

Chapter 2

Continuum Thermomechanics

Abstract The core of this chapter is continuum mechanics and the principle of constitutive equation. Equilibrium and nonequilibrium thermodynamics are also included because these disciplines are necessary to understand the principle of constitutive equation. The introduction to some classical constitutive equations is also addressed for easier understanding of the principle of constitutive equation.

Materials consist of atoms and molecules. Although materials are collection of discrete particles, it is more convenient to treat them as a continuum because the constituent particles are extremely small and the number of the particles is hugely large. Continuum is an uncountable set of points which are continuously distributed. It is assumed that there exist points between any pair of points in the continuum. Hence, continuum can be considered a subset of three-dimensional Euclidian space, E^3 (O'Neill 2006). The point of continuum is called material particle. However, it does not mean a physical particle such as atom and molecule. The material particle is as small as a point from macroscopic viewpoint, while it is so large to contain a number of molecules from microscopic viewpoint.

A macroscopic quantity is assigned to individual material particles and is interpreted as an average over the molecules in the material particle. This means that the macroscopic quantity is related to a function of microscopic quantities which varies faster in both time and space than the macroscopic quantity. Through averaging process, the faster variations of microscopic quantities are canceled mutually, and then, the average of the function of microscopic quantities becomes a smoothly varying function of both space and time (Callen 1985). This is the reason why the macroscopic quantity can be described by a field.

1 Kinematics

1.1 Material and Spatial Coordinates

When classical mechanics is described in terms of particles, the main object is to predict the position of each particle as a function of time. The curves describing the motion of particles can be denoted by $\mathbf{x}_\alpha(t)$ where the subscript indicates the particles. In the case of discrete particle system, the index α is an integer. However, in the case of continuum, integer cannot be used as an indicator of material particles because there is no one-to-one correspondence between integers and material particles.

Imagine that we observe how a lump of materials moves. Since we can construct a coordinate system and have a clock, we can assign every material particle to a coordinate at every time. If we choose a time as the reference time among the interval of observation, then we can identify each material particle by the coordinate at the reference time. The coordinate at the reference time is an indicator of material particle and is called *material coordinate*. Let the material coordinate be denoted by the vector $\tilde{\mathbf{x}}$. As time flows, each material particle moves and is found at \mathbf{x} at the time of t . If we collect all positions at corresponding time, then we have a mapping from $\tilde{\mathbf{x}}$ to \mathbf{x} at every moment:

$$\mathbf{x} = \chi(\tilde{\mathbf{x}}, t) \quad (1.1)$$

Equation (1.1) can be interpreted as the path of the material particle $\tilde{\mathbf{x}}$ as a function of time, which is a spatial curve from the viewpoint of geometry. When time t is fixed, Eq. (1.1) describes the distribution of material particles at time t . The distribution is called *configuration*. The configuration at the reference time is called the *reference configuration*, while the configuration at the present time t is called the *current configuration*. The current configuration is called *deformed configuration* if the body of material is considered to be deformed.

When Newton's second law is written in terms of particle position, it is the equation of motion whose solution is the path of particle motion. From the solution, we can calculate the force exerted on the particle at every moment. Thus, if we know Eq. (1.1), then we come to know everything needed in mechanics. How to obtain Eq. (1.1) will be studied later. For a while, it is assumed that Eq. (1.1) is known.

From the definition of material coordinate, it is clear that when time is the reference time τ , the following is valid:

$$\tilde{\mathbf{x}} = \chi(\tilde{\mathbf{x}}, \tau) \quad (1.2)$$

In continuum mechanics, it is basically assumed that any material particle cannot be created nor annihilated. Then, the mapping Eq. (1.1) is one to one at every moment. Then, we can assume that the mapping has its inverse such that

$$\tilde{\mathbf{x}} = \chi^{-1}(\mathbf{x}, t) \quad (1.3)$$

Since Eq. (1.1) is the path of material particle $\tilde{\mathbf{x}}$, the velocity \mathbf{v} of $\tilde{\mathbf{x}}$ is determined by

$$\mathbf{v} = \frac{\partial \chi(\tilde{\mathbf{x}}, t)}{\partial t} \quad (1.4)$$

Here, the time derivative is the partial differentiation with respect to t at fixed $\tilde{\mathbf{x}}$. Then, the velocity is a vector-valued function of material coordinate and time. Hence, we can write the velocity as follows:

$$\mathbf{v} = \tilde{\mathbf{v}}(\tilde{\mathbf{x}}, t) \quad (1.5)$$

Substitution of Eqs. (1.3)–(1.5) yields

$$\mathbf{v} = \tilde{\mathbf{v}}(\chi^{-1}(\mathbf{x}, t), t) \equiv \mathbf{v}(\mathbf{x}, t) \quad (1.6)$$

Equation (1.5) implies that physical quantity \mathbf{v} is described in terms of material coordinate, while Eq. (1.6) implies that the same quantity is described in terms of current coordinate \mathbf{x} . The former is called *Lagrangian description* or *material description*, and the latter is called *Eulerian description* or *spatial description*.

Lagrangian description of continuum is a direct translation of the Newtonian mechanics of particle because Eq. (1.4) is equivalent to the time derivative of $\mathbf{x}_\alpha(t)$. On the other hand, Eulerian description is more abstract but is more convenient. Since material particle is extremely small in macroscopic scale, it is practically impossible to trace individual material particles experimentally. However, observation of material at a fixed point in space is easier than tracing the material particles. Hence, a kind of translation is necessary when formulating a physical law by Eulerian description.

Acceleration vector is important because it is related to force through the second law of Newtonian mechanics. It is the time derivative of velocity such that

$$\mathbf{a} = \frac{\partial \tilde{\mathbf{v}}}{\partial t} \quad (1.7)$$

Note that Eq. (1.7) is the partial derivative of time at fixed material coordinate. Hence, it is called *material time derivative*. The material time derivative can be calculated easily if the function to be differentiated is expressed in terms of material

coordinate and time. The time derivative of Eq. (1.6) at fixed \mathbf{x} is not the genuine acceleration which can be related to the force exerted on the material particle. Chain rule of differentiation provides the material time derivative from the function expressed in Eulerian description:

$$\mathbf{a} = \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \quad (1.8)$$

where the partial differentiation of time is the one at fixed spatial coordinate \mathbf{x} and the del operator means the differentiation with respect to spatial coordinate. Hence, we define a differential operator called material time derivative as

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \quad (1.9)$$

1.2 Strain

1.2.1 Concept of Strain

If any pair of material particles of a continuum maintains the same distance during motion, the continuum is called *rigid body*. Motion of the rigid body consists of only translation and rotation. Hence, there is no pure deformation in the rigid body. Equation (1.1) describes the motion of material particles. If a continuum body is not a rigid body, then Eq. (1.1) consists of translation, rotation, and pure deformation.

Strain is a measure of pure deformation. Experience of daily life gives a measure of deformation for string such as

$$\varepsilon = \frac{l - l_0}{l_0} \quad (1.10)$$

where l and l_0 are the lengths of string after and before a deformation, respectively. The intuitive strain of string ε is in the interval of $-1 < \varepsilon < \infty$. No deformation is represented by $\varepsilon = 0$. Negative strain means contraction, whereas positive strain means elongation. Various measures of strain can be suggested:

$$\lambda = \frac{l}{l_0}; \quad h = \log \lambda \quad (1.11)$$

However, these strain measures cannot describe three-dimensional deformation. Consider a cylinder which has a small arrow on its lateral surface. The arrow is assumed to be in the direction of the axis of the cylinder. When exerting a

combination of elongation and twist on the cylinder, the deformed arrow has a different direction and length from the original arrow. Hence, a three-dimensional strain measure can describe the change of both direction and length unlike the strain measures of Eqs. (1.10) and (1.11).

1.2.2 Deformation Gradient

Consider a pair of two material coordinates $\tilde{\mathbf{x}}_1$ and $\tilde{\mathbf{x}}_2$. Assume that they are very close to each other. Then, we can write

$$d\tilde{\mathbf{x}} = \tilde{\mathbf{x}}_2 - \tilde{\mathbf{x}}_1 \quad (1.12)$$

When $\mathbf{x}_k = \chi(\tilde{\mathbf{x}}_k, t)$, we have

$$d\mathbf{x} \equiv \chi(\tilde{\mathbf{x}}_2, t) - \chi(\tilde{\mathbf{x}}_1, t) = \mathbf{F} \cdot d\tilde{\mathbf{x}} \quad (1.13)$$

where

$$\mathbf{F} = \tilde{\nabla} \chi \quad (1.14)$$

In Eq. (1.14), $\tilde{\nabla}$ means the differentiation with respect to material coordinate and ∇ represents the differentiation with respect to spatial coordinate. Equation (1.13) implies that *deformation gradient* \mathbf{F} does not contain translational motion because the contributions from translational motion are same for every material particle. However, rotational motion is still imbedded in deformation gradient \mathbf{F} .

1.2.3 Polar Decomposition

The existence of the inverse mapping, Eq. (1.3), implies that the deformation gradient is invertible. The theorem of *polar decomposition* is that any invertible tensor \mathbf{F} can be decomposed to

$$\mathbf{F} = \mathbf{R} \cdot \mathbf{U} = \mathbf{V} \cdot \mathbf{R} \quad (1.15)$$

where \mathbf{R} is an orthogonal tensor and both \mathbf{U} and \mathbf{V} are symmetric and positive definite tensors, respectively. Furthermore, the decomposition is unique.

It is clear that both $\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T$ and $\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F}$ are symmetric and positive definite, respectively. Then, there exist two symmetric and positive definite tensors such that

$$\mathbf{B} = \mathbf{V}^2 \quad \text{and} \quad \mathbf{C} = \mathbf{U}^2 \quad (1.16)$$

because of the spectral decomposition theorem of symmetric and positive definite tensors. The two tensors \mathbf{U} and \mathbf{V} are uniquely determined from the deformation tensor \mathbf{F} . The proof of polar decomposition can be done by showing that $\mathbf{F} \cdot \mathbf{U}^{-1}$ and $\mathbf{V}^{-1} \cdot \mathbf{F}$ are orthogonal tensors and they are identical. The proof of polar decomposition is found in Haupt (2000) and other books of advanced continuum mechanics.

1.2.4 Cauchy–Green Strains

It is not difficult to show that any rotational motion can be determined by an orthogonal tensor whose determinant is positive. Then, polar decomposition provides a way to find a strain measure which excludes both translational and rotational motions. The candidates are

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T \quad (1.17a)$$

and

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F} \quad (1.17b)$$

The tensor \mathbf{B} and \mathbf{C} are called *left Cauchy–Green tensor* and *right Cauchy–Green tensor*, respectively. When deformation gradient represents only rotational motion, \mathbf{F} must be an orthogonal tensor. Then, Eq. (1.17a) implies that $\mathbf{B} = \mathbf{C} = \mathbf{I}$. Of course, both \mathbf{U} and \mathbf{V} can be used as strain measures. However, calculations of \mathbf{B} and \mathbf{C} are easier than those of \mathbf{U} and \mathbf{V} , which is why \mathbf{B} and \mathbf{C} are preferred rather than \mathbf{U} and \mathbf{V} .

