

# Constitutive modeling of macromolecular fluids

Qi Wang

Department of Mathematics  
Florida State University  
Tallahassee, FL 32306-4510

## 1 Introduction

Macromolecular or polymeric liquids consist of polymer solutions, polymer melts, particle suspension fluids, and many biological fluids. Polymer solutions are made of polymers dissolved in solutions or solvent; polymer melts are molten polymers; particle suspension fluids consist of solid particles suspended in a matrix fluid which may be a viscous or viscoelastic fluid, blood flows consist of deformable suspensions (red and white blood cells), and mucus is characteristically viscoelastic. Given the large molecular weight and size in polymers, polymeric liquids are capable of forming a variety of meso-phases, in which partial positional as well as orientational order can be present. These meso-phases are termed liquid crystalline phases. The polymeric liquids in the meso-phases are called liquid crystalline polymers. When the meso-phases are created above some critical concentration in solutions, the polymeric liquids are called lyotropic liquid crystal polymers. When the phases are attained at certain low temperature in melts, the materials are called thermotropic liquid crystal polymers. Not only miscible polymeric solutions and melts are capable of forming the liquid crystalline phase, immiscible polymer blends, emulsions, polymer-particle nanocomposites, which are liquid mixtures of polymer solutions or melts and solid nano-sized particles, are all candidates for forming liquid crystalline phases. Polymeric liquids exhibit a host of distinctive features from the isotropic liquids consisting of small molecules like water, cooking oils, etc. in flows. They may exhibit several well-known phenomena such as rod-climbing, extruded swell, and tubeless siphon [3]. When a gas bubble is trapped within a polymeric liquid, its geometry is distinct from that of a gas bubble trapped within a Newtonian fluid. These fascinating phenomena, distinctive of the polymeric liquids, have spurred a significant amount of research activities over the past few decades. Theories and models developed for polymers are now applied to biofluids and materials, making it a fast growing interdiscipli-

nary research area. In the lecture notes, we will first give a crash course on the basics in the continuum mechanics, which is the foundation of the more sophisticated polymer models, survey the existing models for various polymeric liquids and explore a systematic approach for flexible polymers using the framework of the kinetic theory.

## 2 Introduction to Continuum Mechanics

Continuum mechanics study the motion and deformation of a continuum, which can be a solid or a liquid, following a set of well-established principles. It provides a self-consistent way to establish a continuum theory describing the motion of the continuum for various materials at the macroscopic scale. Currently, it has been extended to handle multiple scales and multiple physics such as electromagnetics and thermodynamics in the continuum [?, 7]. In this notes, we focus on the basic thermomechanical principles at the macroscopic scale for continua.

### 2.1 Material, referential, and spatial description of motions, and deformation tensors

We consider a volume of continuum materials occupying a region  $\mathbf{P} \in \mathbf{R}^3$ . Let  $\mathbf{Y}$  denote the coordinate describing the material configuration in  $\mathbf{P}$ , called the material coordinate. We assume there exists a referential configuration occupying  $\mathbf{P}_R \in R^3$ , which can be the material configuration at certain time or completely irrelevant to the material configuration at all as long as there exists a bijection between  $\mathbf{P}$  and  $\mathbf{P}_R$ . Let  $\mathbf{X}$  describe the coordinate for the referential configuration of the material called Lagrangian coordinate, and  $\mathbf{x}$  the coordinate describing the spatial configuration of the material in the current spatial region  $\mathcal{P} \in \mathbf{R}^3$ , called the Eulerian coordinate. The fundamental assumption in continuum mechanics is that there exists a bijective mapping (one-to-one)  $\mathcal{K}$  such that

$$X = \mathcal{K}(Y) \tag{1}$$

and one between  $\mathbf{x}$  and  $\mathbf{X}$ ,  $\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$ , which denotes the position of the material with referential coordinate  $\mathbf{X}$  at time  $t$ , for some short time  $t$ . We denote vectors as column vectors throughout the notes. So, the inner product is defined as

$$\mathbf{a} \cdot \mathbf{b} = \mathbf{a}^T \cdot \mathbf{b}. \tag{2}$$

We assume the mappings are differentiable. The gradient tensor

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} = \frac{\partial x_i}{\partial X_j} \tag{3}$$

is called the deformation gradient tensor, which is assumed invertible. Similarly, the gradient tensor

$$\mathcal{H} = \frac{\partial \mathbf{X}}{\partial \mathbf{Y}} \quad (4)$$

is assumed invertible as well. The Green's deformation tensor is defined by

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F}. \quad (5)$$

Differentials in the Eulerian and Lagrangian coordinate are related by

$$d\mathbf{x} = \mathbf{F} \cdot d\mathbf{X}. \quad (6)$$

The 2-norm of  $d\mathbf{x}$  is given by

$$\|d\mathbf{x}\|^2 = d\mathbf{X}^T \cdot \mathbf{F}^T \cdot \mathbf{F} \cdot d\mathbf{X} = d\mathbf{X}^T \cdot \mathbf{C} \cdot d\mathbf{X}. \quad (7)$$

So, the Green's tensor measures the change of the measure (metric) from the Lagrangian coordinate to the Eulerian coordinate. Since  $\mathbf{F}^{-1}$  always exists, the Cauchy deformation tensor is defined by

$$\mathbf{c} = (\mathbf{F}^{-1})^T \cdot \mathbf{F}^{-1}. \quad (8)$$

Notice that

$$\|d\mathbf{X}\|^2 = d\mathbf{x}^T \cdot \mathbf{c} \cdot d\mathbf{x}. \quad (9)$$

So, the Cauchy tensor measures the change of measure from the Eulerian to Lagrangian coordinate. The finger tensor is defined by

$$\mathbf{B} = \mathbf{c}^{-1} = \mathbf{F} \cdot \mathbf{F}^T, \quad (10)$$

which is the inverse of the Cauchy tensor. To some extent, the Finger tensor can be viewed as a measure for the change from the Lagrangian coordinate to the Eulerian coordinate as well. Normally, the strain tensors are used to describe the deformation in short time given that the mapping between the Eulerian coordinate and the Lagrange or the material coordinate are not guaranteed bijective for all time. Assuming the referential coordinate is the spatial coordinate at time  $t_0$ , the deformation gradient tensor  $\mathbf{F}$  is identity at  $t = t_0$ . The relative strain tensors are then introduced to measure the relative deformations with respect to the configuration at  $t_0$ .

$$\mathbf{E} = \frac{1}{2}(\mathbf{C} - \mathbf{I}) \quad (11)$$

is the Lagrangian strain tensor measuring the deformation relative to the Lagrangian coordinate (or referential coordinate at  $t_0$ ).

$$\mathbf{e} = \frac{1}{2}(\mathbf{I} - \mathbf{c}) \quad (12)$$

is the Eulerian strain tensor measuring the deformation relative to the Eulerian coordinate (or the spatial coordinate at  $t$ ). We note that

$$\|d\mathbf{x}\|^2 - \|d\mathbf{X}\|^2 = 2d\mathbf{X} \cdot \mathbf{E} \cdot d\mathbf{X} \quad (13)$$

and

$$\|d\mathbf{x}\|^2 - \|d\mathbf{X}\|^2 = 2d\mathbf{x} \cdot \mathbf{e} \cdot d\mathbf{x}. \quad (14)$$

We define the displacement vector as

$$\mathbf{u} = \mathbf{x} - \mathbf{X} \quad (15)$$

In terms of the displacement vector, the relative strain tensors can be written as

$$\mathbf{E} = \frac{1}{2} \left( \frac{\partial \mathbf{u}}{\partial \mathbf{X}} + \frac{1}{2} \frac{\partial \mathbf{u}}{\partial \mathbf{X}}^T \right) + \frac{1}{2} \frac{\partial \mathbf{u}}{\partial \mathbf{X}} \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{X}}, \quad (16)$$

$$\mathbf{e} = \frac{1}{2} \left( \frac{\partial \mathbf{u}}{\partial \mathbf{x}} + \frac{\partial \mathbf{u}}{\partial \mathbf{x}}^T \right) - \frac{1}{2} \frac{\partial \mathbf{u}}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{x}}. \quad (17)$$

Dropping the quadratic terms, we arrive at the linear measure for the relative deformation

$$\mathbf{E} = \frac{1}{2} \left( \frac{\partial \mathbf{u}}{\partial \mathbf{X}} + \frac{\partial \mathbf{u}}{\partial \mathbf{X}}^T \right), \mathbf{e} = \frac{1}{2} \left( \frac{\partial \mathbf{u}}{\partial \mathbf{x}} + \frac{\partial \mathbf{u}}{\partial \mathbf{x}}^T \right). \quad (18)$$

We note that theories built around the linear strain tensors are called linear elastic theories. Let  $\mathbf{Y} = (\theta^1, \theta^2, \theta^3)$  be the material coordinate. Then, the material point in the reference configuration is denoted by

$$\mathbf{X} = \mathbf{X}(\theta^1, \theta^2, \theta^3), \quad (19)$$

and in the spatial configuration by

$$\mathbf{x} = \mathbf{x}(\theta^1, \theta^2, \theta^3, t). \quad (20)$$

A curvilinear basis in the Lagrangian coordinate is given by

$$\mathbf{G}_i = \frac{\partial \mathbf{X}}{\partial \theta^i}, i = 1, 2, 3, \quad (21)$$

and in the Eulerian coordinate by

$$\mathbf{g}_i = \frac{\partial \mathbf{x}}{\partial \theta^i}, i = 1, 2, 3. \quad (22)$$

We introduce

$$\begin{aligned} \mathcal{F} &= \frac{\partial \mathbf{x}}{\partial \mathbf{Y}} = \left( \frac{\partial \mathbf{x}}{\partial \theta_1}, \frac{\partial \mathbf{x}}{\partial \theta_2}, \frac{\partial \mathbf{x}}{\partial \theta_3} \right) = (\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3), \\ \mathcal{H} &= \frac{\partial \mathbf{X}}{\partial \mathbf{Y}} = \left( \frac{\partial \mathbf{X}}{\partial \theta_1}, \frac{\partial \mathbf{X}}{\partial \theta_2}, \frac{\partial \mathbf{X}}{\partial \theta_3} \right) = (\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3). \end{aligned} \quad (23)$$

