Multiscale Description of Polymer Fluids: Hookean Dumbbells

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1 Molecular

At the microscopic level, inertial effects can be neglected, so that the force balance on each bead is,

\[ \mathbf{F}_i^{\text{drag}} + \mathbf{F}_i^s + \mathbf{F}_i^B = 0, \]  

(1)

where \( \mathbf{F}_i^{\text{drag}} \) is the drag force, \( \mathbf{F}_i^s \) is the spring force and \( \mathbf{F}_i^B \) is the Brownian force.

- **Drag force**

  \[ \mathbf{F}_i^{\text{drag}} = \zeta [\dot{\mathbf{r}}_i - \mathbf{v}(\mathbf{r}_i)], \]

  (2)

  for simple shear flows \( \mathbf{v}(\mathbf{r}_i) = \kappa \cdot \mathbf{r}_i \), where the velocity gradient is \( \kappa = (\nabla \mathbf{v})^T \).

- **Spring force**

  \[ \mathbf{F}_i^s = \pm H \mathbf{Q}, \]

  (3)

  here \( \mathbf{Q} = \mathbf{r}_1 - \mathbf{r}_2 \) is the end-to-end vector.

- **Brownian force** This force is of stochastic nature with the following moments

  \[ \langle \mathbf{F}_i^B(t) \rangle = 0, \]

  \[ \langle \mathbf{F}_i^B(t)\mathbf{F}_i^B(t') \rangle = \frac{A}{4} \delta(t - t'). \]
To find $A$ lets assume a simple Brownian diffusion,

$$\zeta \frac{dr}{dt} = F^B. \tag{4}$$

From Stokes-Einstein relation the mean square displacement is given by,

$$(r(t) - r(0))^2 = \frac{k_B T}{\zeta} t.$$ 

Then Eqn.(4) gives,

$$\begin{align*}
(r(t) - r(0))^2 &= \frac{1}{\zeta^2} \int_0^t \int_0^t \langle F^B(t_1)F^B(t_2) \rangle \, dt_1 dt_2, \\
&= \frac{A}{4\zeta^2} \int_0^t \int_0^t \delta(t_1 - t_2) \, dt_1 dt_2, \\
&= \frac{A}{4\zeta^2} \int_0^t \, dt_2 = \frac{A}{4\zeta^2} t.
\end{align*}$$

So that,

$$A = 4k_B T \zeta.$$ 

With these Eqn.(1) becomes,

$$dr_i = \kappa \cdot r_i - \frac{H}{\zeta} r_i - \sqrt{\frac{k_B T}{\zeta}} \, dW_t,$$

where $W_t \sim N(0, 1)$.

The Langevin equation describing the evolution of the end-to-end vector is,

$$dQ = \kappa \cdot Q - \frac{2H}{\zeta} Q - \sqrt{\frac{4k_B T}{\zeta}} \, dW_t. \tag{5}$$

2 Kinetic

Define the probability density function $\psi(Q, t)$ so that $\psi(Q, t) dQ$ is the probability that a dumbbell has an end-to-end vector in the interval $[Q, Q + dQ]$ at time $t$. Our goal is the use Eqn.(5) to find the evolution equation for $\psi(Q, t)$.

- From Langevin to Fokker-Planck

If a stochastic process $X_t$ is a simple Brownian motion so that,

$$dX_t = b dW_t,$$

then we know that the density function follows a Gaussian distribution and satisfies the diffusion equation:

$$\frac{\partial \psi}{\partial t} = \frac{b^2}{2} \frac{\partial^2 \psi}{\partial X^2}.$$
Now if a stochastic process has the following Langevin equation,

\[ dX_t = a dt, \]

we can use the fact that \( \psi = \delta(X - X_0) \) and the chain rule to show that,

\[ \frac{\partial \psi}{\partial t} = -a \frac{\partial}{\partial X} (\delta(X - X_0)), \]

\[ = -\frac{\partial}{\partial X} (a \delta(X - X_0)), \]

\[ = -\frac{\partial}{\partial X} (a \psi). \]

With these it is easy to show that the evolution equation for the probability distribution function of the dumbbells is,

\[ \frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial Q} \left[ \left( \kappa \cdot Q - \frac{2H}{\zeta} Q \right) \psi \right] - \frac{2k_B T}{\zeta} \frac{\partial^2 \psi}{\partial Q^2}. \]  

(6)

3 Continuum

The macroscopic stress tensor is related to the second moment of the probability density function by Kramers’ relation:

\[ \tau = k_B T I - H \langle QQ \rangle, \]  

(7)

where the second moment is defined as,

\[ \langle QQ \rangle \equiv \int QQ \psi dQ. \]

Eqn.(6) can be rewritten as,

\[ \frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial Q} \left[ \left( \kappa \cdot Q - \frac{2H}{\zeta} Q - \frac{2k_B T}{\zeta} \frac{\partial \ln \psi}{\partial Q} \right) \psi \right] = -\frac{\partial}{\partial Q} \left[ (B) \psi \right]. \]  

(8)

Multiplying Eqn.(8) by \( QQ \) and integrating over the configuration space gives,

\[ \int QQ \frac{\partial \psi}{\partial t} dQ = -\int \left[ \frac{\partial}{\partial Q} \cdot (B) \psi \right] QQ dQ, \]

\[ = -\int \left[ \frac{\partial}{\partial Q} \cdot (B) \psi \right] QQ dQ + \int (B) \psi \cdot \frac{\partial}{\partial Q} QQ dQ, \]

\[ = \int_{\text{surface } Q=\infty} \mathbf{n} \cdot [(B)\psi QQ] dS + \int (B) \psi \cdot \frac{\partial}{\partial Q} QQ dQ, \]

\[ = \int (B) \psi \cdot \frac{\partial}{\partial Q} QQ dQ. \]
Finally note that,
\[
\int \left[ \frac{\partial}{\partial Q} \ln \psi \cdot \frac{\partial}{\partial Q} QQ \right] \psi \, dQ = \int \left[ \frac{\partial}{\partial Q} \psi \cdot \frac{\partial}{\partial Q} Q \right] \, dQ,
\]
\[
= \int \left[ \frac{\partial}{\partial Q} \cdot \left( \psi \frac{\partial}{\partial Q} QQ \right) \right] \, dQ - \int \psi \left[ \frac{\partial}{\partial Q} \cdot \frac{\partial}{\partial Q} QQ \right] \, dQ,
\]
\[
= \int_{\text{surface} Q=\infty} \left[ \mathbf{n} \cdot \psi \frac{\partial}{\partial Q} QQ \right] \, dS - \left\langle \frac{\partial}{\partial Q} \cdot \frac{\partial}{\partial Q} QQ \right\rangle,
\]
\[
= - \left\langle \frac{\partial}{\partial Q} \cdot \frac{\partial}{\partial Q} QQ \right\rangle.
\]

With these we get,
\[
\frac{d}{dt} \langle QQ \rangle - \{ \kappa \cdot \langle QQ \rangle \} - \{ \langle QQ \rangle \cdot \kappa^T \} = \frac{4k_B T}{\zeta} I - \frac{4H}{\zeta} \langle QQ \rangle.
\]

And the evolution equation for the stress tensor is
\[
\frac{d\tau}{dt} - \kappa \cdot \tau - \tau \cdot \kappa^T + \frac{4H}{\zeta} \tau = -k_B T \dot{\gamma},
\]
(9)

where \( \dot{\gamma} = \kappa + \kappa^T \).