Consider a line element imbedded in the reference configuration $d\tilde{\mathbf{x}} = d\tilde{l}\mathbf{n}$ where \mathbf{n} is the unit vector and $d\tilde{l}$ is the length of the material line element. The material line element becomes $d\mathbf{x} = \mathbf{F} \cdot d\tilde{\mathbf{x}}$ after deformation. Then, the length of the deformed line element is given by

$$(dl)^2 = d\mathbf{x} \cdot d\mathbf{x} = d\tilde{\mathbf{x}} \cdot \mathbf{C} \cdot d\tilde{\mathbf{x}} = (d\tilde{l})^2 \mathbf{n} \cdot \mathbf{C} \cdot \mathbf{n} \quad (1.18)$$

Arrangement of Eq. (1.18) yields

$$\lambda_n^2 \equiv \left(\frac{dl}{d\tilde{l}} \right)^2 = \mathbf{n} \cdot \mathbf{C} \cdot \mathbf{n} \quad (1.19)$$

Hence, the diagonal component of \mathbf{C} is the square of the ratio of deformed length to undeformed length when the line element is in the direction of the axis of the coordinate of the reference configuration.

Consider two material line elements which are mutually orthogonal: $d\tilde{\mathbf{x}}_1 = d\tilde{l}\mathbf{n}_1$, $d\tilde{\mathbf{x}}_2 = d\tilde{l}\mathbf{n}_2$, and $\mathbf{n}_1 \cdot \mathbf{n}_2 = 0$. When $d\mathbf{x}_k$ indicates the deformed line element of $d\tilde{\mathbf{x}}_k$, we have

$$d\mathbf{x}_1 \cdot d\mathbf{x}_2 = d\tilde{\mathbf{x}}_1 \cdot \mathbf{C} \cdot d\tilde{\mathbf{x}}_2 = (d\tilde{l})^2 \mathbf{n}_1 \cdot \mathbf{C} \cdot \mathbf{n}_2 \quad (1.20)$$

Note that the angle θ_{12} between $d\mathbf{x}_1$ and $d\mathbf{x}_2$ is given by

$$\cos \theta_{12} = \frac{d\mathbf{x}_1 \cdot d\mathbf{x}_2}{\sqrt{d\mathbf{x}_1 \cdot d\mathbf{x}_1} \sqrt{d\mathbf{x}_2 \cdot d\mathbf{x}_2}} = \frac{\mathbf{n}_1 \cdot \mathbf{C} \cdot \mathbf{n}_2}{\sqrt{\mathbf{n}_1 \cdot \mathbf{C} \cdot \mathbf{n}_1} \sqrt{\mathbf{n}_2 \cdot \mathbf{C} \cdot \mathbf{n}_2}} \quad (1.21)$$

Equation (1.21) implies that the off-diagonal component $\mathbf{n}_1 \cdot \mathbf{C} \cdot \mathbf{n}_2$ is related to the distortion of shape if both $d\tilde{\mathbf{x}}_1$ and $d\tilde{\mathbf{x}}_2$ do not conduct length change.

Both \mathbf{B} and \mathbf{C} are three-dimensional generalization of λ of Eq. (1.11). Since the two Cauchy–Green tensors are symmetric and positive definite, $\log \mathbf{B}$ and $\log \mathbf{C}$ can be defined. These strain measures are generalization of h of Eq. (1.11).

1.2.5 Infinitesimal Strain

For rigid solid, small deformation is more interesting. A convenient measure of strain is *infinitesimal strain* which is also called *engineering strain*. When deformation is infinitesimal, the difference between the reference and deformed configuration is very small. Then, we are interested in *displacement vector* field defined as

$$\mathbf{u}(\tilde{\mathbf{x}}, t) = \mathbf{x}(\tilde{\mathbf{x}}, t) - \tilde{\mathbf{x}} \quad (1.22)$$

Then, the gradient of displacement vector field is given by

$$\left(\tilde{\nabla} \mathbf{u} \right)^T = \mathbf{F} - \mathbf{I} \quad (1.23)$$

Expression of \mathbf{C} in terms of \mathbf{u} is given by

$$\mathbf{C} = \left[\mathbf{I} + \left(\tilde{\nabla} \mathbf{u} \right)^T \right]^T \cdot \left[\mathbf{I} + \left(\tilde{\nabla} \mathbf{u} \right)^T \right] = \mathbf{I} + 2\mathbf{E} + \tilde{\nabla} \mathbf{u} \cdot \left(\tilde{\nabla} \mathbf{u} \right)^T \quad (1.24)$$

where

$$\mathbf{E} = \frac{1}{2} \left[\tilde{\nabla} \mathbf{u} + \left(\tilde{\nabla} \mathbf{u} \right)^T \right] \quad (1.25)$$

When deformation is infinitesimally small, the second-order term of Eq. (1.24) can be neglected. Then, we have

$$\mathbf{E} \approx \frac{1}{2}(\mathbf{C} - \mathbf{I}) \quad (1.26)$$

Consider $d\tilde{\mathbf{x}} = d\tilde{l}\mathbf{n}$ as before. Since $dl + d\tilde{l} \approx 2d\tilde{l}$ for infinitesimal deformation, we have

$$\frac{(dl)^2 - (d\tilde{l})^2}{(d\tilde{l})^2} = \frac{(dl - d\tilde{l})(dl + d\tilde{l})}{(d\tilde{l})^2} \approx 2 \frac{dl - d\tilde{l}}{d\tilde{l}} \quad (1.27)$$

On the other hand, the left-hand side of Eq. (1.27) is equal to

$$\frac{(dl)^2 - (d\tilde{l})^2}{(d\tilde{l})^2} = \frac{d\mathbf{x} \cdot d\mathbf{x} - d\tilde{\mathbf{x}} \cdot d\tilde{\mathbf{x}}}{d\tilde{\mathbf{x}} \cdot d\tilde{\mathbf{x}}} = \mathbf{n} \cdot \mathbf{C} \cdot \mathbf{n} - 1 \approx 2\mathbf{n} \cdot \mathbf{E} \cdot \mathbf{n} \quad (1.28)$$

Then, we have

$$\mathbf{n} \cdot \mathbf{E} \cdot \mathbf{n} = \frac{(dl + d\tilde{l})(dl - d\tilde{l})}{2(d\tilde{l})^2} = \frac{dl - d\tilde{l}}{d\tilde{l}} \quad (1.29)$$

Here, we used the approximation of $dl + d\tilde{l} \approx 2d\tilde{l}$. Equation (1.29) implies that \mathbf{E} can be considered as the generalization of ε of Eq. (1.10). Application of Eqs. (1.26)–(1.21) yields

$$\cos \theta_{12} \approx \mathbf{n}_1 \cdot \mathbf{E} \cdot \mathbf{n}_2 \quad (1.30)$$

Hence, the off-diagonal components of infinitesimal strain have the same meaning with those of \mathbf{C} .

Compared with infinitesimal strain, \mathbf{B} and \mathbf{C} are called finite strains. When rubbery materials are considered, finite strains must be used.

1.3 Deformation of Area and Volume

Consider an area element $d\tilde{\mathbf{a}}$ in the reference configuration. From Eq. (4.64) in Chap. 1, we know that

$$d\tilde{\mathbf{a}} = (\tilde{\mathbf{t}}_p \times \tilde{\mathbf{t}}_q) dp dq \quad (1.31)$$

Since the two tangent vectors $\tilde{\mathbf{t}}_p$ and $\tilde{\mathbf{t}}_q$ are imbedded in a surface in the reference configuration, the two vectors become

$$\mathbf{t}_p = \mathbf{F} \cdot \tilde{\mathbf{t}}_p \quad \text{and} \quad \mathbf{t}_q = \mathbf{F} \cdot \tilde{\mathbf{t}}_q \quad (1.32)$$

Then, the area element in a deformed configuration becomes

$$d\mathbf{a} = \mathbf{t}_p \times \mathbf{t}_q \, dp dq \quad (1.33)$$

Now, we will use the identity Eq. (5.a) in Chap. 1 of Problem 5

$$\mathbf{F}^T \cdot [(\mathbf{F} \cdot \mathbf{u}) \times (\mathbf{F} \cdot \mathbf{v})] = \det(\mathbf{F}) \mathbf{u} \times \mathbf{v} \quad (1.34)$$

Note that $\tilde{\mathbf{t}}_p$ and $\tilde{\mathbf{t}}_q$ are linearly independent. If setting $\mathbf{u} = \tilde{\mathbf{t}}_p$ and $\mathbf{v} = \tilde{\mathbf{t}}_q$, then Eqs. (1.31), (1.33), and (1.34) give

$$d\mathbf{a} = \det(\mathbf{F}) \mathbf{F}^{-T} \cdot d\tilde{\mathbf{a}} \quad (1.35)$$

For right-handed coordinate system, the volume element is given by the triple scalar product of three tangent vectors of coordinate:

$$d\tilde{V} = \tilde{\mathbf{g}}_1 \cdot (\tilde{\mathbf{g}}_2 \times \tilde{\mathbf{g}}_3) d\tilde{\xi}^1 d\tilde{\xi}^2 d\tilde{\xi}^3 \quad (1.36)$$

As before, the tilde implies the reference configuration. Since deformation can be understood as a coordinate change, the chain rule of differentiation gives

$$\mathbf{g}_k = \mathbf{F} \cdot \tilde{\mathbf{g}}_k \quad (1.37)$$

Then, the deformed volume element is given by

$$dV = (\mathbf{F} \cdot \tilde{\mathbf{g}}_1) \cdot [(\mathbf{F} \cdot \tilde{\mathbf{g}}_2) \times (\mathbf{F} \cdot \tilde{\mathbf{g}}_3)] d\tilde{\xi}^1 d\tilde{\xi}^2 d\tilde{\xi}^3 = \det(\mathbf{F}) d\tilde{V} \quad (1.38)$$

Here, Eq. (5.d) in Chap. 1 of Problem 5 is used.

1.4 Rate of Deformation

1.4.1 Deformation Rate Tensor and Spin Tensor

Now, we are interested in quantitative description of how fast deformation occurs. The velocity gradient in Lagrangian description is given by

$$d\mathbf{v} = \left(\tilde{\nabla} \tilde{\mathbf{v}} \right)^T \cdot d\tilde{\mathbf{x}} \quad (1.39)$$

Using the chain rule of differentiation, we have the identity such that

$$\frac{d\mathbf{F}}{dt} = (\tilde{\nabla}\tilde{\mathbf{v}})^T = (\nabla\mathbf{v})^T \cdot \mathbf{F} \quad (1.40)$$

Note that

$$\left(\tilde{\nabla}\tilde{\mathbf{v}}\right)^T = \frac{\partial \tilde{v}_i}{\partial \tilde{x}_k} \mathbf{e}_i \mathbf{e}_k; \quad (\nabla\mathbf{v})^T = \frac{\partial v_i}{\partial x_k} \mathbf{e}_i \mathbf{e}_k \quad (1.41)$$

Combining the above three equations, we have

$$d\mathbf{v} = (\nabla\mathbf{v})^T \cdot d\mathbf{x} \quad (1.42)$$

We call the *velocity gradient* in Eulerian description just velocity gradient and denote it by

$$\mathbf{L} \equiv (\nabla\mathbf{v})^T \quad (1.43)$$

Then, the material time derivative of deformation gradient is given by

$$\dot{\mathbf{F}} \equiv \frac{d\mathbf{F}}{dt} = \mathbf{L} \cdot \mathbf{F} \quad (1.44)$$

This identity is important in the development of the nonlinear viscoelastic constitutive equations.