The differentials are denoted by

$$d\mathbf{x} = \mathbf{g}_i d\theta^i, d\mathbf{X} = \mathbf{G}_i d\theta^i. \quad (24)$$

The change in length from the Lagrange to the Eulerian coordinate is given by

$$\|d\mathbf{x}\|^2 - \|d\mathbf{X}\|^2 = d\theta^i (\mathbf{g}_i \cdot \mathbf{g}_j - \mathbf{G}_i \cdot \mathbf{G}_j) d\theta^j. \quad (25)$$

The convected coordinate is defined as the material coordinate with base vectors given in the Eulerian coordinate. In convected coordinates, the coordinates of the material particles are held constant, the relative deformation from the reference to the current spatial configuration is effectively measured by the convected strain tensor

$$\gamma_{ij} = (\mathbf{g}_i \cdot \mathbf{g}_j - \mathbf{G}_i \cdot \mathbf{G}_j), \quad (26)$$

where

$$(\mathbf{g}_i \cdot \mathbf{g}_j) = \mathcal{F}^T \cdot \mathcal{F}, (\mathbf{G}_i \cdot \mathbf{G}_j) = \mathcal{H}^T \cdot \mathcal{H} \quad (27)$$

are called the metric tensors. This is the analogue of the Lagrange strain tensor. The reciprocal basis are given by

$$\mathbf{g}^i = \nabla \theta^i = \frac{\partial \theta^i}{\partial \mathbf{x}}, \mathbf{G}^i = \nabla \theta^i = \frac{\partial \theta^i}{\partial \mathbf{X}}, i = 1, 2, 3, \quad (28)$$

where

$$\mathbf{g}_i \cdot \mathbf{g}^j = \delta_{ij}, \mathbf{G}_i \cdot \mathbf{G}^j = \delta_{ij}. \quad (29)$$

In fact, we have

$$(\mathbf{g}^1, \mathbf{g}^2, \mathbf{g}^3)^T = \mathcal{F}^{-1}, (\mathbf{G}^1, \mathbf{G}^2, \mathbf{G}^3)^T = \mathcal{H}^{-1}. \quad (30)$$

For the differentials, we have

$$d\mathbf{x} = (d\mathbf{x} \cdot \mathbf{g}_i) \mathbf{g}^i, d\mathbf{X} = (d\mathbf{X} \cdot \mathbf{G}_i) \mathbf{G}^i. \quad (31)$$

Another strain measure, analogous to the negative of the Eulerian strain tensor, can be defined as

$$\gamma^{ij} = -(\mathbf{g}^i \cdot \mathbf{g}^j - \mathbf{G}^i \cdot \mathbf{G}^j) = -(\mathcal{F}^{-1} \cdot \mathcal{F}^{-T} - \mathcal{H}^{-1} \cdot \mathcal{H}^{-T}). \quad (32)$$

The two strain measures (tensors) are the variables used to describe the deformation of the material in convected coordinates. The constitutive equations for fluids must be formulated in the convected coordinates. The base vectors  $\mathbf{g}_i$  are called covariant base vectors while  $\mathbf{g}^i$  are called contravariant base vectors. For an arbitrary vector  $\mathbf{v}$ ,

$$\mathbf{v} = v^i \mathbf{g}_i = \mathcal{F} \cdot \begin{pmatrix} v^1 \\ v^2 \\ v^3 \end{pmatrix}, v^i = \mathbf{v} \cdot \mathbf{g}^i, i = 1, 2, 3. \quad (33)$$

$v^i, i = 1, 2, 3$  are called the contravariant coordinates (or components) since  $v^i = \mathbf{v} \cdot \mathbf{g}^i$  varies with respect to  $\mathbf{g}^i$  and  $v_i$  the covariant coordinates (or components) since they vary with respect to  $\mathbf{g}_i$ . The tensors  $g_{ij} = \mathbf{g}_i \cdot \mathbf{g}_j = \mathcal{F}^T \cdot \mathcal{F}$ ,  $g_i^j = \mathbf{g}_i \cdot \mathbf{g}^j = \mathcal{F}^T \cdot (\mathcal{F}^{-1})^T$ ,  $g_j^i = \mathbf{g}^i \cdot \mathbf{g}_j = \mathcal{F}^{-1} \cdot \mathcal{F}$ ,  $g^{ij} = \mathbf{g}^i \cdot \mathbf{g}^j = \mathcal{F}^{-1} \cdot \mathcal{F}^{-T}$  are called metric tensors that define measures in the space with curvilinear base vectors. In fact,

$$\mathbf{g}_i = g_{ij} \mathbf{g}^j, \mathbf{g}^i = g^{ij} \mathbf{g}_j. \quad (34)$$

For any second order tensor

$$\tau = \tau^{ij} \mathbf{g}_i \mathbf{g}_j = \mathcal{F} \cdot (\tau^{ij}) \cdot \mathcal{F}^T = \tau_{ij} \mathbf{g}^i \mathbf{g}^j = \mathcal{F}^{-T} \cdot (\tau_{ij}) \cdot \mathcal{F}^{-1}, \quad (35)$$

where  $\mathbf{g}_i \mathbf{g}_j$  denotes the tensor product. In some books the tensor product is denoted by  $\mathbf{g}_i \otimes \mathbf{g}_j$  or  $\mathbf{g}_i \mathbf{g}_j^T$ , where  $\mathbf{g}_i$  is a column vector. Similarly in the Lagrange coordinate,

$$\sigma = \sigma^{ij} \mathbf{G}_i \mathbf{G}_j = \sigma_{ij} \mathbf{G}^i \mathbf{G}^j. \quad (36)$$

We next define various derivatives. Let  $\Phi(\mathbf{x}, t)$  be a function of  $\mathbf{x}$ , we define the derivative of the function with respect to the vector  $\mathbf{x}$  as

$$\frac{\partial \Phi}{\partial \mathbf{x}} \cdot \mathbf{u} = \lim_{\alpha \rightarrow 0} \frac{\Phi(\mathbf{x} + \alpha \mathbf{u}, t) - \Phi(\mathbf{x}, t)}{\alpha}, \quad (37)$$

where  $\mathbf{u}$  is an arbitrary nonzero vector. Let  $\mathbf{v}$  be a function of  $\mathbf{x}$ . We can define the derivative of  $\mathbf{v}$  with respect to  $\mathbf{x}$  as follows:

$$\frac{\partial \mathbf{v}}{\partial \mathbf{x}} \cdot \alpha = \lim_{t \rightarrow 0} \frac{\mathbf{v}(\mathbf{x} + t\alpha) - \mathbf{v}(\mathbf{x})}{t}, \quad (38)$$

for an arbitrary vector  $\alpha$ . In the convected coordinate, let

$$\mathbf{v} = v^i \mathbf{g}_i = v_i \mathbf{g}^i \quad (39)$$

be a vector function of  $\mathbf{x}$ . Its derivative with respect to  $\mathbf{x}$  is given by

$$\frac{\partial \mathbf{v}}{\partial \mathbf{x}} = \left[ \frac{\partial v^i}{\partial \theta^j} + \Gamma_{mj}^i v^m \right] \mathbf{g}_i \mathbf{g}^j = \left[ \frac{\partial v_i}{\partial \theta^j} - \Gamma_{ij}^m v_m \right] \mathbf{g}^i \mathbf{g}^j, \quad (40)$$

where  $\mathbf{x} = \theta^j \mathbf{g}_j$  and

$$\frac{\partial \mathbf{g}_i}{\partial \theta^j} = \Gamma_{ij}^k \mathbf{g}_k, \quad \frac{\partial \mathbf{g}^i}{\partial \theta^j} = -\Gamma_{kj}^i \mathbf{g}^k, \quad (41)$$

$\Gamma_{ij}^k$  are called the Christoffel symbols of the second kind [3]. Analogously, we can define the derivative with respect to higher order tensors.

## 2.2 Transformation under the motion $\mathbf{x}(\mathbf{X}, t)$

We discuss how the differential elements transform under the motion  $\mathbf{x}(\mathbf{X}, t)$  in the line integral, surface integral, and volume integral, respectively. These transformation formulae will be useful in the derivation of conservation equations for various physical quantities.

### 2.2.1 Line element

Consider a curve in  $P_R \in \mathbf{R}^3$  parametrized by its own arclength  $L$  and the corresponding one in the Eulerian coordinate, mapped by  $\mathbf{x}(\mathbf{X}, t)$ , is parametrized by  $l$ . The line element is denoted as  $d\mathbf{x} = \mathbf{t} dl$  in the Eulerian coordinate, where  $\mathbf{t} = \frac{d\mathbf{x}}{dl}$  is the tangent vector, and the one in the Lagrangian coordinate is given by  $d\mathbf{X} = \mathbf{T} dL$ , where  $\mathbf{T}$  is the tangent vector in the Lagrange coordinate of the curve. By definition

$$\mathbf{F} \cdot d\mathbf{X} = d\mathbf{x}. \quad (42)$$

We arrive at

$$\mathbf{F} \cdot \mathbf{T} = \mathbf{t} \frac{dl}{dL}. \quad (43)$$

$\mathbf{F}$  maps the tangent vector in the Lagrangian coordinate to another tangent vector (not necessarily a unit vector) in the Eulerian coordinate.

