the identity matrix. We can see appear a "**fading memory**" with a **characteristic time scale** of $\frac{\zeta}{2h}$.

■ If the fluid is **at rest**, that is, $[L] = [0]$, we obtain

$$E\{\boldsymbol{Q}(t)\}$$
$$= \exp\left(-\frac{2h}{\zeta}t\right)E\{\boldsymbol{Q}(0)\},$$
$$E\{\left(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\right)\left(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\right)^{\mathrm{T}}\}$$
$$= \exp\left(-2\frac{2h}{\zeta}t\right)E\{\left(\boldsymbol{Q}(0) - E\{\boldsymbol{Q}(0)\}\right)\left(\boldsymbol{Q}(0) - E\{\boldsymbol{Q}(0)\}\right)^{\mathrm{T}}\} + \frac{k_{\mathrm{B}}T}{h}\left(1 - \exp\left(-2\frac{2h}{\zeta}t\right)\right)[I].$$

Thus, in a fluid at rest, the Hookean dumbbell will tend to evolve randomly over time in such a way that the long-time behavior ($t \to +\infty$) of its connector vector is governed by a multivariate Gaussian probability density function with mean zero and covariance matrix $\frac{k_{\mathrm{B}}T}{h}[I]$:

$$\rho(\boldsymbol{r}^{(2)} - \boldsymbol{r}^{(1)}) = \left(\frac{1}{2\pi\frac{k_{\mathrm{B}}T}{h}}\right)^{3/2} \exp\left(-\frac{\|\boldsymbol{r}^{(2)} - \boldsymbol{r}^{(1)}\|^2}{2\frac{k_{\mathrm{B}}T}{h}}\right).$$

The covariance matrix being diagonal and the diagonal elements being equal indicates that **in the fluid at rest, the orientation of the Hookean dumbbell evolves randomly over time without preferred orientation**.

■ If the fluid is in the **shear flow**, that is, $\dot{\gamma} \neq 0$ and therefore $[L] \neq [0]$, and if the connector vector is distributed initially as a multivariate Gaussian with mean zero and covariance matrix $\frac{k_{\mathrm{B}}T}{h}[I]$:

$$E\{\boldsymbol{Q}(t)\}$$
$$= \boldsymbol{0},$$

$$E\big\{\big(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\big)\big(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\big)^{\mathrm{T}}\big\}$$

$$= \exp\left(-2\frac{2h}{\zeta}t\right)\frac{k_{\mathrm{B}}T}{h}\exp\left([L]t\right)\exp\left([L]^{\mathrm{T}}t\right)$$

$$+ \int_0^t \exp\left(-2\frac{2h}{\zeta}(t-s)\right)\frac{2k_{\mathrm{B}}T}{\zeta}\exp\left([L](t-s)\right)\exp\left([L]^{\mathrm{T}}(t-s)\right)2ds.$$

Because the matrix exponential of $[L]$ reads as

$$\exp([L]) = \exp\left(\begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}\right) = \begin{bmatrix} 1 & \dot{\gamma} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

the covariance matrix $E\big\{\big(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\big)\big(\boldsymbol{Q}(t) - E\{\boldsymbol{Q}(t)\}\big)^{\mathrm{T}}\big\}$ is no longer diagonal and its diagonal elements are no longer equal, so that **in the fluid in the shear flow, the orientation still evolves randomly, but this time the shear flow induces a preferred orientation.**

- From the aforementioned solution to the system of SDEs, quantities relevant to the **constitutive behavior** can be determined by **evaluating probabilistic averages**. Following a method of calculation proposed by Kramers, the polymer contribution to the stress tensor is obtained as

Plane of unit area with unit normal $\boldsymbol{n}$

$\|\boldsymbol{Q}\|$
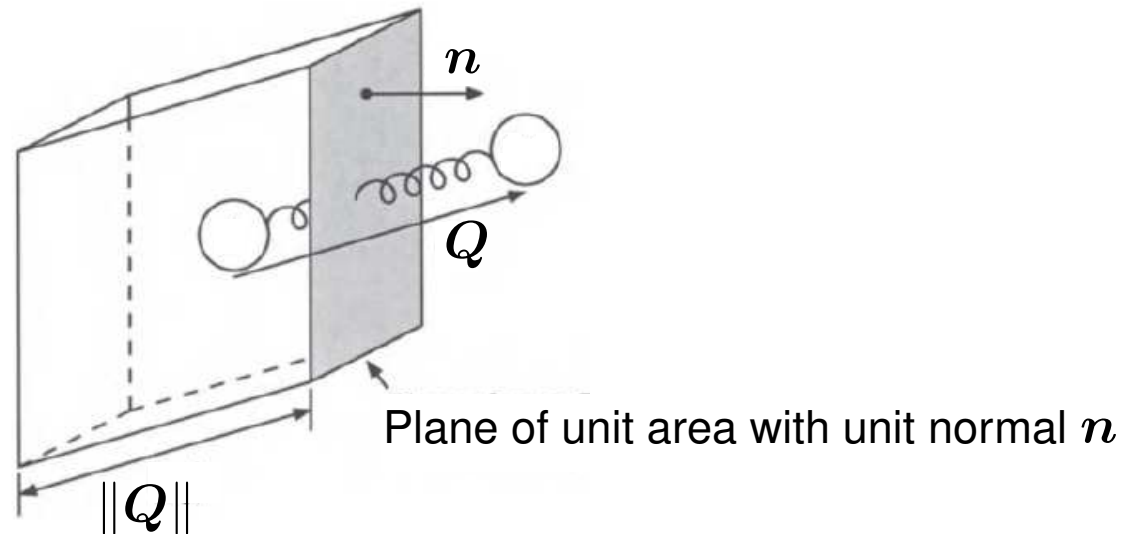
$$[\sigma^{\mathsf{p}}]\boldsymbol{n} = \underbrace{-\nu k_{\mathsf{B}}T\boldsymbol{n}}_{\substack{\text{osmotic} \\ \text{pressure}}} + \underbrace{E}_{\substack{\text{macroscale stress} \\ \text{obtained} \\ \text{as average} \\ \text{over microscale} \\ \text{configurations}}} \left\{ \underbrace{m}_{\substack{\text{number} \\ \text{of polymers} \\ \text{in solution}}} \underbrace{\frac{\boldsymbol{n} \cdot \boldsymbol{Q}}{V}}_{\substack{\text{probability of finding} \\ \text{polymer with connector vector } \boldsymbol{Q} \\ \text{intersecting the unit area plane}}} \underbrace{h\boldsymbol{Q}}_{\text{spring force}} \right\},$$