We shall show that the total differential of velocity field $d\mathbf{v}$ is the material time derivative of the infinitesimal difference $d\mathbf{x}$ in the current configuration. Consider the total differential of \mathbf{v} :

$$d\mathbf{v} = \mathbf{v}(\mathbf{x} + d\mathbf{x}, t) - \mathbf{v}(\mathbf{x}, t) = \tilde{\mathbf{v}}(\tilde{\mathbf{x}} + d\tilde{\mathbf{x}}, t) - \tilde{\mathbf{v}}(\tilde{\mathbf{x}}, t) \quad (1.45)$$

The first equality is the Eulerian description, and the second is the Lagrangian description. From the definition of velocity, we obtain

$$d\mathbf{v} = \frac{d}{dt} [\mathbf{x}(\tilde{\mathbf{x}} + d\tilde{\mathbf{x}}, t) - \mathbf{x}(\tilde{\mathbf{x}}, t)] = \frac{d}{dt} d\mathbf{x} \quad (1.46)$$

and

$$d\mathbf{v} = \frac{d}{dt} (\mathbf{F} \cdot d\tilde{\mathbf{x}}) = \frac{d\mathbf{F}}{dt} \cdot d\tilde{\mathbf{x}} = \frac{d\mathbf{F}}{dt} \cdot (\mathbf{F}^{-1} \cdot d\mathbf{x}) = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} \cdot d\mathbf{x} \quad (1.47)$$

In Eq. (1.47), it is used that $d\tilde{\mathbf{x}}$ can be considered as constant vector with respect to material time differentiation. Comparison of Eq. (1.42) with Eq. (1.47) gives Eq. (1.44) again. This result is not more important than Eq. (1.46) because

Eq. (1.46) gives a new insight on velocity gradient. The infinitesimal arc length in the current configuration can be defined as $(dl)^2 = d\mathbf{x} \cdot d\mathbf{x}$. Then, we have

$$\frac{1}{2} \frac{d}{dt} (dl)^2 = dl \frac{d}{dt} dl = d\mathbf{x} \cdot \frac{d}{dt} d\mathbf{x} = d\mathbf{x} \cdot d\mathbf{v} = d\mathbf{x} \cdot \mathbf{L} \cdot d\mathbf{x} \quad (1.48)$$

The last term is the quadratic form of velocity gradient. The Problem 5 (McQuarrie 2000), Eq. (5.k), in Chap. 1 let us know that

$$\frac{d}{dt} (dl)^2 = d\mathbf{x} \cdot \mathbf{D} \cdot d\mathbf{x} \quad (1.49)$$

where \mathbf{D} is the symmetric part of velocity gradient and is called *deformation rate tensor*. The unique decomposition of tensor shown in Eq. (5.36) in Chap. 1 gives

$$\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T) \quad \text{and} \quad \mathbf{W} = \frac{1}{2} (\mathbf{L} - \mathbf{L}^T) \quad (1.50)$$

The skew-symmetric tensor \mathbf{W} is called *spin tensor*.

Differential geometry of a curve illustrates that when the curve is parameterized by its arc length, the tangent vector $d\mathbf{x}/dl$ is a unit vector. Then, Eq. (1.49) becomes

$$\frac{1}{2} \frac{d}{dt} dl = \frac{d}{dt} \log(dl) = \frac{d\mathbf{x}}{dl} \cdot \mathbf{D} \cdot \frac{d\mathbf{x}}{dl} \quad (1.51)$$

Thus, \mathbf{D} indicates how fast the infinitesimal line element is extended or contracted. More detailed analysis is found in Aris (1962).

With the help of Eq. (1.44) and the polar decomposition, we have

$$\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = \dot{\mathbf{V}} + \mathbf{V} \cdot (\dot{\mathbf{R}} \cdot \mathbf{R}^T) \cdot \mathbf{V}^{-1} \quad (1.52)$$

Note that $\dot{\mathbf{V}} = d\mathbf{V}/dt$ is symmetric because \mathbf{V} is symmetric and the last term in the right-hand side of Eq. (1.52) is skew-symmetric because of skew-symmetric $\dot{\mathbf{R}} \cdot \mathbf{R}^T$. Equation (1.50) gives

$$\mathbf{D} = \frac{d\mathbf{V}}{dt} \quad (1.53)$$

and

$$\mathbf{W} = \mathbf{V} \cdot \left(\frac{d\mathbf{R}}{dt} \cdot \mathbf{R}^T \right) \cdot \mathbf{V}^{-1} \quad (1.54)$$

Note that the polar decomposition implies that \mathbf{U} and \mathbf{V} represent pure deformation. Thus, Eq. (1.53) also means that \mathbf{D} represents deformation rate as shown in

Eq. (1.51). When the motion of continuum is pure rotation, the deformation gradient becomes an orthogonal tensor. Putting $\mathbf{F} = \mathbf{R}$ into Eq. (1.52), we have $\mathbf{L} = \dot{\mathbf{R}} \cdot \mathbf{R}^T$. The tensors \mathbf{V} and \mathbf{V}^{-1} in \mathbf{W} play the role that pure deformation is canceled when \mathbf{W} transforms $d\mathbf{x}$ to $\mathbf{W} \cdot d\mathbf{x}$. In other words, \mathbf{W} is related to the rotation only. Hence, we call \mathbf{W} spin tensor. Furthermore, for any vector \mathbf{x} , the following is an identity:

$$\mathbf{W} \cdot \mathbf{x} = -(\nabla \times \mathbf{v}) \times \mathbf{x} \quad (1.55)$$

This implies that the curl of velocity represents the rotation in flow.

It is interesting that the representative strain tensors \mathbf{B} and \mathbf{C} have different forms of material time derivatives:

$$\dot{\mathbf{B}} = \mathbf{L} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{L}^T \quad (1.56)$$

and

$$\dot{\mathbf{C}} = 2\mathbf{F}^T \cdot \mathbf{D} \cdot \mathbf{F} \quad (1.57)$$

1.5 Relative Deformation Gradient

1.5.1 Relativity of Deformation

If the macroscopic properties of a continuum are functions of the states of the body, then we can choose the reference configuration in a definite manner. For an example, the lowest energy state may give the reference configuration. Solid was believed as such a material body. As for such solids, we often experience a state of material in equilibrium without deformation. It is not much difficult to control the state of the solid materials in order to choose the reference configuration at will. However, a tiny perturbation makes fluid flow. Although it is difficult to find the well-defined reference configuration of fluid, imagination of the concrete reference configuration allows us to describe mechanical phenomena well if we are equipped with mathematical tools such as material time derivative and if it is a reasonable assumption that the macroscopic properties of the fluid are functions of suitable state variables. However, if the macroscopic properties depend on not only current state but also how materials experience the variation of state in past, the choice of reference configuration loses a foundation. The reference configuration becomes relative. Viscoelastic materials are ones that their history determines their present just as human.

The use of the current configuration as the reference one is more convenient in the description of viscoelastic deformation, because viscoelastic behavior is

determined by the effects of past deformation. Effect of far past is less than that of near past, which is called *fading memory*.

1.5.2 Relative Deformation Measures

As before, \mathbf{x} is the position vector of a material particle at current time and the position of the particle at time τ is denoted by $\hat{\mathbf{x}}$. The configuration characterized by $\hat{\mathbf{x}}$ shall be called past configuration. Then, we have a one-to-one mapping such that

$$\hat{\mathbf{x}} = \chi_t(\mathbf{x}, \tau), \quad \mathbf{x} = \chi_t(\mathbf{x}, t) = \chi_t^{-1}(\hat{\mathbf{x}}, \tau) \quad (1.58)$$

Note that the subscript t emphasizes that the configuration at t is the reference configuration.

The use of Eq. (1.58) gives *relative deformation gradient* defined by

$$\mathbf{F}_t(\tau) = (\nabla \hat{\mathbf{x}})^T \quad (1.59)$$

Equation (1.59) also means that

$$d\hat{\mathbf{x}} = \mathbf{F}_t(\tau) \cdot d\mathbf{x}; \quad d\mathbf{x} = \mathbf{F}_t^{-1}(\tau) \cdot d\hat{\mathbf{x}} \quad (1.60)$$

Application of polar decomposition to relative deformation gradient gives

$$\mathbf{F}_t(\tau) = \mathbf{R}_t(\tau) \cdot \mathbf{U}_t(\tau) = \mathbf{V}_t(\tau) \cdot \mathbf{R}_t(\tau) \quad (1.61)$$

Of course, it is clear that

$$\mathbf{F}_t(t) = \mathbf{R}_t(t) = \mathbf{U}_t(t) = \mathbf{V}_t(t) = \mathbf{I} \quad (1.62)$$

This is the result from that the current configuration is chosen as the reference configuration. Deformation measures such as \mathbf{F} , \mathbf{U} , and \mathbf{V} are defined from the reference configuration represented by $\tilde{\mathbf{x}}$ and those such as \mathbf{F}_t , \mathbf{U}_t , and \mathbf{V}_t are given from the current configuration. Carefully considering the definitions of the deformation measures, it can be understood that they represent the quantitative description of deformation relative to the reference configurations under consideration. Hence, Eq. (1.62) holds. If we denote t_R as the reference time of \mathbf{F} , \mathbf{U} , and \mathbf{V} , then we have

$$\mathbf{F}(t_R) = \mathbf{R}(t_R) = \mathbf{U}(t_R) = \mathbf{V}(t_R) = \mathbf{I} \quad (1.63)$$

As we did in Sect. 1.2, we can define the various strain measures such as

$$\mathbf{B}_t(\tau) = \mathbf{F}_t(\tau) \cdot \mathbf{F}_t^T(\tau) \quad (1.64a)$$

and

$$\mathbf{C}_t(\tau) = \mathbf{F}_t^T(\tau) \cdot \mathbf{F}_t(\tau) \quad (1.64b)$$

The *relative Finger deformation tensor* is defined as $\mathbf{C}_t^{-1}(\tau)$, and the *relative Piola deformation tensor* is defined as $\mathbf{B}_t^{-1}(\tau)$.