### 2.2.2 Surface element

Consider a surface in  $P_R \in R^3$ . Let  $d\mathbf{X}_i, i = 1, 2$  be two surface vectors defining the surface element  $\mathbf{N} dS = d\mathbf{X}_1 \times d\mathbf{X}_2$ , where  $dS$  is the surface area element. The differentials  $d\mathbf{X}_i, i = 1, 2$  are transformed by

$$\mathbf{F} \cdot d\mathbf{X}_i = d\mathbf{x}_i, i = 1, 2. \quad (44)$$

The mapped surface element in the Eulerian coordinate is

$$\mathbf{F} \cdot d\mathbf{X}_1 \times \mathbf{F} \cdot d\mathbf{X}_2 = d\mathbf{x}_1 \times d\mathbf{x}_2 = \mathbf{n}ds, \quad (45)$$

where  $ds$  is the surface area element in the Eulerian coordinate. We find

$$\mathbf{F}^T \cdot \mathbf{n}ds = \det(\mathbf{F})\mathbf{N}dS. \quad (46)$$

We denote  $J = \det(\mathbf{F})$ ; then

$$\mathbf{F}^T \cdot \mathbf{n} = J\mathbf{N}\frac{dS}{ds}, (\mathbf{F}^T)^{-1} \cdot \mathbf{N} = \frac{1}{J}\mathbf{n}\frac{ds}{dS}. \quad (47)$$

$$ds = \frac{J}{\|\mathbf{F}^T \cdot \mathbf{n}\|}dS \quad (48)$$

We note that the following identity is used in the above derivation:

$$F_{i\alpha}F_{j\beta}F_{k\gamma}\epsilon_{ijk} = \epsilon_{\alpha\beta\gamma}\det(\mathbf{F}). \quad (49)$$

### 2.2.3 Volume element

Let  $d\mathbf{X}_i, i = 1, 2, 3$  be three differential vectors defining the volume element in the Lagrange coordinate. The volume element in the Eulerian coordinate in  $\mathbf{R}^3$  is given by

$$d\mathbf{v} = (d\mathbf{x}_1 \times d\mathbf{x}_2) \cdot d\mathbf{x}_3. \quad (50)$$

$$\begin{aligned} d\mathbf{v} &= (d\mathbf{x}_1 \times d\mathbf{x}_2) \cdot d\mathbf{x}_3 = (\mathbf{F} \cdot d\mathbf{X}_1 \times \mathbf{F} \cdot d\mathbf{X}_2) \cdot \mathbf{F} \cdot d\mathbf{X}_3 \\ &= J(d\mathbf{X}_1 \times d\mathbf{X}_2) \cdot d\mathbf{X}_3 = JdV. \end{aligned} \quad (51)$$

Here  $dV$  is the volume element in the Lagrange coordinate. It follows that  $J = 1$  if the transformation  $\mathbf{x}(\mathbf{X}, t)$  is volume preserving.

### 2.2.4 Material derivative

The material time derivative of a function  $f$  is defined as partial derivative with respect to time while the material coordinate  $\mathbf{Y}$  or the reference coordinate  $\mathbf{X}$  is held fixed:

$$\dot{f} = \frac{d}{dt}f = \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}}\right)f = \frac{\partial}{\partial t}f|_{\mathbf{Y}} = \frac{\partial}{\partial t}f|_{\mathbf{X}}, \quad (52)$$

where  $\mathbf{v} = \frac{\partial}{\partial t}\mathbf{x}(\mathbf{X}, \mathbf{t})$  is the velocity vector. We denote the velocity gradient tensor by  $\mathbf{L} = \nabla\mathbf{v}$ . The time derivative of the deformation tensor and the Jacobian are given by

$$\begin{aligned} \dot{\mathbf{F}} &= \mathbf{L} \cdot \mathbf{F}, \\ \dot{J} &= J\text{div}\mathbf{v}. \end{aligned} \quad (53)$$

Thus, the volume preserving transformation requires

$$\text{div} \mathbf{v} = \nabla \cdot \mathbf{v} = 0. \quad (54)$$

We derive the equations that the material derivative of the deformation tensor and the associated strain tensors satisfy. We recall the material derivative of the deformation tensor

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{F} = \mathbf{L} \cdot \mathbf{F}. \quad (55)$$

The material derivative of its inverse is

$$\dot{\mathbf{F}}^{-1} = -\mathbf{F}^{-1} \cdot \mathbf{L}. \quad (56)$$

From this, we can easily calculate the time derivative of the Finger tensor and the Cauchy tensor:

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{B} - [\mathbf{L} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{L}^T] = 0, \quad (57)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{c} + [\mathbf{L}^T \cdot \mathbf{c} + \mathbf{c} \cdot \mathbf{L}] = 0.$$

We decompose the strain rate tensor  $\mathbf{L}$  into the symmetric ( $\mathbf{D}$ ) and antisymmetric part ( $\mathbf{W}$ ):

$$\mathbf{L} = \mathbf{D} + \mathbf{W}, \mathbf{D}^T = \mathbf{D}, \mathbf{W}^T = -\mathbf{W}. \quad (58)$$

(57) can be rewritten into

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{B} - \mathbf{W} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{W} - [\mathbf{D} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{D}] = 0, \quad (59)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{c} - \mathbf{W} \cdot \mathbf{c} + \mathbf{c} \cdot \mathbf{W} + [\mathbf{D} \cdot \mathbf{c} + \mathbf{c} \cdot \mathbf{D}] = 0.$$

The left hand side expressions are called the upper-convected and lower convected derivative, respectively. A linear interpolation of the upper and lower convected derivative yields a new derivative

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) \mathbf{E} - \mathbf{W} \cdot \mathbf{E} + \mathbf{E} \cdot \mathbf{W} - a[\mathbf{D} \cdot \mathbf{E} + \mathbf{E} \cdot \mathbf{D}], \quad (60)$$

where  $\mathbf{E}$  is a second order tensor. For  $-1 \leq a \leq 1$ , this is known as the Gordon-Shoemaker derivative or Jaumann derivative [9]. Using the analogy between  $\mathbf{F}$  and  $\mathcal{F}$ , we have

$$\dot{\mathcal{F}} = \mathbf{L} \cdot \mathcal{F}. \quad (61)$$

The time derivative of  $\tau$  is

$$\begin{aligned} \dot{\tau} &= \overline{\mathcal{F} \cdot (\tau^{ij}) \cdot \mathcal{F}^T} = \dot{\mathcal{F}} \cdot (\tau^{ij}) \cdot \mathcal{F}^T + \mathcal{F} \cdot (\dot{\tau}^{ij}) \cdot \mathcal{F}^T + \mathcal{F} \cdot (\tau^{ij}) \cdot \dot{\mathcal{F}}^T \\ &= \mathcal{F} \cdot [\dot{\tau} + \mathbf{L} \cdot \tau + \tau \cdot \mathbf{L}^T]^{ij} \cdot \mathcal{F}^T. \end{aligned} \quad (62)$$

Similarly,

$$\dot{\mathcal{F}}^{-1} = -\mathcal{F}^{-1} \cdot \mathbf{L} \quad (63)$$

and

$$\hat{\tau} = \overline{\mathcal{F}^{-1T} \tau_{ij} \mathcal{F}^{-1}} = \mathcal{F}^{-1T} \dot{\tau}_{ij} \mathcal{F}^{-1} - [\mathbf{L}^T \cdot \mathcal{F}^{-1T} \tau_{ij} \cdot \mathcal{F}^{-1} + \mathcal{F}^{-1T} \tau_{ij} \cdot \mathcal{F}^{-1} \cdot \mathbf{L}]. \quad (64)$$

If we choose the material coordinate as the Eulerian coordinate at  $t_0$ ,  $\mathcal{F}|_{t_0} = \mathbf{I}$ . Then,  $\hat{\tau}$  is also known as the contravariant convected derivative and  $\check{\tau}$  is the covariant convected derivative.

### 2.2.5 Transport theorem

Let  $\mathcal{G}$  be a finite material volume in the Eulerian coordinate and  $f(\mathbf{x}, t)$  be a differentiable function. Then,

$$\frac{d}{dt} \int_{\mathcal{G}} f(\mathbf{x}, t) d\mathbf{x} = \int_{\mathcal{G}} \left( \frac{d}{dt} f + \operatorname{div} \mathbf{v} f \right) d\mathbf{x} = \int_{\mathcal{G}} \left( \frac{\partial}{\partial t} f + \nabla(\mathbf{v} f) \right) d\mathbf{x}. \quad (65)$$

The integral on the right hand side can be rearranged into

$$\frac{d}{dt} \int_{\mathcal{G}} f d\mathbf{x} = \int_{\mathcal{G}} \frac{\partial}{\partial t} f d\mathbf{x} + \int_{\partial \mathcal{G}} f \mathbf{v} \cdot \mathbf{n} ds, \quad (66)$$

where  $\mathbf{n}$  is the unit external normal of  $\partial \mathcal{G}$ .

## 2.3 Conservation laws

Several conservation laws are postulated, including the conservation of mass, linear momentum, angular momentum, and energy. We present them in both the Eulerian coordinate and the Lagrange coordinate, respectively.

### 2.3.1 Eulerian description

Let  $\mathcal{P}$  be a material volume in  $\mathbf{R}^3$ . We denote the velocity by  $\mathbf{v}$ , the Cauchy stress tensor by  $\tau$  and the internal energy density per unit mass by  $\epsilon$ . Conservation of mass

$$\frac{d}{dt} \int_{\mathcal{P}} \rho d\mathbf{v} = 0, \quad (67)$$

where  $\rho$  is the density in the Eulerian coordinate. Conservation of linear momentum

$$\frac{d}{dt} \int_{\mathcal{P}} \rho \mathbf{v} d\mathbf{v} = \int_{\partial \mathcal{P}} \tau \cdot \mathbf{n} ds + \int_{\mathcal{P}} \mathbf{b} d\mathbf{v}, \quad (68)$$

where  $\mathbf{b}$  is the body force density per unit volume. Conservation of angular momentum

$$\frac{d}{dt} \int_{\mathcal{P}} \rho \mathbf{x} \times \mathbf{v} d\mathbf{v} = \int_{\partial\mathcal{P}} \mathbf{x} \times (\boldsymbol{\tau} \cdot \mathbf{n}) ds + \int_{\mathcal{P}} \mathbf{x} \times \mathbf{b} d\mathbf{v}, \quad (69)$$

where  $\mathbf{x}$  is the position vector. Conservation of energy

$$\frac{d}{dt} \int_{\mathcal{P}} \rho \left[ \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \epsilon \right] d\mathbf{v} = \int_{\mathcal{P}} \rho (\mathbf{b} \cdot \mathbf{v} + r) d\mathbf{v} + \int_{\partial\mathcal{P}} (\mathbf{t} \cdot \mathbf{v} - h) ds. \quad (70)$$

where  $h$  is the heat flux per unit volume and  $r$  is the heat source density. The traction and the heat flux are given, respectively, by

$$\mathbf{t} = \boldsymbol{\tau} \cdot \mathbf{n}, h = \mathbf{q} \cdot \mathbf{n}, \quad (71)$$

where  $\mathbf{q}$  is the flux vector.