so that

$$[\sigma^{\mathsf{p}}] = -\nu k_{\mathsf{B}}T[I] + \nu h E\{\boldsymbol{Q}\boldsymbol{Q}^{\mathsf{T}}\};$$

here, ν is the concentration of polymers (supposed homogeneous, that is, $\nu = \frac{m}{V}$ with m the total number of polymers in the total volume V occupied by the fluid).

■ In our case of the Hookean dumbbell in the shear flow, we obtain

$$
[\sigma^{\mathsf{p}}](t) = -\nu k_{\mathsf{B}} T[I] + \nu h E\{\boldsymbol{Q}\boldsymbol{Q}^{\mathrm{T}}\}
$$

$$
= -\nu k_{\mathsf{B}} T[I] + \nu k_{\mathsf{B}} T \exp\left(-\frac{4h}{\zeta}t\right) \exp\left([L]t\right) \exp\left([L]^{\mathrm{T}}t\right)
$$

$$
+ \nu k_{\mathsf{B}} T \frac{4h}{\zeta} \int_0^t \exp\left(-\frac{4h}{\zeta}(t-s)\right) \exp\left([L](t-s)\right) \exp\left([L]^{\mathrm{T}}(t-s)\right) ds.
$$

With the help of the expression for the matrix exponential given previously, we obtain

$$
\sigma_{12}^{\mathsf{p}}(t) = \nu k_{\mathsf{B}} T \exp\left(-\frac{4h}{\zeta}t\right) \dot{\gamma}t + \nu k_{\mathsf{B}} T \frac{4h}{\zeta} \int_0^t \exp\left(-\frac{4h}{\zeta}(t-s)\right) \dot{\gamma}(t-s) ds
$$

$$
= \nu k_{\mathsf{B}} T \exp\left(-\frac{4h}{\zeta}t\right) \dot{\gamma}t + \nu k_{\mathsf{B}} T \frac{4h}{\zeta}\left(-\dot{\gamma}t\frac{\zeta}{4h}\exp\left(-\frac{4h}{\zeta}t\right) + \dot{\gamma}\left(\frac{\zeta}{4h}\right)^2 - \dot{\gamma}\left(\frac{\zeta}{4h}\right)^2 \exp\left(-\frac{4h}{\zeta}t\right)\right).
$$

Increased viscosity

- In the limit as $t \to +\infty$, we obtain

$$\lim_{t \to +\infty} \sigma^{\mathsf{p}}_{12}(t) = \nu \, k_{\mathsf{B}} T \, \frac{4h}{\zeta} \dot\gamma \left(\frac{\zeta}{4h} \right)^2$$

$$= \nu \, k_{\mathsf{B}} T \, \frac{\zeta}{4h} \, \dot\gamma.$$

so that the total shear stress in the polymeric fluid reads as

$$\lim_{t \to +\infty} \sigma_{12}(t) = \left(\underbrace{\mu_{\mathsf{v}}}_{\substack{\text{viscosity of fluid} \\ \text{in which polymers are dissolved}}} + \underbrace{\nu \, k_{\mathsf{B}} T \, \frac{\zeta}{4h}}_{\substack{\textbf{increased viscosity} \\ \textbf{due to presence of polymers}}} \right) \dot\gamma.$$

Assignment

1. Implement, by using the explicit Euler method, the Langevin dynamics

$$\zeta\left(\frac{d\boldsymbol{Q}}{dt} - [L]\boldsymbol{Q}\right) = -2h\boldsymbol{Q} + \sqrt{4k_\text{B}T\zeta}\frac{d\boldsymbol{V}}{dt}$$

where $[L]$ is the velocity gradient corresponding to the shear flow defined on Slide 15/24, and $\{\boldsymbol{V}(t),\ t \in \mathbb{R}^+\}$ is a Wiener process.

Use values for the physical properties such that $\frac{\zeta}{4h} = 1$, $\frac{k_\text{B}T}{h} = 1$, and $\nu k_\text{B}T = 1$.

Plot a few sample paths (components of $\boldsymbol{Q}$, angle that $\boldsymbol{Q}$ makes with the horizontal,...), first for the case wherein the fluid is at rest, that is, $[L] = [0]$, and then for the case wherein the fluid is in the shear flow, that is, $\dot{\gamma} \neq 0$ and therefore $[L] \neq [0]$. Interpret your results, perhaps with the help of additional figures, such as scatter plots, histograms,...

How would you use your implementation of these Langevin dynamics to estimate the increased viscosity due to the presence of polymers? Illustrate your answer with numerical results.

2. Formulate yourself an additional question that you find interesting, related to the Brownian motion, the Wiener process, the Langevin equation, or polymeric fluids, and provide an appropriate answer.

References

Suggested reading material

■ V. Denoel. Eléments de processus stochastiques. Université de Liège. Lecture notes.

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