1.5.3 Velocity Gradient Revisited

The velocity of a material particle is the time derivative of $\hat{\mathbf{x}}(\mathbf{x}, \tau)$ at fixed \mathbf{x} and can be denoted by $\hat{\mathbf{v}}(\mathbf{x}, \tau)$. Then, the velocity at present is $\mathbf{v}(\mathbf{x}, t) = \hat{\mathbf{v}}(\mathbf{x}, t)$. The velocity gradient at time of τ is given by $\mathbf{L}(\mathbf{x}, \tau) = (\nabla \hat{\mathbf{v}})^T$. Replacement of τ by t gives the velocity gradient at present time. The time derivative of relative deformation gradient is given by

$$\frac{\partial}{\partial \tau} \mathbf{F}_t(\tau) = \frac{\partial}{\partial \tau} \frac{\partial \hat{x}_i}{\partial x_k} \mathbf{e}_i \mathbf{e}_k = \frac{\partial \hat{v}_i}{\partial x_k} \mathbf{e}_i \mathbf{e}_k = \mathbf{L}(\mathbf{x}, \tau) \quad (1.65)$$

Equation (1.65) implies that although $\mathbf{F}_t(t) = \mathbf{I}$, the time derivative of relative deformation gradient at present time is the velocity gradient at present time:

$$\left. \frac{\partial}{\partial \tau} \mathbf{F}_t(\tau) \right|_{\tau=t} = \mathbf{L}(\mathbf{x}, t) \quad (1.66)$$

Application of the polar decomposition of Eq. (1.61) gives

$$\mathbf{L}(\mathbf{x}, t) = \left[\mathbf{R}_t(\tau) \cdot \frac{\partial \mathbf{U}_t(\tau)}{\partial \tau} + \frac{\partial \mathbf{R}_t(\tau)}{\partial \tau} \cdot \mathbf{U}_t(\tau) \right]_{\tau=t} = \dot{\mathbf{U}}_t(t) + \dot{\mathbf{R}}_t(t) \quad (1.67)$$

where Eq. (1.62) is used. It is noteworthy that the time derivatives of $\mathbf{F}_t(\tau)$, $\mathbf{U}_t(\tau)$, $\mathbf{V}_t(\tau)$, and $\mathbf{R}_t(\tau)$ at $\tau = t$ may not be the identity tensor even though Eq. (1.62) is valid. Since $\mathbf{R}_t(\tau)$ is an orthogonal tensor, its time derivative with respect to τ must be skew-symmetric [see Problem 1 (Huang 1963)]. Compared with Eqs. (1.53) and (1.54), we have

$$\mathbf{D} = \dot{\mathbf{U}}_t(t) = \left. \frac{\partial \mathbf{U}_t}{\partial \tau} \right|_{\tau=t} = \frac{d\mathbf{V}}{dt} \quad (1.68)$$

and

$$\mathbf{W} = \dot{\mathbf{R}}_t(t) = \left. \frac{\partial \mathbf{R}_t}{\partial \tau} \right|_{\tau=t} = \mathbf{V} \cdot \left(\frac{d\mathbf{R}}{dt} \cdot \mathbf{R}^T \right) \cdot \mathbf{V}^{-1} \quad (1.69)$$

This confirms again that the deformation rate tensor is the rate of pure deformation and the spin tensor is the rate of rotation.

1.5.4 Rivlin–Ericksen Tensor

Strain measure \mathbf{C}_t defined in Eq. (1.64b) is a function of past time τ . One may want to estimate \mathbf{C}_t in terms of the deformation quantities at present time. It can be done by the Taylor expansion such as

$$\mathbf{C}_t(\mathbf{x}, \tau) = \mathbf{C}_t(\mathbf{x}, t) + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{\partial^n \mathbf{C}_t}{\partial \tau^n} \right)_{\tau=t} (\tau - t)^n \quad (1.70)$$

The *Rivlin–Ericksen tensors* are defined as

$$\mathbf{A}_n(\mathbf{x}, t) \equiv \left(\frac{\partial^n \mathbf{C}_t}{\partial \tau^n} \right)_{\tau=t} \quad (1.71)$$

The use of Eqs. (1.63) and (1.71) gives

$$\mathbf{C}_t(\mathbf{x}, \tau) = \mathbf{I} + (\tau - t)\mathbf{A}_1 + \frac{(\tau - t)^2}{2}\mathbf{A}_2 + \dots \quad (1.72)$$

From the definition of \mathbf{C}_t , it is clear that

$$(\hat{dl})^2 \equiv d\hat{\mathbf{x}} \cdot d\hat{\mathbf{x}} = d\mathbf{x} \cdot \mathbf{C}_t \cdot d\mathbf{x} \quad (1.73)$$

Differentiation of Eq. (1.73) with respect to τ at a fixed \mathbf{x} gives

$$\frac{\partial^n}{\partial \tau^n} (\hat{dl})^2 = d\mathbf{x} \cdot \frac{\partial^n \mathbf{C}_t}{\partial \tau^n} \cdot d\mathbf{x} \quad (1.74)$$

Substitution of $\tau = t$ gives

$$\left[\frac{\partial^n}{\partial \tau^n} (\hat{dl})^2 \right]_{\tau=t} = \frac{d^n}{dt^n} (dl)^2 = d\mathbf{x} \cdot \mathbf{A}_n \cdot d\mathbf{x} \quad (1.75)$$

where

$$(\hat{dl})^2_{\tau=t} = (dl)^2 = d\mathbf{x} \cdot d\mathbf{x} \quad (1.76)$$

is used. Note that Eqs. (1.48) and (1.49) give

$$\frac{d}{dt} \mathbf{dx} = d\mathbf{v} = \mathbf{L} \cdot \mathbf{dx} \quad (1.77)$$

Finally, we have

$$\begin{aligned} \frac{d^{n+1}}{dt^{n+1}} \mathbf{dx} \cdot \mathbf{dx} &= \mathbf{dx} \cdot \mathbf{A}_{n+1} \cdot \mathbf{dx} = \frac{d}{dt} \mathbf{dx} \cdot \mathbf{A}_n \cdot \mathbf{dx} \\ &= \mathbf{dx} \cdot \left(\mathbf{L}^T \cdot \mathbf{A}_n + \frac{d\mathbf{A}_n}{dt} + \mathbf{A}_n \cdot \mathbf{L} \right) \cdot \mathbf{dx} \end{aligned} \quad (1.78)$$

Comparison of Eq. (1.75) with Eq. (1.78) yields

$$\mathbf{A}_{n+1} = \frac{d\mathbf{A}_n}{dt} + \mathbf{L}^T \cdot \mathbf{A}_n + \mathbf{A}_n \cdot \mathbf{L} \quad (1.79)$$

Equation (1.79) holds when n is any positive integers. For $n = 1$, we have

$$\frac{d}{dt} \mathbf{dx} \cdot \mathbf{dx} = \mathbf{dx} \cdot (\mathbf{L} + \mathbf{L}^T) \cdot \mathbf{dx} = \mathbf{dx} \cdot \mathbf{A}_1 \cdot \mathbf{dx} \quad (1.80)$$

Hence, we know that

$$\mathbf{A}_1 = 2\mathbf{D} \quad (1.81)$$

If \mathbf{A}_n is symmetric, then \mathbf{A}_{n+1} is also symmetric. It can be proved easily by the use of Eq. (1.79). Since \mathbf{A}_1 is symmetric, mathematical induction gives all the Rivlin–Ericksen tensors are symmetric.

Problem 1

- [1] Simple shear is a motion defined by

$$\mathbf{x} = \tilde{\mathbf{x}} + \gamma(t)(\tilde{\mathbf{x}} \cdot \mathbf{n})\mathbf{m} \quad (1.a)$$

where γ is called shear strain, \mathbf{m} and \mathbf{n} are constant unit vectors, and $\mathbf{m} \cdot \mathbf{n} = 0$. Let $\mathbf{k} = \mathbf{m} \times \mathbf{n}$. Then, \mathbf{m} , \mathbf{n} , and \mathbf{k} form an orthonormal basis. Calculate \mathbf{F} , \mathbf{B} , \mathbf{C} , \mathbf{U} , \mathbf{V} , \mathbf{R} , \mathbf{L} , \mathbf{D} , and \mathbf{W} .

- [2] Prove that $\text{tr}(\mathbf{E}) \approx (dV - d\tilde{V})/d\tilde{V}$ for infinitesimal deformation.
 [3] Show that $I_{\mathbf{B}} = I_{\mathbf{C}}$, $II_{\mathbf{B}} = II_{\mathbf{C}}$, and $III_{\mathbf{B}} = III_{\mathbf{C}}$.
 [4] Prove that

$$(I_{\mathbf{U}})^2 = I_{\mathbf{C}} + 2II_{\mathbf{U}}; \quad (II_{\mathbf{U}})^2 = II_{\mathbf{C}} + I_{\mathbf{U}}\sqrt{III_{\mathbf{U}}}; \quad (III_{\mathbf{U}})^2 = III_{\mathbf{C}} \quad (1.b)$$

- [5] Consider the unit vector \mathbf{n} which is in the direction of the rotation axis. Then, it is not difficult to find a unit vector \mathbf{m} which is perpendicular to \mathbf{n} . From the two unit vectors, define $\mathbf{k} = \mathbf{m} \times \mathbf{n}$. It is clear that the three unit vectors form an orthonormal basis. Then, show that the following tensor is an orthogonal tensor.

$$\mathbf{Q} = \mathbf{nn} + \cos \theta (\mathbf{mm} + \mathbf{kk}) + \sin \theta (\mathbf{km} - \mathbf{mk}) \quad (1.c)$$

- [6] Show that $\dot{\mathbf{R}} \cdot \mathbf{R}^T$ is skew-symmetric. Use $\mathbf{R} \cdot \mathbf{R}^T = \mathbf{I}$.
 [7] Consider the velocity field given as $\mathbf{v} = r\omega(z)\mathbf{e}_z$ where cylindrical coordinate system is assumed and find deformation rate tensor \mathbf{D} .
 [8] Prove that

$$\frac{d}{dt}dV = (\nabla \cdot \mathbf{v})d\tilde{V} \quad (1.d)$$

- [9] Consider the case that the reference configuration uses generalized basis $\{\tilde{\mathbf{g}}^k\}$ and the current configuration uses generalized basis $\{\mathbf{g}_k\}$. Then, show that deformation gradient is given by

$$\mathbf{F} = \frac{\partial \xi^i}{\partial \tilde{\xi}^k} \mathbf{g}_i \tilde{\mathbf{g}}^k \quad (1.e)$$

- [10] Prove that

$$\frac{d\mathbf{F}^{-1}}{dt} = -\mathbf{F}^{-1} \cdot \mathbf{L} \quad (1.f)$$

- [11] Prove Eq. (1.47).
 [12] Show that time derivative of any orthogonal tensor is skew-symmetric.
 [13] Show that the Rivlin–Ericksen tensors are symmetric.
 [14] Show that

$$\mathbf{F}_t(\tau) = \mathbf{F}(\tilde{\mathbf{x}}, \tau) \cdot \mathbf{F}^{-1}(\tilde{\mathbf{x}}, t) \quad (1.g)$$

- [15] Derive

$$\frac{d}{dt}\mathbf{F}_t(\tau) = -\mathbf{F}_t(\tau) \cdot \mathbf{L}(t) \quad (1.h)$$

- [16] Derive

$$\frac{d}{dt}\mathbf{C}_t(\tau) + \mathbf{L}^T(t) \cdot \mathbf{C}_t(\tau) + \mathbf{C}_t(\tau) \cdot \mathbf{L}(t) = \mathbf{0} \quad (1.i)$$

[17] Derive

$$\frac{d}{dt} \mathbf{C}_t^{-1}(\tau) - \mathbf{L}(t) \cdot \mathbf{C}_t^{-1}(\tau) - \mathbf{C}_t^{-1}(\tau) \cdot \mathbf{L}^T(t) = \mathbf{0} \quad (1.j)$$

2 Balance Equations

We shall deal with four balance equations of mass, linear momentum, angular momentum, and energy for single-component materials. As for multicomponent versions, refer to De Groot (1984). Entropy balance equation will be discussed in Sect. 4.