### 2.3.2 Lagrangian description

We denote the density in the Lagrange coordinate by  $\rho_R$  and same notation for velocity and internal energy density. Conservation of mass

$$\rho_R(t) = \rho_R. \quad (72)$$

Conservation of linear momentum

$$\frac{d}{dt} \int_{\mathcal{P}_R} \rho_R \mathbf{v} d\mathbf{V} = \int_{\mathcal{P}_R} \mathbf{b}_R d\mathbf{V} + \int_{\partial\mathcal{P}_R} \mathbf{t}_R dS, \quad (73)$$

where  $\mathbf{t}_R$  is the traction force and  $\mathbf{b}_R$  is the body force density per unit volume in the Lagrange coordinate. Conservation of angular momentum

$$\frac{d}{dt} \int_{\mathcal{P}} \rho_R \mathbf{X} \times \mathbf{v} d\mathbf{V} = \int_{\partial\mathcal{P}} \mathbf{X} \times \mathbf{t}_R dS + \int_{\mathcal{P}} \mathbf{X} \times \mathbf{b}_R d\mathbf{V}, \quad (74)$$

where  $\mathbf{X}$  is the position vector in the Lagrange coordinate. Conservation of energy

$$\frac{d}{dt} \int_{\mathcal{P}_R} \rho_R \left[ \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \epsilon \right] d\mathbf{X} = \int_{\mathcal{P}_R} \rho_R (\mathbf{b}_R \cdot \mathbf{v} + r) d\mathbf{X} + \int_{\partial\mathcal{P}_R} (\mathbf{t}_R \cdot \mathbf{v} - h_R) dS, \quad (75)$$

where  $h_R$  is the heat flux.

$$\mathbf{t}_R = \mathbf{P} \cdot \mathbf{N}, h_R = \mathbf{q} \cdot \mathbf{N}, \quad (76)$$

$\mathbf{P}$  is the Piola-Kirchhoff stress tensor. There is a relationship between the Cauchy stress tensor and the Piola-Kirchhoff tensor:

$$\mathbf{P} = J_{\mathcal{T}} \cdot \mathbf{F}^{-T}. \quad (77)$$

As you can see, the Piola-Kirchhoff tensor is normally not symmetric even though  $\boldsymbol{\tau}$  is.

## 2.4 Superimposed rigid body motion (SRBM) and invariant principles

Two motions  $(\mathbf{x} = \mathbf{x}(\mathbf{X}, t), t)$  and  $(\mathbf{x}^+ = \mathbf{x}^+(\mathbf{X}, t^+), t^+)$  are said to be related by a superimposed rigid body motion (SRBM) if

$$\mathbf{x}^+ = \mathbf{Q}(t) \cdot \mathbf{x} + \mathbf{c}(t), t^+ = t + c. \quad (78)$$

The gradient operator between the two Eulerian coordinates is transformed according to

$$\nabla^+ = \mathbf{Q} \cdot \nabla. \quad (79)$$

Under the SRBM, we have

$$\begin{aligned} \mathbf{v}^+ &= \Omega \cdot \mathbf{Q} \cdot \mathbf{x} + \mathbf{Q} \cdot \mathbf{v} + \dot{\mathbf{c}}(t), \mathbf{F}^+ = \mathbf{Q} \cdot \mathbf{F}, \mathbf{C}^+ = \mathbf{C}, \mathbf{B}^+ = \mathbf{F} \cdot \mathbf{B} \cdot \mathbf{F}^T, \\ \mathbf{L}^+ &= \mathbf{Q} \cdot \mathbf{L} \cdot \mathbf{Q} + \Omega, \mathbf{D}^+ = \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T, \mathbf{W}^+ = \mathbf{Q} \cdot \mathbf{W} \cdot \mathbf{Q}^T + \Omega, \end{aligned} \quad (80)$$

where

$$\Omega = \dot{\mathbf{Q}} \cdot \mathbf{Q}^T, \quad (81)$$

is an antisymmetric tensor. Let  $\mathbf{n}$  be a vector and  $\mathbf{n}^+$  the vector in the "+" coordinate with the same coordinates. Then,

$$\mathbf{n}^+ = \mathbf{Q} \cdot \mathbf{n}. \quad (82)$$

The time derivative of the vector  $\mathbf{n}^+$  is given by

$$\dot{\mathbf{n}}^+ = \Omega \cdot \mathbf{Q} \cdot \mathbf{n} + \mathbf{Q} \cdot \dot{\mathbf{n}}. \quad (83)$$

Let  $\mathbf{G}$  be a second order tensor in the coordinate system  $\mathbf{x}$  and  $\mathbf{G}^+$  the "same" tensor with the same components in the coordinate system  $\mathbf{x}^+$ , i.e.,

$$\mathbf{G} = g^{ij} \mathbf{e}_i \mathbf{e}_j, \mathbf{G}^+ = g^{ij} \mathbf{e}_i^+ \mathbf{e}_j^+, \quad (84)$$

where

$$\mathbf{e}_i^+ = \mathbf{Q} \cdot \mathbf{e}_i. \quad (85)$$

Then

$$\mathbf{G}^+ = \mathbf{Q} \cdot \mathbf{G} \cdot \mathbf{Q}^T, G_{kl}^+ = Q_{ki} Q_{lj} G_{ij}. \quad (86)$$

Let  $\mathcal{L}_{i_1 \dots i_n}$  be an n-th order tensor and  $\mathcal{L}_{i_1 \dots i_n}^+$  the same order in the transformed space with the same coordinates.

$$\mathcal{L}_{k_1 \dots k_n}^+ = Q_{k_1 i_1} \cdots Q_{k_n i_n} \mathcal{L}_{i_1 \dots i_n}. \quad (87)$$

If  $\mathcal{L}^+$  and  $\mathcal{L}$  satisfy the above equation, they are said to transform like an nth order tensor under the SRBM. Any constitutive law must be invariant under the SRBM. In addition, we impose the following invariant assumptions. For the physical variables, the scalar and the angle between any two vectors should be invariant. In addition, the difference between the inertia force and the body force transforms like a vector. The following are assumed in continuum mechanics:

$$\begin{aligned} \mathbf{t} \cdot (\mathbf{x} - \mathbf{y}) &= \mathbf{t}^+ \cdot (\mathbf{x}^+ - \mathbf{y}^+), \mathbf{t}^+ = \mathbf{Q} \cdot \mathbf{t}, \\ h^+ &= h, \rho^+ = \rho, \epsilon^+ = \epsilon, r^+ = r, \mathbf{b}^+ - \rho \ddot{\mathbf{x}}^+ = \mathbf{Q} \cdot (\mathbf{b} - \rho \ddot{\mathbf{x}}), \eta^+ = \eta, \theta^+ = \theta. \end{aligned} \quad (88)$$

Here  $\eta$  is the entropy and  $\theta$  the temperature.

## 2.5 Invariant time derivatives

Let  $\mathbf{S}$  be a second order tensor. The corotational derivative defined by

$$\hat{\mathbf{S}} = \dot{\mathbf{S}} - \mathbf{W} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{W}, \quad (89)$$

is an invariant time derivative in that it transforms like a second order tensor under a SRBM, i.e.

$$\hat{\mathbf{S}}^+ = \mathbf{Q} \cdot \hat{\mathbf{S}} \cdot \mathbf{Q}^T. \quad (90)$$

Let  $\mathcal{L}$  be the third order tensor. Then,

$$\begin{aligned} \dot{\mathcal{L}}_{ijk}^+ - \mathbf{W}_{i\alpha}^+ \mathcal{L}_{\alpha jk}^+ - \mathbf{W}_{j\alpha}^+ \mathcal{L}_{i\alpha k}^+ - \mathbf{W}_{k\alpha}^+ \mathcal{L}_{ij\alpha}^+ &= Q_{in} Q_{jm} Q_{kp} [\dot{\mathcal{L}}_{nmp} - \\ \mathbf{W}_{n\alpha} \mathcal{L}_{\alpha mp} - \mathbf{W}_{m\alpha} \mathcal{L}_{n\alpha p} - \mathbf{W}_{p\alpha} \mathcal{L}_{nm\alpha}]. \end{aligned} \quad (91)$$

The invariant time derivative is defined as

$$\hat{\mathcal{L}}_{ijk} = \dot{\mathcal{L}}_{ijk} - \mathbf{W}_{i\alpha} \mathcal{L}_{\alpha jk} - \mathbf{W}_{j\alpha} \mathcal{L}_{i\alpha k} - \mathbf{W}_{k\alpha} \mathcal{L}_{ij\alpha}. \quad (92)$$

For n-th order tensor, the invariant time derivative is defined as

$$\hat{\mathcal{L}}_{i_1 \dots i_n} = \dot{\mathcal{L}}_{i_1 \dots i_n} - \sum_{k=1}^n W_{i_k \alpha} \mathcal{L}_{i_1 \dots \alpha \dots i_n}. \quad (93)$$

Namely, it transforms like an n-th order tensor. The invariant time derivative for a vector is

$$\mathbf{N} = \dot{\mathbf{n}} - \mathbf{W} \cdot \mathbf{n}, \quad (94)$$

namely,  $\mathbf{N}$  transforms like a vector:

$$\mathbf{N}^+ = \mathbf{Q} \cdot \mathbf{N}. \quad (95)$$

In constitutive equations, only the invariant derivatives can be used.

## 2.6 Material symmetry

Consider two referential descriptions of the same material volume denoted by the coordinate  $\mathbf{X}, \mathcal{X}$ , respectively, that yields the same constitutive function or functional  $f$ . We denote

$$\mathbf{H} = \frac{\partial \mathcal{X}}{\partial \mathbf{X}}. \quad (96)$$

$\mathbf{H}$  is called a symmetry transformation. All symmetry transformations form a group called the symmetry group, denoted by  $\mathcal{G}$ . The density in the two Lagrangian coordinates are related by

$$\rho_R |det(H)| = \rho_{\mathcal{R}}. \quad (97)$$

By requiring  $\rho_R = \rho_{\mathcal{R}}$ , we arrive at

$$det(H) = \pm 1. \quad (98)$$

So the symmetry group consists of all uni-modular matrices. Let  $f(\mathbf{F}, \dots)$  be a constitutive function depending on the deformation tensor  $\mathbf{F}$  with respect to the two referential descriptions. Then,

$$f(\mathbf{F}, \dots) = f(\mathbf{F} \cdot \mathbf{H}, \dots). \quad (99)$$

We define

$$\mu = \{\mathbf{H} | det(\mathbf{H}) = \pm 1\}, O(3) = \{\mathbf{H} | \mathbf{H}^T = \mathbf{H}^{-1}\}. \quad (100)$$

If  $\mathcal{G} = \mu$ , the material is called a fluid; if  $\mathcal{G} = O(3)$ , it is called an isotropic solid; if  $\mathcal{G} \subset O(3)$ , it is called an anisotropic solid. If  $O(3) \not\subset \mathcal{G}$ , the material is neither a fluid nor a solid. The invariant assumptions along with the material symmetry can be used together to derive constitutive relations for the material in question.

### 3 Second law of thermodynamics, Clausius-Duhem inequality

The conservation laws, material symmetry and the invariant principles are not sufficient to determine the necessary relations between physical variables. Thermodynamical considerations must be accounted for then. Let  $\eta$  be the entropy density per unit mass. The second law of thermodynamics in the form of Clausius-Duhem inequality is given by

$$\frac{d}{dt} \int_{\mathcal{P}} \rho \eta d\mathbf{x} \geq \int_{\mathcal{P}} \frac{r}{\theta} d\mathbf{x} - \int_{\partial\mathcal{P}} \frac{h}{\theta} ds, \quad (101)$$

where  $\mathcal{P}$  is an arbitrary material volume. This states that the total entropy production rate exceeds the rate of heat generated internally per unit temperature minus the heat loss per temperature through the boundary in material volume  $\mathcal{P}$ . The equivalent Lagrangian form is

$$\frac{d}{dt} \int_{\mathcal{P}_R} \rho_R \eta d\mathbf{x} \geq \int_{\mathcal{P}_R} \frac{r_R}{\theta} d\mathbf{x} - \int_{\partial\mathcal{P}_R} \frac{h_R}{\theta} ds, \quad (102)$$

where  $\mathcal{P}_R$  is the material volume in the referential configuration. For a thermodynamical process, both the internal energy and the entropy are fundamental physical variables. However, the absolute temperature in many occasions is more convenient to apply than the entropy in formulating a theory. In order to use the absolute temperature, we need to introduce the Helmholtz free energy through a Legendre transformation:

$$\psi = \epsilon - \theta \eta. \quad (103)$$

Namely, the relationship between  $\eta$  and  $\theta$  is through  $\theta = \frac{\partial \epsilon}{\partial \eta}$ . Solving the implicit equation for  $\eta$  and substitute it into the definition, we obtain the functional dependence of  $\psi$  on  $\theta$ . With the Helmholtz free energy, the Clausius-Duhem inequality in its point-wise or localized form becomes

$$-\rho \dot{\psi} - \rho \eta \dot{\theta} + \mathbf{T} \cdot \mathbf{D} - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \geq 0. \quad (104)$$

The invariant principles, the material symmetry, the second law of thermodynamics, and a constitutive assumption allow us to derive the constitutive relation for the stress and other thermodynamical variables. As examples, we illustrate how to derive the stress constitutive law for viscous fluids under isothermal and nonisothermal conditions, respectively. **Example 1: isothermal viscous fluids** We consider a purely mechanical theory for isothermal viscous fluids. We assume the stress tensor depends on the history of motion only through  $\rho, \mathbf{v}, \mathbf{L}$ :

$$\mathbf{T} = \mathbf{T}(\rho, \mathbf{v}, \mathbf{L}) = \mathbf{T}(\rho, \mathbf{v}, \mathbf{D}, \mathbf{W}). \quad (105)$$

We apply SRBM on the stress tensor to obtain

$$\mathbf{T}^+ = \mathbf{Q} \cdot \mathbf{T} \mathbf{Q}^T = \mathbf{T}(\rho, \Omega \cdot \mathbf{Q} \mathbf{x} + \mathbf{Q} \cdot \mathbf{v} + \dot{\mathbf{c}}, \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T, \mathbf{Q} \cdot \mathbf{W} \cdot \mathbf{Q}^T + \Omega) \quad (106)$$

for an arbitrary orthogonal function of  $\mathbf{Q}(\mathbf{t})$ , where  $\Omega = \dot{\mathbf{Q}} \cdot \mathbf{Q}$ .

- We first choose thermomechanical processes such that  $\mathbf{Q}(t) = I, \dot{\mathbf{Q}}(0) = 0$  and  $\dot{\mathbf{c}}$  arbitrary. Then,  $\mathbf{T}(\rho, \mathbf{v} + \dot{\mathbf{c}}, \mathbf{D}, \mathbf{W}) = \mathbf{T}(\rho, \mathbf{v}, \mathbf{D}, \mathbf{W})$  for an arbitrary vector  $\dot{\mathbf{c}}$ . This implies that  $\mathbf{T}$  does not depend on  $\mathbf{v}$ .
- Next, we consider  $\mathbf{Q} = e^{\Omega t}$ . Then,  $\mathbf{T}(\rho, \mathbf{D}, \mathbf{W}) = \mathbf{T}(\rho, \mathbf{D}, \mathbf{W} + \Omega)$  for an arbitrary antisymmetric tensor  $\Omega$  at  $t = 0$ . Hence,  $\mathbf{T}$  does not depend on  $\mathbf{W}$  either, i.e.,  $\mathbf{T} = \mathbf{T}(\rho, \mathbf{D})$ . Moreover,

$$\mathbf{T}(\rho, \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T) = \mathbf{Q} \cdot \mathbf{T}(\rho, \mathbf{D}) \cdot \mathbf{Q}^T, \quad (107)$$

according to SRBM. Namely,  $\mathbf{T}$  must be an isotropic tensor function of  $\mathbf{D}$ .

*Reiner-Rivlin fluids:* if we assume  $\mathbf{T}$  is given by a power series of  $\mathbf{D}$ , we arrive at the Reiner-Rivlin fluid. From Cauchy-Hamilton theorem, we have

$$\mathbf{T} = \alpha_0 \mathbf{I} + \alpha_1 \mathbf{D} + \alpha_2 \mathbf{D}^2, \quad (108)$$

where  $\alpha_i, i = 0, 1, 2$  are functions of  $\rho$  and invariants of  $\mathbf{D}$  ( $tr(\mathbf{D}), \mathbf{D} : \mathbf{D}, det(\mathbf{D})$ ). *Linear viscous fluids:* if we assume

$$\mathbf{T} = \mathcal{C}(\rho) : \mathbf{D} - \mathbf{A}(\rho), \quad (109)$$

where  $\mathcal{C}$  is a fourth order tensor; then

$$\mathcal{C} : \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T - \mathbf{A} = \mathbf{Q} \cdot [\mathcal{C} : \mathbf{D} - \mathbf{A}] \cdot \mathbf{Q}^T \quad (110)$$

for all orthogonal tensors  $\mathbf{Q}$ . A sufficient condition for this is

$$\mathcal{C} : \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T = \mathbf{Q} \cdot \mathcal{C} : \mathbf{D} \cdot \mathbf{Q}^T, \mathbf{A} = \mathbf{Q} \cdot \mathbf{A} \cdot \mathbf{Q}^T. \quad (111)$$

This implies

$$\mathbf{A} = -p \mathbf{I}, \mathcal{C}_{ijkl} = a \delta_{ij} \delta_{kl} + b \delta_{il} \delta_{jk} + c \delta_{il} \delta_{jk}, \quad (112)$$

where  $p, a, b, c$  are functions of  $\rho$ . Finally, the stress tensor can be written into

$$\mathbf{T} = -p + \lambda(tr \mathbf{D}) \mathbf{I} + 2\mu \mathbf{D}, \quad (113)$$

with  $p, \lambda, \mu$  functions of  $\rho$ . The theory as is is not complete, an equation of state, a relation between  $p$  and  $\rho$ , is needed to complete the theory. This can only be done by accounting for the thermodynamics. **Example 2: nonisothermal viscous fluids** We assume the Cauchy stress tensor  $\mathbf{T}$ , the heat flux  $\mathbf{q}$ , the free energy  $\psi$ , and the entropy are functions of  $(\rho, \mathbf{v}, \mathbf{L}, \theta, \mathbf{g})$ , where  $\mathbf{g} = \nabla\theta$  is the temperature gradient. Using the same SRBM argument, we deduce that these thermodynamical quantities only depend on  $(\rho, \mathbf{D}, \theta, \mathbf{g})$ . Substitution of the thermodynamical quantities into the Clausius-Duhem inequality yields

$$-\rho\left(\frac{\partial\psi}{\partial\theta} + \dot{\eta}\right)\dot{\theta} + (\mathbf{T} + \rho^2\frac{\partial\psi}{\partial\rho}\mathbf{I}) \cdot \mathbf{D} - \rho\frac{\partial\psi}{\partial\mathbf{D}} \cdot \dot{\mathbf{D}} - \rho\frac{\partial\psi}{\partial\mathbf{g}} \cdot \dot{\mathbf{g}} - \frac{1}{\theta}\mathbf{q} \cdot \mathbf{g} \geq 0, \quad (114)$$

where we have used the conservation of mass:  $\dot{\rho} = -\rho \text{tr} \mathbf{D} = -\rho \mathbf{I} : \mathbf{D}$ . This inequality should be valid for any thermomechanical processes. We can choose the special thermomechanical process such as

$$\dot{\theta} = \text{arbitrary constant}, \mathbf{D} = \dot{\mathbf{D}} = \mathbf{0}, \dot{\mathbf{g}} = \mathbf{g} = \mathbf{0}. \quad (115)$$

to deduce

$$\eta = -\frac{\partial\psi}{\partial\theta}. \quad (116)$$

Analogously, we find

$$\frac{\partial\psi}{\partial\mathbf{D}} = \mathbf{0}, \frac{\partial\psi}{\partial\mathbf{g}} = \mathbf{0}. \quad (117)$$

Thus,

$$\psi = \psi(\rho, \theta) \quad (118)$$

and the Clausius-Duhem inequality reduces to

$$(\mathbf{T} + \rho^2\frac{\partial\psi}{\partial\rho}\mathbf{I}) \cdot \mathbf{D} - \frac{1}{\theta}\mathbf{q} \cdot \mathbf{g} \geq 0. \quad (119)$$