2.1 Mass Balance

It is the basic assumption of continuum theory that there exists a scalar field called mass density such that

$$M = \iiint_{\tilde{\Omega}} \tilde{\rho}(\tilde{\mathbf{x}}, t) d\tilde{V} \quad (2.1)$$

where M is the total mass of material particles in the region of $\tilde{\Omega}$. Note that $\tilde{\Omega}$ is the region in the reference configuration. Since all material particles in $\tilde{\Omega}$ move to the region Ω at time t , mass conservation law implies

$$M = \iiint_{\Omega} \rho(\mathbf{x}, t) dV \quad (2.2)$$

No mass change during any motion gives

$$\frac{dM}{dt} = \frac{d}{dt} \iiint_{\Omega} \rho(\mathbf{x}, t) dV = \iiint_{\Omega} \left(\frac{d\rho}{dt} dV + \rho \frac{d}{dt} dV \right) = 0 \quad (2.3)$$

Application of Eq. (1.d) of Problem 1 gives

$$\iiint_{\Omega} \left[\frac{d\rho}{dt} + (\nabla \cdot \mathbf{v})\rho \right] dV = 0 \quad (2.4)$$

Since Eqs. (2.1) and (2.2) hold for arbitrary subset of the reference configuration, it is clear that

$$\frac{d\rho}{dt} + (\nabla \cdot \mathbf{v})\rho = 0 \quad (2.5)$$

Application of Eq. (1.9), the definition of material time derivative, gives

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad (2.6)$$

Equations (2.5) and (2.6) are called continuity equation or mass balance equation.

When volume does not vary during motion, the motion is called incompressible. Incompressible condition is equivalent to constant density field. Compared with gas, compression of liquid requires huge pressure. Hence, incompressible condition is a good approximation for flow of liquid. Rubbery material is observed as incompressible material because its change in shape is easier than the volumetric change for moderate loading. Then, application of constant density to Eq. (2.5) or (2.6) gives

$$\nabla \cdot \mathbf{v} = 0 \quad (2.7)$$

Similar approximation can be used for liquid fluids. If flow field is given by $\mathbf{v} = v(x, y, t)\mathbf{e}_3$, Eq. (2.7) holds. Hence, it can be said that incompressible condition can be considered as a material property for certain materials. It is noteworthy that certain special deformation of compressible material may not change volume.

The most important feature of mass balance equation is that it holds for every material. This feature holds for the balance equation to be introduced later. Hence, these balance equations are called governing equations, too.

2.1.1 Reynolds Transport Theorem

Consider $\Phi(\mathbf{x}, t)$ is a tensorial quantity of any order. Then, the corresponding quantity for the region Ω can be given by

$$\Phi(\mathbf{x}, t) = \iiint_{\Omega} \rho(\mathbf{x}, t)\Phi(\mathbf{x}, t)dV \quad (2.8)$$

Then, the material time derivative of $\Phi(\mathbf{x}, t)$ is given by

$$\begin{aligned} \frac{d}{dt}\Phi(\mathbf{x}, t) &= \frac{d}{dt} \iiint_{\Omega} \rho(\mathbf{x}, t)\Phi(\mathbf{x}, t)dV = \iiint_{\Omega} \left[\frac{d\rho}{dt}\Phi dV + \rho \frac{d\Phi}{dt}dV + \rho\Phi \frac{d}{dt}dV \right] \\ &= \iiint_{\Omega} \left\{ \rho \frac{d\Phi}{dt} + \left[\frac{d\rho}{dt} + (\nabla \cdot \mathbf{v})\rho \right] \Phi \right\} dV \end{aligned} \quad (2.9)$$

Here, Eq. (1.d) was used. Application of the mass balance equation, Eq. (2.5), gives

$$\frac{d}{dt} \iiint_{\Omega} \rho \phi dV = \iiint_{\Omega} \rho \frac{d\phi}{dt} dV \quad (2.10)$$

This identity is called the *Reynolds transport theorem*. This theorem is very important because it will be used when we derive various balance equations.

2.2 Momentum Balance

2.2.1 Linear Momentum Balance

There are two kinds of forces exerted on a material body: *contact force* and *body force*. The action of contact force is carried through the contact surface, while that of body force is carried at a distance. The representative body forces are gravitational and electrostatic forces.

Newton's second law implies that the total force exerted on a body is the time rate of the total linear momentum of the body. This holds for any part of the whole body. The mathematical expression of the second law of Newtonian mechanics is given by

$$\frac{d}{dt} \iiint_{\Omega} \rho \mathbf{v} dV = \iint_{\partial\Omega} \mathbf{t} da + \iiint_{\Omega} \rho \mathbf{b} dV \quad (2.11)$$

where \mathbf{t} is the contact force per unit area, called *stress vector*, and \mathbf{b} is the body force per unit mass. The left side can be expanded as follows:

$$\frac{d}{dt} \iiint_{\Omega} \rho \mathbf{v} dV = \iiint_{\Omega} \rho \frac{d\mathbf{v}}{dt} dV \quad (2.12)$$

Here, we used the Reynolds transport theorem.

Cauchy proved that there exists a second-order tensor called *stress* such that

$$\mathbf{t} = \mathbf{T} \cdot \mathbf{n} \quad (2.13)$$

where \mathbf{n} is the unit vector normal to the surface element da . Then, the surface integral of Eq. (2.11) becomes

$$\iint_{\partial\Omega} \mathbf{t} da = \iint_{\partial\Omega} \mathbf{T} \cdot \mathbf{n} da = \iint_{\partial\Omega} \mathbf{T} \cdot \mathbf{d}\mathbf{a} = \iiint_{\Omega} \operatorname{div} \mathbf{T} dV \quad (2.14)$$

Substitution of Eqs. (2.12) and (2.14) into Eq. (2.11) yields

$$\iiint_{\Omega} \left[\rho \frac{d\mathbf{v}}{dt} - \operatorname{div} \mathbf{T} - \rho \mathbf{b} \right] dV = \mathbf{0} \quad (2.15)$$

Since this must be valid for any region Ω , the integrand of Eq. (2.15) must be the zero vector:

$$\rho \frac{d\mathbf{v}}{dt} = \operatorname{div} \mathbf{T} + \rho \mathbf{b}, \quad (2.16)$$

which is the local form (or differential form) of linear momentum balance. This equation is also valid for any materials.

The two governing equations are actually four scalar equations because the continuity equation is a scalar equation, while the linear momentum balance equation is a vector equation. However, these equations contain thirteen unknown fields: one for mass density field; three for velocity vector field; and nine for stress tensor field. Only four equations cannot determine the thirteen unknown fields uniquely. Hence, we need nine more equations. The nine equations correspond to *constitutive equation* which relates stress tensor to deformation. The constitutive equation is a tensor equation and will be discussed in Sect. 3. Different from governing equations, the constitutive equation represents material properties.

2.2.2 Stress Tensor

To understand what stress is, we consider a body of materials as a collection of molecules. If forces exerting on the body do not give rise to any deformation, then the body moves as a rigid body. Assume that a tiny probe is installed in the body and it can detect any variation of the force field around the point where the probe is installed. The probe averages out the variation whose wavelength is shorter than the size of material particle hypothesized in continuum theory and also does the variation whose frequency is higher than the inverse of the minimum characteristic time concerned in continuum theory. Then, it can be said that the tiny probe can detect the variation of the force field in the scale of continuum theory. Let us call the force field in the scale of continuum theory the macroscopic force field. On the other hand, microscopic force field is the object to be averaged by the probe.

The microscopic force field varies due to the changes in intermolecular potential and momentum rates of molecules. These changes must be deeply related to the changes in relative positions of molecules, which is deformation in terminology of continuum theory. Thus, stress cannot be generated without any deformation.

Consider a small volume Ω in a deformed body and divide the volume into two parts: A and B. The volume Ω is enveloped by the surface $\partial\Omega$. The surface $\partial\Omega$ is the union of $\partial\Omega_A$ and $\partial\Omega_B$ which belong to A and B, respectively. Suppose that the two subsets A and B are distinguished by the flat plane $\partial\Omega_{AB}$ between the subsets. Suppose that a macroscopic force field is distributed on $\partial\Omega$. Then, force exerted on $\partial\Omega_A$ results in the force exerted on $\partial\Omega_{AB}$ of B. Let the force on $\partial\Omega_{AB}$ of B be denoted by $\delta\mathbf{f}_{AB}$. The force on $\partial\Omega_B$ generates the force $\delta\mathbf{f}_{BA}$ on $\partial\Omega_{AB}$ of A. The action–reaction law implies that $\delta\mathbf{f}_{AB} = -\delta\mathbf{f}_{BA}$. It is assumed that there exists the limit such that

$$\mathbf{t}(\mathbf{x}, t, \mathbf{n}) = \lim_{\delta a \rightarrow 0} \frac{\delta\mathbf{f}_{AB}}{\delta a} \quad (2.17a)$$

where \mathbf{x} is the center of $\partial\Omega_{AB}$, δa is the area of $\partial\Omega_{AB}$, and \mathbf{n} is the unit normal vector of $\partial\Omega_{AB}$, whose direction is outward from B. Similarly, we have

$$\mathbf{t}(\mathbf{x}, t, -\mathbf{n}) = \lim_{\delta a \rightarrow 0} \frac{\delta\mathbf{f}_{BA}}{\delta a} \quad (2.17b)$$

The action–reaction law gives

$$\mathbf{t}(\mathbf{x}, t, -\mathbf{n}) = -\mathbf{t}(\mathbf{x}, t, \mathbf{n}) \quad (2.18)$$

The force field $\mathbf{t}(\mathbf{x}, t, \mathbf{n})$ is called *stress vector*.

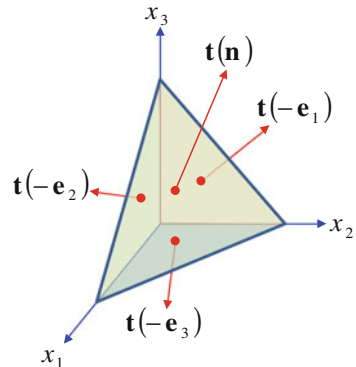
Cauchy proved that

$$\mathbf{t}(\mathbf{x}, t, \mathbf{n}) = \mathbf{T}(\mathbf{x}, t) \cdot \mathbf{n} \quad (2.19)$$

by the use of the tiny tetrahedron as shown in Fig. 1.