We note that the free energy is invariant under the SRBM:  $\psi^+ = \psi$ . For linear viscous fluids, we assume

$$\begin{aligned} \mathbf{T} + \rho^2\frac{\partial\psi}{\partial\rho}\mathbf{I} &= \mathcal{A}_1 + \mathcal{A}_2 \cdot \mathbf{g} + \mathcal{A}_3 : \mathbf{D}, \\ \mathbf{q} &= \mathcal{K}_1 + \mathcal{K}_2 \cdot \mathbf{g} + \mathcal{K}_3 : \mathbf{D}, \end{aligned} \quad (120)$$

where the coefficients are functions of  $(\rho, \theta)$ ,  $\mathcal{A}_1$  is a second order tensor,  $\mathcal{A}_2$  is a third order tensor,  $\mathcal{A}_3$  a fourth order tensor, and  $\mathcal{K}_1$  is a vector,  $\mathcal{K}_2$  a second order tensor,  $\mathcal{K}_3$  a third order tensor, respectively. We consider the impact of a SRBM:

$$\mathbf{T}^+ = \mathbf{Q} \cdot \mathbf{T} \cdot \mathbf{Q}^T, \mathbf{q}^+ = \mathbf{Q} \cdot \mathbf{q}, \mathbf{g}^+ = \mathbf{Q} \cdot \mathbf{g}, \mathbf{D}^+ = \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T \quad (121)$$

for all orthogonal tensors  $\mathbf{Q}$ . This demands

$$\begin{aligned}\mathcal{A}_{1,ij} &= -p\delta_{ij}, \mathcal{A}_{2,ijk} = c\epsilon_{ijk}, \\ \mathcal{A}_{3,ijkl} &= \lambda\delta_{ij}\delta_{kl} + \mu\delta_{ik}\delta_{jl} + \gamma\delta_{il}\delta_{jk}, \\ \mathcal{K}_1 &= \mathbf{0}, \mathcal{K}_{2,ij} = -K\delta_{ij}, \mathcal{K}_{3,i,j,k} = E\epsilon_{ijk}.\end{aligned}\tag{122}$$

This gives us

$$\mathbf{T} + \rho^2 \frac{\partial \psi}{\partial \rho} = -p\mathbf{I} + \lambda(\text{tr}\mathbf{D})\mathbf{I} + 2\mu\mathbf{D}, \mathbf{q} = -K\mathbf{g},\tag{123}$$

where we have replaced  $\mu + \lambda$  by  $2\mu$  in the final expression of the stress tensor. From (119), we have

$$\mathbf{q} \cdot \mathbf{g} \leq 0, [\mathbf{T} + \rho^2 \frac{\partial \psi}{\partial \rho}] : \mathbf{D} \geq 0,\tag{124}$$

which implies

$$K \geq 0.\tag{125}$$

We rescale the second inequality by  $\alpha\mathbf{D}$  so that

$$[-p\mathbf{I} + \rho^2 \frac{\partial \psi}{\partial \rho} \mathbf{I} + \alpha\lambda \text{tr}(\mathbf{D})\mathbf{I} + 2\alpha\mu\mathbf{D}] : \mathbf{D} \geq 0\tag{126}$$

for all  $\alpha$ . Then, we have

$$\begin{aligned}(-p + \rho^2 \frac{\partial \psi}{\partial \rho})\mathbf{I} : \mathbf{D} &\geq 0, \\ (\lambda \text{tr}(\mathbf{D})\mathbf{I} + 2\mu\mathbf{D}) : \mathbf{D} &\geq 0.\end{aligned}\tag{127}$$

Notice that

$$\mathbf{D} = \frac{1}{3}\text{tr}(\mathbf{D})\mathbf{I} + \mathbf{S},\tag{128}$$

where  $\text{tr}(\mathbf{S}) = 0$ .

$$[\lambda \text{tr}(\mathbf{D})\mathbf{I} + 2\mu\mathbf{D}] : \mathbf{D} = (\lambda + \frac{2\mu}{3})(\text{tr}(\mathbf{D}))^2 + 2\mu\mathbf{S} : \mathbf{S} \geq 0.\tag{129}$$

Thus,

$$p = -\rho^2 \frac{\partial \psi}{\partial \rho}, \lambda + \frac{2\mu}{3} \geq 0, \mu \geq 0.\tag{130}$$

This completes the theory for compressible (linear) viscous fluids. Without the second law of thermodynamics, we would never be able to derive the equation of state for the pressure [2]

## 4 Constitutive models for flexible polymers

In the modeling of complex fluids, we assume the materials incompressible. The governing system of equations for the material system consists of the continuity equation, the balance of linear momentum equation, the constitutive equation for the elastic stress tensor. **Continuity equation**

$$\nabla \cdot \mathbf{v} = 0, \quad (131)$$

where  $\mathbf{v}$  is the velocity vector.

**Balance of linear momentum equation**

$$\rho \frac{\partial}{\partial t} \mathbf{v} = \nabla(-p\mathbf{I} + \tau) + \mathbf{F}, \quad (132)$$

where  $\rho$  is the density for the polymeric fluid,  $p$  is the pressure,  $\tau$  is the extra stress tensor, and  $\mathbf{F}$  is the external force.

**Constitutive equation of stress**

$$f(\mathbf{D}, \tau) = 0, \quad (133)$$

where  $f$  is a function or functional of the strain rate tensor  $\mathbf{D}$  and extra stress tensor  $\tau$ . The constitutive modeling is the process of establishing the functional relationship between  $\mathbf{D}$  and  $\tau$ . There are several approaches to modeling of complex fluids. These include the models of the generalized Newtonian Fluids, linear viscoelastic models, retarded-motion expansion, memory-integral expansion, continuum mechanics models, kinetic (molecular) theories, and GENERIC/Poisson bracket formulation. We list the first a few in a chronological order below.

### **Generalized Newtonian Fluids:**

In order to model the strain-rate dependent viscosity exhibited in the polymeric fluids, the viscosity in the extra stress is expressed as a nonlinear function of the strain rate tensor  $\mathbf{D}$  and the extra stress is proportional to the strain rate nonlinearly:

$$\tau = \eta(\mathbf{D})\mathbf{D}. \quad (134)$$

**Examples:** (i). Carreau-Yasuda model:

$$\eta(\mathbf{D}) = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\lambda\sqrt{\mathbf{D} : \mathbf{D}/2})^a]^{(n-1)/a}, \quad (135)$$

where  $\eta_0$  is the zero-shear-rate viscosity,  $\eta_\infty$  is the infinite-shear-rate viscosity,  $\lambda$  is a time constant,  $n$  is the power-law-exponent,  $a$  is a dimensionless parameter that characterizes the

transitional region between the zero-shear-rate region and the power-law region [3].

(ii). Power law model

$$\eta = m(\mathbf{D} : \mathbf{D})^{(n-1)/2}, \quad (136)$$

where  $n$  is the power-law-exponent and  $m$  is dimensional parameter ( $Pa.s^n$ ).

Both models can be fine-tuned to capture the shear thinning behavior in shear. However, they are after all phenomenological models, thus often fail to model the complex relaxation phenomenon in the complex fluids such as in shear reversal, step-strain, step-stress shear experiments.

### Linear viscoelastic models

Generalizing the linear viscoelastic theories developed for solids to complex fluids, one can derive the linear viscoelastic models, in which the extra stress tensor is a linear functional of the strain rate history or strain history.

$$\tau = \int_{-\infty}^t G(t-t')\mathbf{D}(t')dt' = - \int_{-\infty}^t M(t-t')\gamma(t,t')dt', \quad (137)$$

where  $G(t)$  is the elastic relaxation modulus,  $M(t)$  is the memory function, and  $\gamma(t,t') = \int_t^{t'} \mathbf{D}(t'')dt''$  is the strain tensor  $t'$  to  $t$  [3].

**Example:** (i). The linear Maxwell model is given by  $G(t) = \frac{\eta}{\lambda}e^{-t/\lambda}$ , where  $\eta$  is called the polymer viscosity and  $\lambda$  is the relaxation time.

(ii). The Jeffreys model is given by  $\frac{\eta_0}{\lambda_1}(1 - \frac{\lambda_2}{\lambda_1})e^{-t/\lambda_1} - \frac{2\eta_0\lambda_2}{\lambda_1}\delta(t)$ , where the additional time parameter  $\lambda_2$  is called the retardation time.

### Quasilinear viscoelastic models

The quasilinear viscoelastic models are obtained by replacing the time derivative in the linear viscoelastic models by the convected time derivatives. [3].

### Retarded-motion expansion

In the retarded-motion expansion, the extra stress tensor is expanded in the convected derivatives of the rate of strain tensor:

$$\tau = b_1\mathbf{D} + b_2\mathbf{D}_{(2)} + b_{11}\mathbf{D} \cdot \mathbf{D} + b_3\mathbf{D}_{(3)} + b_{12}(\mathbf{D} \cdot \mathbf{D}_{(2)} + \mathbf{D}_{(2)} \cdot \mathbf{D}) + b_{111}\mathbf{D} : \mathbf{D}\mathbf{D} + \dots, \quad (138)$$

where  $\mathbf{D}_{(i)}$  is the  $i$ th convected derivative of the strain tensor with  $\mathbf{D} = \mathbf{D}_{(1)}$  and  $b_j$  are the retarded-motion constants.  $\mathbf{D}_{(i+1)} = \frac{d\mathbf{D}_{(i)}}{dt} - [\nabla\mathbf{v} \cdot \mathbf{D}_{(i)} + \mathbf{D}_{(i)} \cdot \nabla\mathbf{v}^T]$ . For example, the model for the second order fluid is given by the first three terms in the retarded-motion expansion [3].

### Memory-integral expansion

The stress is assumed a functional of the strain history, in which the stress is represented

as the Frechet series of the convected derivatives of the strain tensor. The retarded-motion expansion can be derived from this more general method as a matter of fact.

$$\begin{aligned} \tau = & - \int_{-\infty}^t M(t-t')\gamma(t')dt' - \int_{-\infty}^t \int_{-\infty}^t M_{II}(t-t', t-t'')(\gamma' \cdot \gamma'' + \gamma'' \cdot \gamma')dt''dt' + \\ & \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t M_{III}(t-t', t-t'', t-t''')\gamma'\gamma'' : \gamma''' dt''' dt'' dt' + \dots, \end{aligned} \quad (139)$$

where  $\gamma' = \gamma(t, t')$  is the strain tensor and M's are the memory functions [3].

### Macroscopic models:

A large class of constitutive equations for the stress tensor can be written into the form

$$\begin{aligned} \tau &= 2\eta\mathbf{D} + \tau_p, \\ \tau_p + \lambda\hat{\tau}_p + f(\mathbf{D}, \tau_p) &= 2\eta\mathbf{D}, \end{aligned} \quad (140)$$

where

$$\hat{\tau}_p = \frac{d\tau_p}{dt} - \Omega \cdot \tau_p + \tau_p \cdot \Omega - a[\mathbf{D} \cdot \tau_p + \tau_p \cdot \mathbf{D}] \quad (141)$$

is the Gordon-Schowalter derivative; a=-1: lower convected, a=1: upper convected, a=0: corotational, is the vorticity tensor; the choice of f specifies the model. **Examples:** (i). f=0 yields the Johnson Segalman model. (ii).  $f = c\tau \cdot \tau$  gives the Giesekus model, where c is a constant. (iii).  $f = c\mathbf{D} : \tau(\tau + G\mathbf{I})$ , where c and G are constants, gives the Larson model. (iv).  $f = 0$ ,  $\lambda = \lambda(\sqrt{\mathbf{D} : \mathbf{D}})$  and  $\eta = \eta(\sqrt{\mathbf{D} : \mathbf{D}})$  yield the white metzner model. (v). Phan-Thien/Tanner model corresponds to  $f = Y(tr(\tau))\tau$ , where Y is a scalar function. The Poisson bracket formulation and the Generic formulation can be found in the book [1]

## 5 Kinetic theory and the Rouse model for flexible polymers

In this section, we give a crash course on the development of kinetic theories for polymeric liquids. We derive the kinetic theory using a phenomenological approach, which can be called a poor man's kinetic theory. We begin with the conservation of polymer number density. This is the most fundamental conservation law in the development of kinetic theories. Let  $\psi$  be the number density of some polymer and  $\mathbf{F}$  the flux of the polymer flow in the generalized coordinate or phase space  $x$ . The conservation law for the number of polymers in any "material volume" in the phase space yields

$$\frac{\partial\psi}{\partial t} + \frac{\partial\mathbf{F}}{\partial x} = 0. \quad (142)$$

Using the instantaneous velocity  $\mathbf{v}$  at  $x$ , we can rewrite the flux as

$$\mathbf{F} = \mathbf{v}\psi. \quad (143)$$

Assume the motion of polymers are due to a force generated by an external field  $U$  and the Brownian force. The inertialess force balance equation reads

$$L^{-1} \cdot \mathbf{v} + \frac{\partial}{\partial x} \mu = 0, \mu = kT \ln \rho + U, \quad (144)$$

where  $\mu$  is the chemical potential and  $L^{-1}$  the friction coefficient matrix, which is assumed invertible. Then,

$$\mathbf{v} = -L \cdot \frac{\partial \mu}{\partial x}. \quad (145)$$

(142) becomes

$$\frac{\partial \psi}{\partial t} - \frac{\partial}{\partial x} \cdot (L \cdot \frac{\partial \mu}{\partial x} \psi) = 0. \quad (146)$$

This equation is called the Smoluchowski equation or the kinetic equation. For a system in which the molecule is described by  $x = \{\mathbf{x}_i\}_1^N$ , where  $\mathbf{x}_i \in \mathcal{R}^3$ , the Smoluchowski equation is usually written as

$$\frac{\partial \psi}{\partial t} + \sum_{n=1}^N \frac{\partial}{\partial \mathbf{x}_n} \cdot (\mathbf{v}_n \psi) = 0, \mathbf{v}_n = - \sum_m L_{nm} \frac{\partial \mu}{\partial \mathbf{x}_m}, \quad (147)$$

where  $L = (L_{nm})$  is the mobility matrix and  $L_{nm} = L_{mn}$ ,  $(L_{mn}) > 0$ . When the particle system  $x$  is immersed in a viscous solvent, each particle is going to be subject to a drag exerted by the solvent and additional forces on each particle caused by the perturbation of the flow field due to the motion of the particles. This is called the hydrodynamic effect. When hydrodynamic effect is included, the total velocity consists of two parts:

$$\mathbf{v}_n = \mathbf{v}_n^e + \mathbf{v}_n^v, \mathbf{v}_n^e = - \sum_m L_{nm} \cdot \frac{\partial \mu}{\partial \mathbf{x}_m}, \quad (148)$$

where the mobility matrix depends on the location of the particles and the second part  $\mathbf{v}_n^v$  is due to the existence of the macroscopic flow field and often it is well approximated by

$$\mathbf{v}_n^v = \nabla \mathbf{v} \cdot \mathbf{x}_n, \quad (149)$$

where  $\mathbf{v}$  is the averaged velocity field. We assume  $\nabla \mathbf{v}$  is a slowly varying function in space in the length scale of the system  $x$ . Thus, in the process of finding the velocity due to external forces, it is assumed a space-independent function. In the following, we assume the particle is approximated by a sphere. Due to the presence and motion of the spheres, the flow field around each particle is perturbed, which in turn affect the motion of the other spheres. This phenomenon is called the hydrodynamic interaction. For very dilute solution where the distance between spheres are sufficiently far so that the hydrodynamic interaction

can be neglected, the velocity of the sphere is determined by the external force acting on it alone and the mobility matrix is given by

$$L_{mn} = \frac{\delta_{mn}}{\zeta} \mathbf{I}, \quad (150)$$

where  $\zeta = 6\pi\eta_s a$  for spheres of radius  $a$ . In the general case, we have to solve the fluid velocity  $\mathbf{v}(\mathbf{x})$  with the given external force  $\mathbf{F}_n$  exerted on the sphere at  $\mathbf{x}_n$ , which can be expressed as

$$\mathbf{g}(\mathbf{x}) = \sum_n \mathbf{F}_n \delta(\mathbf{x} - \mathbf{x}_n). \quad (151)$$

We simplify the problem by treating the sphere as a point mass. We assume the solvent is incompressible  $\nabla \cdot \mathbf{v} = 0$  and governed by the Stokes equation

$$\nabla \cdot \boldsymbol{\tau} + \mathbf{g} = 0, \quad (152)$$

where the stress tensor is given by

$$\boldsymbol{\tau} = -p \mathbf{I} + 2\eta_s \mathbf{D}. \quad (153)$$

A solution of the equation is

$$\mathbf{v} = K \cdot \mathbf{x} + \sum_m \mathbf{H}(\mathbf{x} - \mathbf{x}_m) \cdot \mathbf{F}_m, \quad (154)$$

where  $K = \nabla \mathbf{v}$  is treated as a spatially homogeneous tensor and

$$\mathbf{H}(\mathbf{x}) = \frac{1}{8\eta_s \pi x} (\mathbf{I} + \frac{\mathbf{x}\mathbf{x}}{x^2}) \quad (155)$$

is called the Oseen tensor, where  $x = \|\mathbf{x}\|$ . This tensor is singular at  $\mathbf{x} = 0$ , which is due to the assumption that the particle is a point. For finite size sphere, this singularity would be removed. However, the exact solution of the Stokes equation is not feasible. A compromise is to approximate the Oseen tensor for point mass by

$$\hat{\mathbf{H}}(\mathbf{x}) = \begin{cases} \frac{\mathbf{I}}{\zeta}, & \mathbf{x} = 0, \\ \mathbf{H}(\mathbf{x}), & \mathbf{x} \neq 0. \end{cases} \quad (156)$$

The mobility matrix is then calculated by

$$L_{mn} = \hat{\mathbf{H}}(\mathbf{x}_n - \mathbf{x}_m). \quad (157)$$

The Smoluchowski equation then becomes

$$\frac{\partial \psi}{\partial t} = \sum_{n=1}^N \frac{\partial}{\partial \mathbf{x}_n} \cdot \left[ \sum_m L_{nm} \frac{\partial \mu}{\partial \mathbf{x}_m} - \nabla \mathbf{v} \cdot \mathbf{x}_n \right]. \quad (158)$$

The elastic stress in the polymer system can be derived from a virtual work principle. Let

$$\mathcal{A} = \int_V \int \mu \psi dx dv \quad (159)$$

be the free energy over the material volume  $V$ . (We remark that this free energy formulation is based on that the potential  $U$  is independent of  $\psi$ ; if  $U$  depends on  $\psi$  as well,  $\mathcal{A}$  has to be modified such that  $\frac{\delta \mathcal{A}}{\delta \psi} = \mu$ .) We consider an infinitesimal deformation given by

$$\delta \psi = \frac{d\psi}{dt} \delta t = - \sum_n \frac{\partial}{\partial \mathbf{x}_n} \cdot [\nabla \mathbf{v} \cdot \mathbf{x}_n] \delta t. \quad (160)$$

Take the variation of the free energy and assume  $vol(V)$  small, we have

$$\delta \mathcal{A} = vol(V) \tau^e : \delta t \nabla \mathbf{v} = - \delta t \nabla \mathbf{v}_{\alpha\beta} \sum_n \langle \mathbf{F}_n \mathbf{x}_{n\beta} \rangle, \quad (161)$$

where

$$\mathbf{F}_n = - \frac{\partial \mu}{\partial \mathbf{x}_n} \quad (162)$$

is the force exerted on the part of the polymer at  $\mathbf{x}_n$ . The elastic part of stress is then given by

$$\tau^e = - \frac{1}{vol(V)} \sum_n \langle \mathbf{F}_n \mathbf{x}_n \rangle, \quad (163)$$

where

$$\langle (\bullet) \rangle = \int_V \int (\bullet) dx dv. \quad (164)$$

## 5.1 Langevin equation

An alternative description of the molecular motion is the Langevin equation. For each particle  $\mathbf{x}_n$ , there is a stochastic differential equation

$$\dot{\mathbf{x}}_n = \sum_m L_{nm} \left( - \frac{\partial U}{\partial \mathbf{x}_n} + f_m(t) \right) + \frac{1}{2} kT \frac{\partial}{\partial \mathbf{x}_m} L_{nm}, \quad (165)$$

where  $f_m(t)$  is a random force subject to the Gaussian distribution and

$$\langle f_m \rangle = 0, \langle f_n f_m \rangle = 2(L^{-1})_{nm} kT \delta(t - t'). \quad (166)$$