The tetrahedron shown in Fig. 1 has four flat planes whose normal vectors are $-\mathbf{e}_1$, $-\mathbf{e}_2$, $-\mathbf{e}_3$, and \mathbf{n} . We can choose \mathbf{n} freely. The plane of $-\mathbf{e}_1$ is the projection of the plane of \mathbf{n} on the x_2x_3 plane. Hence, if the area of the plane of \mathbf{n} is Δa , then the

Fig. 1 Cauchy's tetrahedron



area Δa_1 of the plane of $-\mathbf{e}_1$ is given by $(\mathbf{n} \cdot \mathbf{e}_1)\Delta a$. Similarly, the area Δa_k of the plane of $-\mathbf{e}_k$ is given by $(\mathbf{n} \cdot \mathbf{e}_k)\Delta a$. The volume of the tetrahedron can be calculated by $\Delta V = \frac{1}{3}h\Delta a$ where h is the height of the tetrahedron from the plane of \mathbf{n} . Then, the force balance for the tetrahedron is given by

$$\rho\Delta V \frac{d\mathbf{v}}{dt} = \mathbf{t}(\mathbf{n}) + \sum_{k=1}^3 \mathbf{t}(-\mathbf{e}_k)\Delta a(\mathbf{n} \cdot \mathbf{e}_k) + \rho\mathbf{g}\Delta V \quad (2.20)$$

If taking $\Delta V \rightarrow 0$ which means $\Delta a \rightarrow 0$ and $h \rightarrow 0$, we have

$$\mathbf{t}(\mathbf{n}) + \sum_{k=1}^3 \mathbf{t}(-\mathbf{e}_k)(\mathbf{n} \cdot \mathbf{e}_k) = \mathbf{0} \quad (2.21)$$

Using Eq. (2.18), we have

$$\mathbf{t}(\mathbf{n}) = \mathbf{t}(\mathbf{e}_k)(\mathbf{e}_k \cdot \mathbf{n}) \quad (2.22)$$

where summation convention was used as before. Since $\mathbf{t}(\mathbf{e}_k)$ is a vector, we can write

$$\mathbf{t}(\mathbf{e}_k) = T_{ik}\mathbf{e}_i \quad (2.23)$$

Substitution of Eq. (2.23) into Eq. (2.22) gives

$$\mathbf{t}(\mathbf{n}) = T_{ik}\mathbf{e}_i\mathbf{e}_k \cdot \mathbf{n} \quad (2.24)$$

Equation (2.13) is proven.

When a force is exerted on small area, the effect of the force on the body is larger than that of the same force exerted on larger area. Even though force vector and area are fixed, the effect of the force can be different depending on the orientation of the surface. Thus, the effect of force exerted on a body differs depending on both the area and orientation of the contact surface. Hence, we can consider a piece of surface as a vector when we consider the effect of force on a body. We want the effect of force to be represented by the force normalized by oriented area (area vector). Although a vector cannot be divided by another vector, we can use

$$\mathbf{f} = \mathbf{T} \cdot \mathbf{a} \quad (2.25)$$

where \mathbf{f} is the force vector, \mathbf{a} is the area vector, and the second-order tensor \mathbf{T} is the normalized effect of the force. Hence, stress has the dimension of force per unit area. When dividing both sides of Eq. (2.25) by the area $a = \|\mathbf{a}\|$ and taking $a \rightarrow 0$, Eq. (2.13) is recovered.

2.2.3 Angular Momentum Balance

When linear momentum and position of a particle are given, respectively, as \mathbf{p} and \mathbf{x} , the angular momentum of the particle is given by $\mathbf{l} = \mathbf{x} \times \mathbf{p}$. The torque of the particle is the time rate of angular momentum. Then, we have

$$\frac{d\mathbf{l}}{dt} = \frac{d}{dt}(\mathbf{x} \times \mathbf{p}) = \mathbf{x} \times \mathbf{f} \quad (2.26)$$

Note that the time rate of angular momentum is equal to the moment of force.

Consider a body denoted by Ω . The total angular momentum is given by

$$\mathbf{L} = \iiint_{\Omega} \mathbf{x} \times \rho \mathbf{v} dV \quad (2.27)$$

Continuum version of the moment of force is given by

$$\mathbf{M} = \iint_{\partial\Omega} \mathbf{x} \times \mathbf{t} da + \iiint_{\Omega} \mathbf{x} \times \rho \mathbf{b} dV \quad (2.28)$$

Then, we have the continuum version of Eq. (2.26):

$$\frac{d\mathbf{L}}{dt} = \iiint_{\Omega} \mathbf{x} \times \rho \frac{d\mathbf{v}}{dt} dV = \mathbf{M} \quad (2.29)$$

Note that $d\mathbf{x}/dt = \mathbf{v}$ and $\mathbf{v} \times \mathbf{v} = \mathbf{0}$. Equation (2.27) can be derived by the use of the Reynolds transport theorem.

In Sect. 5, we have learned that a vector product can be replaced by the corresponding skew-symmetric tensor [see Eqs. (5.27) and (5.28) in Chap. 1]. Then, we have

$$\mathbf{x} \times \mathbf{t} = \mathbf{G} \cdot \mathbf{t} = \mathbf{G} \cdot \mathbf{T} \cdot \mathbf{n} \quad (2.30)$$

Note that Eq. (2.13) is used and the skew-symmetric tensor \mathbf{G} is given by

$$\mathbf{G} = G_{ik} \mathbf{e}_i \mathbf{e}_k = -\varepsilon_{ikp} x_p \mathbf{e}_i \mathbf{e}_k \quad (2.31)$$

Then, the divergence theorem gives

$$\begin{aligned} \iint_{\partial\Omega} \mathbf{x} \times \mathbf{t} dS &= \iiint_{\Omega} \text{div}(\mathbf{G} \cdot \mathbf{T}) dV = \iiint_{\Omega} \nabla \cdot (\mathbf{T}^T \cdot \mathbf{G}^T) dV \\ &= \iiint_{\Omega} \left[\mathbf{G} \cdot (\nabla \cdot \mathbf{T}^T) + \frac{\partial G_{ik}}{\partial x_j} T_{kj} \mathbf{e}_i \right] dV \end{aligned} \quad (2.32)$$

Note that

$$\frac{\partial G_{ik}}{\partial x_j} T_{kj} = -\varepsilon_{ikp} \frac{\partial x_p}{\partial x_j} T_{kj} = -\varepsilon_{ikp} T_{kp} \quad (2.33)$$

With the help of Eqs. (2.32) and (2.33), Eq. (2.29) can be rewritten by

$$\iiint_{\Omega} \mathbf{G} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \nabla \cdot \mathbf{T}^T - \rho \mathbf{b} \right) dV = - \iiint_{\Omega} \varepsilon_{ikp} T_{kp} \mathbf{e}_i dV \quad (2.34)$$

The left side of Eq. (2.34) is zero vector because of the equation of linear momentum balance. Hence, we have

$$\varepsilon_{ikp} T_{kp} = 0 \quad (2.35)$$

Equation (2.35) is equivalent to $T_{ik} = T_{ki}$. Finally, we come to know that the symmetry of stress tensor is the consequence from angular momentum conservation.

2.2.4 Piola–Kirchhoff Stress

The stress \mathbf{T} is called *Cauchy stress* or *true stress*. Cauchy stress is a linear transform from the outward normal vector \mathbf{n} of the current configuration to the stress vector which is exerted on the infinitesimal surface element of the current configuration. With the help of Eq. (1.37), we have

$$\mathbf{t} da = \mathbf{T} \cdot d\mathbf{a} = \tilde{\mathbf{P}} \cdot d\tilde{\mathbf{a}} \quad (2.36)$$

where

$$\tilde{\mathbf{P}} \equiv \det(\mathbf{F}) \mathbf{T} \cdot \mathbf{F}^{-T} \quad (2.37)$$

The tensor $\tilde{\mathbf{P}}$ is called *Piola–Kirchhoff stress of the 1st kind*, which is a linear transform from the infinitesimal surface element of the reference configuration to the force exerted on the infinitesimal surface element of the current configuration. Note that $\tilde{\mathbf{P}}$ is not symmetric, while Cauchy stress \mathbf{T} is symmetric. *Piola–Kirchhoff stress of the 2nd kind* is defined by

$$\tilde{\mathbf{T}} = \mathbf{F}^{-1} \cdot \tilde{\mathbf{P}} = \det(\mathbf{F}) \mathbf{F}^{-1} \cdot \mathbf{T} \cdot \mathbf{F}^{-T} \quad (2.38)$$

Note that $\tilde{\mathbf{T}}^T = \tilde{\mathbf{T}}$ from the definition.

2.3 Energy Balance: The First Law of Thermodynamics

2.3.1 Heat Transfer

There are three ways of heat transfer: conduction, convection, and radiation. Conduction occurs through mediation of materials irrespective of solid and fluid. Convection occurs by flow in fluid. On the other hand, radiation does not need any mediation of materials because it transfers energy through propagation of electromagnetic wave. Since convection is an energy transfer coupled with flow motion, we consider conduction and radiation here.

Since materials absorb and radiate electromagnetic wave, the net energy rate \dot{Q}_{rad} for only radiation is given by

$$\dot{Q}_{\text{rad}} = \iiint_{\Omega} \rho r \, dV \quad (2.39)$$

where r is a scalar field representing the rate of the energy gain per unit mass by absorbance and radiation of electromagnetic wave.

According to Fourier, the heat flux of conduction is given in terms of temperature gradient:

$$\mathbf{q} = -\kappa \nabla T \quad (2.40)$$

where \mathbf{q} is the *heat flux*, κ is the *heat conductivity*, and T is the absolute temperature. Then, net energy rate \dot{Q}_{cond} for only heat conduction is given by

$$\dot{Q}_{\text{cond}} = - \iint_{\partial\Omega} \mathbf{q} \cdot \mathbf{da} \quad (2.41)$$

2.3.2 Energy Balance

When a body of continuum exchanges mechanical work and heat with its surroundings, the rate of the net energy gain of the body dE/dt is given by

$$\frac{dE}{dt} = \frac{dW}{dt} + \frac{dQ}{dt} \quad (2.42)$$

where dW/dt is the rate of mechanical work given to the body and dQ/dt is the rate of heat gain.

The rate of mechanical work is called the mechanical power which can be calculated by

$$\frac{dW}{dt} = \iint_{\partial\Omega} \mathbf{t} \cdot \mathbf{v} \, da + \iiint_{\Omega} \rho \mathbf{b} \cdot \mathbf{v} \, dV \quad (2.43)$$

Application of Eq. (2.13) gives

$$\frac{dW}{dt} = \iiint_{\Omega} \text{tr}(\mathbf{L} \cdot \mathbf{T}) \, dV + \iiint_{\Omega} \mathbf{v} \cdot (\nabla \cdot \mathbf{T} + \rho \mathbf{b}) \, dV \quad (2.44)$$

Here, we used divergence theorem and symmetry of stress tensor. The use of Eq. (2.16) gives

$$\frac{dW}{dt} = \frac{dK}{dt} + \iiint_{\Omega} \text{tr}(\mathbf{L} \cdot \mathbf{T}) \, dV \quad (2.45)$$

where K is the kinetic energy of the body:

$$K = \iiint_{\Omega} \frac{\rho}{2} \mathbf{v} \cdot \mathbf{v} \, dV \quad (2.46)$$

Note that the Reynolds transport theorem gives

$$\frac{dK}{dt} = \iiint_{\Omega} \rho \mathbf{v} \cdot \frac{d\mathbf{v}}{dt} \, dV \quad (2.47)$$

We define stress power as the second term in the right-hand side of Eq. (2.45). Note that

$$\text{tr}(\mathbf{L} \cdot \mathbf{T}) = \text{tr}(\mathbf{D} \cdot \mathbf{T}) = \text{tr}(\mathbf{T} \cdot \mathbf{D}) = \text{tr}(\mathbf{T} \cdot \mathbf{L}) = \mathbf{T} : \mathbf{D} \quad (2.48)$$

It is clear that the rate of heat gain dQ/dt is the sum of \dot{Q}_{cond} and \dot{Q}_{rad} . Then, we have

$$\frac{dE}{dt} = \frac{dK}{dt} + \iiint_{\Omega} \mathbf{T} : \mathbf{D} \, dV - \iiint_{\Omega} \nabla \cdot \mathbf{q} \, dV + \iiint_{\Omega} \rho r \, dV \quad (2.49)$$

The total energy E can be considered as the sum of the kinetic energy and the energy stored in the material called *internal energy*:

$$E = U + K \quad (2.50)$$

where U is the internal energy. For the internal energy U , we can define internal energy density u such that

$$U = \iiint_{\Omega} \rho u \, dV \quad (2.51)$$

Substitution of Eq. (2.50) into Eq. (2.49) and rearrangement give

$$\iiint_{\Omega} \left[\rho \frac{du}{dt} + \nabla \cdot \mathbf{q} - \rho r - \mathbf{T} : \mathbf{D} \right] dV = 0 \quad (2.52)$$

Since Eq. (2.52) is valid for arbitrary region of Ω , it can be concluded that

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} \quad (2.53)$$

The term including stress, $\mathbf{T} : \mathbf{D}$, is called *stress power*. Equation (2.53) implies that the rate of internal energy is equal to the sum of the rate of net gain of heat and the stress power. The first law of equilibrium thermodynamics reads

$$du = dq + dw \quad (2.54)$$

where du is the differential of internal energy, dq is the infinitesimal heat entering the system, and dw is the infinitesimal work done on the system. Comparison of Eq. (2.53) with Eq. (2.54) tells us that the stress power and the rate of heat gain correspond to dw and dq , respectively.

As for rigid body with constant heat capacity, it is clear that

$$\mathbf{T} : \mathbf{D} = 0; \quad du = c_V dT \quad (2.55)$$

where c_V is the *specific heat capacity* at constant volume. In this case, rigid body implies $c_V = c_P$, too. Of course, c_P is the specific heat capacity at constant pressure. Then, with the help of Eq. (2.40), Eq. (2.53) becomes

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_P} \nabla^2 T + \frac{r}{c_P} \quad (2.56)$$

It is usual that r depends on position and time through temperature. Then, Eq. (2.56) is a nonlinear equation of temperature because r is proportional to T^4 (the Stefan–Boltzmann law). At a moderate temperature, it is a good approximation the term involving r is negligible compared with other terms in Eq. (2.56). Then, we obtain a diffusion equation of temperature such that

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_P} \nabla^2 T \quad (2.57)$$

As for deformable body, we need the second law and suitable constitutive equation for internal energy to derive temperature equation similar to Eqs. (2.56) and (2.57). This will be discussed when we study irreversible thermodynamics.

2.4 Balance Equations in Terms of Flux

We have derived several balance equations on the basis of the motion of material particles. The same equations can be derived from another basis called flux (Deen 1998; Bird 2002; De Groot 1984). Although the use of flux in the derivation of balance equation is easily understood and is made of direct parlance to physical meaning, physical quantities may need their ways to finding the corresponding fluxes. Furthermore, it is additionally necessary to consider source term. However, the use of flux provides a unified way to balance equations of various physical quantities. Therefore, we give general forms of balance equation in terms of flux and then interpret the balance equations derived before from the viewpoint of flux.

Consider a physical quantity, say Φ which is defined by

$$\Phi = \iiint_{\Omega} \rho \phi \, d\hat{V} \quad (2.58)$$

where $\hat{\Omega}$ represents an arbitrary region fixed in space, ϕ is the field such that $\rho\phi$ is the density of Φ , ρ is the mass density, and $d\hat{V}$ is the infinitesimal volume element of $\hat{\Omega}$. Thus, $d\hat{V}$ is independent of time. Hence, the rate of Φ is given by

$$\frac{d\Phi}{dt} = \iiint_{\hat{\Omega}} \left(\frac{\partial}{\partial t} \rho \phi \right) d\hat{V} \quad (2.59)$$

Introduction of flux and source gives

$$\frac{d\Phi}{dt} = - \iint_{\partial\hat{\Omega}} \mathbf{J}_{\phi} \cdot \hat{\mathbf{n}} d\hat{S} + \iiint_{\hat{\Omega}} \Pi_{\phi} d\hat{V}; \quad \frac{\partial \rho \phi}{\partial t} = -\text{div} \mathbf{J}_{\phi} + \Pi_{\phi} \quad (2.60)$$

where \mathbf{J}_{ϕ} is the flux of the physical quantity Φ (or ϕ) and Π_{ϕ} is the source term. The minus sign of surface integral is originated from the convention that unit normal vector $\hat{\mathbf{n}}$ of surface element is given by the outward normal vector. Equation (2.60) is the general form of balance equations.

Equation (2.4), the balance equation of mass, can be obtained when $\phi = 1$ and the flux and the source are identified by

$$\mathbf{J}_{\rho} = \rho \mathbf{v}; \quad \Pi_{\rho} = 0 \quad (2.61)$$

Since mass is conserved, it is obvious that the source term of mass is zero. When linear momentum balance is considered, we know that $\phi = \mathbf{v}$ and

$$\mathbf{J}_v = \rho \mathbf{v} \mathbf{v} - \mathbf{T}; \quad \Pi_v = \rho \mathbf{b} \quad (2.62)$$

Equation (2.50) leads us to that the energy density is given by

$$\rho \varepsilon = \rho u + \frac{1}{2} \rho \|\mathbf{v}\|^2 \quad (2.63)$$

Since energy is conserved, it is obvious that the source term of energy must be zero. Then, the flux and source term of energy are given by

$$\mathbf{J}_\varepsilon = \rho \varepsilon \mathbf{v} + \mathbf{q}_T - \mathbf{T} \cdot \mathbf{v}; \quad \Pi_\varepsilon = 0 \quad (2.64)$$

where \mathbf{q}_T is the total heat flux which includes heat transfer by both conduction and radiation:

$$\nabla \cdot \mathbf{q}_T = \nabla \cdot \mathbf{q} - \rho r \quad (2.65)$$

From Eq. (2.65), thermal energy density or heat energy density ρq can be defined as

$$Q = \iiint_{\Omega} \rho q \, dV \quad (2.66)$$

and

$$\rho \frac{dq}{dt} = -\nabla \cdot \mathbf{q}_T \quad (2.67)$$

Then, energy balance equation can be rewritten by

$$\frac{\partial \rho \varepsilon}{\partial t} + \nabla \cdot \mathbf{J}_\varepsilon = 0 \quad (2.68)$$

or

$$\frac{du}{dt} = \frac{dq}{dt} - \hat{p} \frac{dv}{dt} + v \mathbf{T}' : \mathbf{L} \quad (2.69)$$

where v is the specific volume such that $v = \rho^{-1}$, $\hat{p} = -\frac{1}{3} \text{tr}(\mathbf{T})$, and \mathbf{T}' is the deviatoric stress such that $\mathbf{T} = -\hat{p} \mathbf{I} + \mathbf{T}'$.

Note that the conservative quantities such as mass and energy have no source term, whereas the nonconservative quantity such as linear momentum has nonzero source term. This viewpoint suggests that the entropy of nonequilibrium has the following formal balance equation:

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \Pi_s \quad (2.70)$$

The second law of thermodynamics demands the nonnegativeness of the source term of entropy: $\Pi_s \geq 0$. The essence of irreversible thermodynamics is to find the formulation of flux and source term of entropy in terms of measurable field variables. This will be discussed in Sect. 4.

It is noteworthy that the flux of momentum is a second-order tensor and the flux of mass is a vector, which implies that if a physical quantity is an n th-order tensor, then the corresponding flux is a tensorial quantity with the order of $n+1$. Meanwhile, the source term has the same order as the physical quantity.

Problem 2

- [1] Derive Eq. (2.29) by use the Reynolds transport theorem.
- [2] Derive

$$\rho(\mathbf{x}, t) = \frac{\tilde{\rho}(\tilde{\mathbf{x}}, t_R)}{\det(\mathbf{F})} \quad (2.a)$$

where ρ is the mass density field in the current configuration, $\tilde{\rho}$ is the mass density in the reference configuration, and t_R is the reference time.

- [3] Derive the equation of motion in terms of Piola–Kirchhoff stress of the first kind.
- [4] The case of $\mathbf{T} = T_{11}\mathbf{e}_1\mathbf{e}_1 + T_{22}\mathbf{e}_2\mathbf{e}_2 + T_{12}(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)$ is called the state of plane stress. Suppose that the body is in the state of plane stress and in equilibrium: $\nabla \cdot \mathbf{T} = \mathbf{0}$. Show the existence of $\psi(x_1, x_2)$ such that

$$\frac{\partial^2 \psi}{\partial x_2^2} = T_{11}; \quad \frac{\partial^2 \psi}{\partial x_1^2} = T_{22}; \quad \frac{\partial^2 \psi}{\partial x_1 \partial x_2} = -T_{12} \quad (2.b)$$

- [5] Show that

$$\text{tr}(\mathbf{T} \cdot \mathbf{L}) = \text{tr} \left(\mathbf{V}^{-1} \cdot \mathbf{T} \cdot \frac{d\mathbf{V}}{dt} \right) \quad (2.c)$$

- [6] Suppose that a material satisfies

$$\frac{df(\mathbf{B})}{dt} = \text{tr}(\mathbf{T} \cdot \mathbf{L}) \quad (2.d)$$

Then, show that

$$\mathbf{T} = 2\mathbf{B} \cdot \frac{\partial f}{\partial \mathbf{B}} \quad (2.e)$$

[7] Derive that

$$\text{tr}(\mathbf{T} \cdot \mathbf{L}) = \frac{1}{\det(\mathbf{F})} \text{tr} \left(\tilde{\mathbf{P}} \cdot \frac{d\mathbf{F}}{dt} \right) \quad (2.f)$$

[8] Derive Eq. (2.53) by the use of Eqs. (2.60) and (2.64).

3 Classical Constitutive Equations

From the viewpoint of rheology, materials can be classified into four groups: elastic body; viscous fluid; plastic body; and viscoelastic body. Stress of elastic body is a function of strain, which means that a current stress is uniquely determined by a strain at the present time. Viscous fluid is a body whose stress is a function of deformation rate and independent of strain. Stress of plastic material is determined by the path of deformation but independent of the deformation rate. This dependence on deformation path implies that different stresses occur when a given strain is conducted by different paths of deformation. For example, the two deformation paths such as the twist after an extension and the extension after a twist give different stresses even if the final strains are same. Since stress of plastic body is independent of the deformation rate, the same stress is obtained from two deformation histories with the same deformation path but different duration times. Stress of viscoelastic material is determined by the history of deformation. Hence, stress of viscoelastic material may depend on both the rate and the path of deformation. Different from plastic body, stress of viscoelastic body may be different for the deformation histories with the same deformation path but different duration times.