This Langevin equation implies the Smoluchowski equation. **Lemma:** The Langevin equation

$$\frac{dx}{dt} = - \frac{1}{\xi} \frac{\partial}{\partial x} U(x) + \sqrt{\frac{kT}{\xi}} g(t) + \frac{1}{2} \frac{d}{dx} \left( \frac{kT}{\xi} \right) \quad (167)$$

implies the distribution density function of  $x$  satisfies

$$\frac{\partial}{\partial t} \psi = \frac{\partial}{\partial x} \frac{1}{\xi} \left( kT \frac{\partial}{\partial x} \psi + \frac{\partial U}{\partial x} \psi \right) = \frac{\partial}{\partial x} \frac{1}{\xi} \left( \frac{\partial}{\partial x} \mu \psi \right), \quad (168)$$

where

$$\langle g(t) \rangle = 0, \langle g(t) g(t') \rangle = 2\delta(t - t'). \quad (169)$$

## 5.2 System of constraint

Assume the motion of the particles is subject to a set of constraints

$$\overline{C_p}(x) = 0, p = 1, \dots, P. \quad (170)$$

Then, the forces exerted on each particle must include the constraining forces

$$\mathbf{F}_n^{(c)} = \lambda_p \frac{\partial}{\partial \mathbf{x}_n} C_p, \quad (171)$$

where  $\lambda_p$  is the Lagrange multiplier. The velocity of the particle is calculated from

$$\mathbf{v}_m = K \cdot \mathbf{x}_m + H_{mn} \cdot (\mathbf{F}_n + \mathbf{F}_n^{(c)}), \quad (172)$$

where  $\mathbf{F}_n = -\frac{\partial}{\partial \mathbf{x}_n} \mu$ . Taking the time derivative on the constraints, we have

$$\frac{\partial C_p}{\partial \mathbf{x}_n} \cdot \mathbf{v}_n = 0. \quad (173)$$

Combining the above equations together, we can solve the Lagrange multiplier

$$\lambda_p = (h^{-1})_{pq} \left[ \frac{\partial C_q}{\partial \mathbf{x}_m} \cdot \mathbf{H}_{mn} \cdot \frac{\partial}{\partial \mathbf{x}_n} \mu - \frac{\partial C_q}{\partial \mathbf{x}_n} \cdot K \cdot \mathbf{x}_n \right]. \quad (174)$$

The Smoluchowski equation with constraints is then

$$\frac{\partial}{\partial t} \psi + \frac{\partial}{\partial \mathbf{x}_n} \cdot (\mathbf{v}_n \psi) = 0. \quad (175)$$

Kirkwood shows that the stress formula is quite general and it applies to any forces acting on the particle. Therefore, it can also be used to calculate the viscous stress due to the particle constraints. We assume each particle is subject to a drag or constraint force linear to the velocity gradient and the velocity gradient is slowly varying,

$$F_{mn}^{(c)} = \mathcal{C}_{mnkl} K_{kl}, \quad (176)$$

where  $m$  is the index for the particle and  $n$  is the index for the component of the force  $\mathbf{F}_m$ . The viscous stress is given by

$$\tau^{(v)}_{ij} = -\frac{1}{\text{vol}(V)} \sum_{m=1}^N \langle \mathcal{C}_{mikl} \mathbf{x}_{mj} \rangle K_{kl}. \quad (177)$$

In addition, we need to add the viscous stress from the contribution of the solvent

$$\tau_s^{(v)} = 2\eta_s \mathbf{D}. \quad (178)$$

Next, we give a specific model for polymers modeled as beads connected by linear elastic springs. This is called the Rouse model [5].

### 5.3 Rouse model

We assume the bead-spring system is described by the phase space coordinate  $\{\mathbf{x}_i\}, i = 1, \dots, N$ . The system can also be uniquely described by the connecting vector and the center of mass

$$\mathbf{x}_c = \frac{1}{N} \sum_{i=1}^N \mathbf{x}_i, \mathbf{q}_i = \mathbf{x}_{i+1} - \mathbf{x}_i, i = 1, \dots, N - 1. \quad (179)$$

The elastic potential of the system is

$$U = \frac{c}{2} \sum_{i=1}^{N-1} \|\mathbf{q}_i\|^2. \quad (180)$$

For the Rouse model, we assume

$$\psi = \nu \phi(\{\mathbf{q}\}_1^{N-1}, t) h(\mathbf{x}_c, t), \quad (181)$$

where  $\nu$  is the constant number density. The Smoluchowski equation reduces to

$$h \frac{\partial \phi}{\partial t} + \phi \frac{\partial h}{\partial t} + \sum_{n=1}^{N-1} \frac{\partial}{\partial \mathbf{q}_n} \cdot (\dot{\mathbf{q}}_n \phi) h + \frac{\partial}{\partial \mathbf{x}_c} (\dot{\mathbf{x}}_c h) \phi = 0. \quad (182)$$

Assuming

$$\frac{\partial h}{\partial t} + \frac{\partial h}{\partial \mathbf{x}_c} \cdot (\dot{\mathbf{x}}_c h) = 0, \quad (183)$$

we end up with a decoupled Smoluchowski equation for  $\psi$ :

$$\frac{\partial \phi}{\partial t} + \sum_{n=1}^{N-1} \frac{\partial}{\partial \mathbf{q}_n} \cdot (\dot{\mathbf{q}}_n \phi) = 0, \quad (184)$$

in which

$$\begin{aligned} \dot{\mathbf{q}}_n &= \nabla \mathbf{v} \cdot \mathbf{q}_n - A_{nm} (kT \frac{\partial}{\partial \mathbf{q}_n} \ln \phi + c \mathbf{q}_n), \\ A_{nm} &= \frac{1}{\zeta} \begin{cases} 2, & n = m, \\ -1, & n = m \pm 1, \\ 0, & \text{otherwise.} \end{cases} \end{aligned} \quad (185)$$

Since  $A$  is symmetric, there exists an eigenvalue-eigenvector decomposition

$$A = \Omega \Lambda \Omega^T, \quad (186)$$

where  $\Lambda = \text{Diag}(\Lambda_{ii})$  with  $\Lambda_{ii} = 4 \sin^2(\frac{i\pi}{2N}), i = 1, \dots, N - 1$ . We introduce a new coordinate  $\mathbf{q}'_n, n = 1, \dots, N - 1$  such that

$$\frac{\partial}{\partial \mathbf{q}_n} \cdot \Omega = \frac{\partial}{\partial \mathbf{q}'_n}. \quad (187)$$

Namely,

$$\mathbf{q}'_n = \sum_m \Omega_{nm} \cdot \mathbf{q}_m. \quad (188)$$

The Smoluchowski equation is transformed into

$$\frac{\partial \phi}{\partial t} + \sum_{n=1}^{N-1} \frac{\partial}{\partial \mathbf{q}'_n} \cdot [\nabla \mathbf{v} \cdot \mathbf{q}'_n - \frac{1}{\zeta} \Lambda_{nn} \frac{\partial \mu}{\partial \mathbf{q}'_n} \phi] = 0. \quad (189)$$

Assume  $\phi = \prod_n^{N-1} \phi_n(\mathbf{q}_n, t)$ ,  $\phi_n$  are solutions of

$$\frac{\partial \phi_n}{\partial t} = -\frac{\partial}{\partial \mathbf{q}'_n} \cdot [\nabla \mathbf{v} \cdot \mathbf{q}'_n \phi_n - \frac{\Lambda_{nn}}{\zeta} \frac{\partial \mu_n}{\partial \mathbf{q}'_n} \phi_n], \mu_n = kT \ln \phi_n + \frac{c}{2} \|\mathbf{q}'_n\|^2. \quad (190)$$

Take the second moment of  $\phi_n$  with respect to  $\mathbf{q}'_n$ , we obtain

$$\langle \hat{\mathbf{q}}'_n \mathbf{q}'_n \rangle = \frac{2\Lambda_{nn}}{\zeta} [kT \mathbf{I} - c \langle \mathbf{q}'_n \mathbf{q}'_n \rangle]. \quad (191)$$

We note that the left hand side of the equation is the upper convected derivative of the second moment tensor  $\langle \mathbf{q}'_n \mathbf{q}'_n \rangle$ . The total elastic stress tensor is

$$\tau^e = \nu c \sum_{n=1}^{N-1} \langle \mathbf{q}'_n \mathbf{q}'_n \rangle. \quad (192)$$

When  $N = 2$ , this is the Oldroyd-B model which is derived from the linear viscoelastic theory by using the convected derivative [3, 4].

## References

- [1] A. N. Beris and B. J. Edwards. *Thermodynamics of flowing system with internal microstructure*, Oxford University Press, New York, 1994.
- [2] S. E. Bechtel, *Advanced continuum mechanics, Lecture Notes*, Ohio State University, 1990.
- [3] R. B. Bird, R. C. Armstrong and O. Hassager. *Dynamics of Polymeric Liquids*, v. 1, John Wiley & Sons, New York, 1987.
- [4] R. B. Bird, C. F. Curtiss, R. C. Armstrong and O. Hassager. *Dynamics of Polymeric Liquids*, v. 2, John Wiley & Sons, New York, 1987.
- [5] M. Doi and S.F. Edwards. *Theory of Polymer Dynamics*, Oxford University Press (Clarendon), 1986.

- [6] A. C. Eringen, *Mechanics of Continua*, Robert E. Krieger Publishing Company, Malabar, Florida, 1980.
- [7] A. C. Eringen, *Microcontinuum Field Theories I: Foundations and Solids, II: Fluent Media*, Springer-Verlag, New York, 1999.
- [8] R. G. Larson. *The structure and Rheology of Complex Fluids*, Oxford University Press, 1999.
- [9] R. G. Larson. *Constitutive Equations for Polymer Melts and Solutions*, Butterworths, Boston, 1988.