In this section, we shall introduce three kinds of classical constitutive equations: those of isotropic linear elastic body; viscous fluid; and linear viscoelastic body. These examples are helpful to understand more advanced theories of constitutive equations for polymeric materials. Some of them are practically important, and the others are conceptually important.

3.1 Elasticity

3.1.1 Constitutive Equation of Linear Elastic Body

Consider only infinitesimal deformation which means that infinitesimal strain is sufficient in describing stress. Isotropic linear elastic constitutive equation is an idealization of material. The constitutive equation is based on the assumptions such that

- [1] Material properties are isotropic.
- [2] Stress depends linearly only on current infinitesimal strain.

When stress is a linear function of infinitesimal strain, we can write the stress as follows:

$$T_{ik} = C_{ikmn}e_{mn} \quad (3.1)$$

where T_{ik} is the component of the stress tensor, C_{ikmn} is the component of fourth-order tensor called *modulus*, and e_{mn} is the component of infinitesimal strain.

Although fourth-order tensor has 81 components, the modulus tensor has only 21 independent components for fully anisotropic materials (Sadd 2009). However, the modulus of isotropic materials has only two independent components. Since material is isotropic, the modulus tensor must be isotropic fourth-order tensor such as

$$C_{ikmn} = \lambda\delta_{ik}\delta_{mn} + G(\delta_{im}\delta_{kn} + \delta_{in}\delta_{km}) + \beta(\delta_{im}\delta_{kn} - \delta_{in}\delta_{km}) \quad (3.2)$$

Application of Eq. (3.2) to Eq. (3.1) gives

$$T_{ik} = \lambda e_{mm}\delta_{ik} + 2G e_{ik} \quad (3.3)$$

Since $e_{ik} = e_{ki}$, the term involving β disappears irrespective of strain tensor. Hence, isotropic linear elastic body has only two independent modulus components.

3.1.2 Moduli of Isotropic Linear Elasticity

Problem 1 [2] provides that the trace of strain is the volumetric strain. Hydrostatic pressure $T_{ik} = p\delta_{ik}$ gives only change of volume without shape change. Taking trace on both sides of Eq. (3.3), we have

$$(3\lambda + 2G)e_V = T_{mm} = 3p \quad (3.4)$$

where $e_V = e_{mm}$. *Bulk modulus* K is defined as the slope in the plot of p as a function of e_V . Then, we have

$$K = \lambda + \frac{2}{3}G \quad (3.5)$$

An example of simple shear is $\mathbf{x} = \tilde{\mathbf{x}} + \gamma x_2 \mathbf{e}_1$. As for this deformation, the volume does not change, but only the shape of material changes. The infinitesimal strain for the *simple shear* is given by

$$\mathbf{E} = \frac{\gamma}{2}(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1) \quad (3.6)$$

Application of Eq. (3.6) to Eq. (3.3) gives

$$\mathbf{T} = \tau(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1) \quad (3.7)$$

where

$$\tau = G\gamma \quad (3.8)$$

Note that γ and τ are called shear strain and *shear stress*, respectively. Hence, G is called *shear modulus* which represents the resistance to shear. Deviatoric strain \mathbf{E}' is defined as

$$\mathbf{E}' = \mathbf{E} - \frac{1}{3}\text{tr}(\mathbf{E})\mathbf{I} \quad (3.9)$$

Equation (3.9) immediately indicates that the deviatoric strain is traceless:

$$\text{tr}(\mathbf{E}') = 0 \quad (3.10)$$

Then, Eq. (3.3) can be rewritten in terms of K and G as follows:

$$\mathbf{T} = Ke_v\mathbf{I} + 2G\mathbf{E}' \quad (3.11)$$

The isotropic term of Eq. (3.11) corresponds to the stress due to volume change, while the term of deviatoric strain corresponds to the stress due to shape change.

One of the most convenient test methods for elastic material is *simple elongation*. If elongation axis is \mathbf{e}_1 , then only nonzero component of stress is T_{11} . Then, we have only three nonzero components of strain:

$$e_{11} = \frac{\lambda + G}{G(3\lambda + 2G)}T_{11}; \quad e_{22} = e_{33} = -\frac{\lambda}{\lambda + G}e_{11} \quad (3.12)$$

Young's modulus is the slope in the plot of T_{11} against e_{11} . Hence, we have

$$E = \frac{G(3\lambda + 2G)}{\lambda + G} \quad (3.13)$$

Simple elongation test provides the measurement of Young's modulus as well as *Poisson's ratio* defined as

$$\nu = -\frac{e_{22}}{e_{11}} = \frac{\lambda}{2(\lambda + G)} \quad (3.14)$$

The constitutive equation can be rewritten in terms of E and ν as follows:

$$\begin{aligned} e_{11} &= \frac{T_{11} - \nu(T_{22} + T_{33})}{E}; & e_{22} &= \frac{T_{22} - \nu(T_{33} + T_{11})}{E}; \\ e_{33} &= \frac{T_{33} - \nu(T_{11} + T_{22})}{E}; & e_{12} &= \frac{T_{12}}{2G}; & e_{23} &= \frac{T_{23}}{2G}; & e_{31} &= \frac{T_{31}}{2G} \end{aligned} \quad (3.15)$$

Bulk modulus and shear modulus can be expressed in terms of Young's modulus and Poisson's ratio as follows:

$$K = \frac{E}{3(1 - 2\nu)}; \quad G = \frac{E}{2(1 + \nu)} \quad (3.16)$$

As Poisson's ratio goes to $\frac{1}{2}$, bulk modulus goes to infinity, which means that volume cannot be changed for any deformation. However, G goes to $\frac{1}{3}E$ as ν approaches to $\frac{1}{2}$. Hence, a material with $K \gg G$ behaves as *incompressible solid*. Rubber has Poisson's ratio very close to $\frac{1}{2}$.

3.1.3 Positiveness of Moduli

Deformation gives rise to the increase of the internal energy of linear elastic body. The minimum internal energy must be achieved at $\mathbf{E} = \mathbf{0}$. Strain energy density is the difference between the internal energies per unit volume of deformed and undeformed configurations. Then, the strain energy density can be calculated by integrating the differential equation such as

$$df = \mathbf{T} : d\mathbf{E} \quad (3.17)$$

This is the infinitesimal work per unit volume.

It is a reasonable assumption that higher strain gives rise to higher strain energy density. Mathematical expression of this notion is

$$f(t_1 \mathbf{E}) \geq f(t_2 \mathbf{E}) \quad (3.18)$$

where \mathbf{E} is arbitrary and $t_1 \geq t_2$ are arbitrary positive real numbers. The strain energy density must be an even function of strain such that $f(\mathbf{E}) = f(-\mathbf{E})$. We can expand $f(t\mathbf{E})$ as follows:

$$f(t\mathbf{E}) = f(\mathbf{0}) + t \left(\frac{\partial f}{\partial \mathbf{E}} \right)_{\mathbf{E}=\mathbf{0}} : \mathbf{E} + \frac{t^2}{2} \mathbf{E} : \left(\frac{\partial^2 f}{\partial \mathbf{E} \partial \mathbf{E}} \right)_{\mathbf{E}=\mathbf{0}} : \mathbf{E} + \cdots \quad (3.19)$$

Since Eq. (3.17) implies $\mathbf{T} = \partial f / \partial \mathbf{E}$, $\mathbf{E} = \mathbf{0}$ implies $(\partial f / \partial \mathbf{E})_{\mathbf{E}=\mathbf{0}} = \mathbf{0}$. Then, the inequality of Eq. (3.18) implies that

$$f(t_1 \mathbf{E}) - f(t_2 \mathbf{E}) = \frac{t_1^2 - t_2^2}{2} \mathbf{E} : \mathbf{C} : \mathbf{E} \geq 0 \quad (3.20)$$

where

$$\left(\frac{\partial^2 f}{\partial \mathbf{E} \partial \mathbf{E}} \right)_{\mathbf{E}=\mathbf{0}} = \left(\frac{\partial f}{\partial e_{ik} \partial e_{mn}} \right)_{\mathbf{E}=\mathbf{0}} \mathbf{e}_i \mathbf{e}_k \mathbf{e}_m \mathbf{e}_n = C_{ikmn} \mathbf{e}_i \mathbf{e}_k \mathbf{e}_m \mathbf{e}_n = \mathbf{C} \quad (3.21)$$

Since $t_1 > t_2$, we have

$$\mathbf{E} : \mathbf{C} : \mathbf{E} = C_{ikmn} e_{ik} e_{mn} \geq 0 \quad (3.22)$$

The inequality must hold for any strain. Note that \mathbf{E} is arbitrary. Hence, Eq. (3.22) implies the modulus tensor is positive definite. Equation (3.22) can be rewritten for isotropic linear elastic body as follows:

$$\mathbf{E} : \mathbf{C} : \mathbf{E} = K(e_V)^2 + 2G\mathbf{E}' : \mathbf{E}' \geq 0 \quad (3.23)$$

Note that $(e_V)^2 > 0$ and $\mathbf{E}' : \mathbf{E}' \geq 0$. Since we can render volume strain to be zero while deviatoric strain is not zero tensor, the inequality gives $G > 0$. Similarly, isotropic stress such as $\mathbf{T} = p\mathbf{I}$ gives $e_V \neq 0$ and $\mathbf{E}' = \mathbf{0}$. Then, we have $K > 0$. Then, it is not difficult to show that $E > 0$, $\lambda > 0$, and

$$-1 < \nu < \frac{1}{2} \quad (3.24)$$

3.1.4 Navier Equation

Modulus of most practical materials is so high that their deformation is nearly independent of gravitation. Hence, neglectation of body force is usually chosen. When deformed elastic body rests in equilibrium, we have the equilibrium equation such as

$$\nabla \cdot \mathbf{T} = 0 \quad (3.25)$$

When deformation is infinitesimal, $\mathbf{x} \approx \tilde{\mathbf{x}}$ holds. Then, we can use $\tilde{\nabla} \approx \nabla$. Hence, Eq. (1.25) can be rewritten by

$$\mathbf{E} = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \quad (3.26)$$

Then, we can express the equilibrium equation in terms of displacement vector:

$$\nabla(\nabla \cdot \mathbf{u}) + \frac{G}{\lambda + G} \nabla^2 \mathbf{u} = \mathbf{0} \quad (3.27)$$

Equation (3.27) is *Navier equation*.

If body force is not neglected, then the Navier equation becomes

$$\nabla^2 \mathbf{u} + \frac{1}{1 - 2\nu} \nabla(\nabla \cdot \mathbf{u}) = - \frac{2(1 + \nu)}{E} \rho \mathbf{b} \quad (3.28)$$

Here, λ and G are replaced by E and ν . A vector identity

$$\nabla(\nabla \cdot \mathbf{u}) = \nabla^2 \mathbf{u} + \nabla \times (\nabla \times \mathbf{u}) \quad (3.29)$$

gives

$$\nabla^2 \mathbf{u} + \frac{1}{2(1 - \nu)} \nabla \times (\nabla \times \mathbf{u}) = - \frac{(1 + \nu)(1 - 2\nu)}{E(1 - \nu)} \rho \mathbf{b} \quad (3.30)$$

If displacement field \mathbf{u} is irrotational, then Eq. (3.30) gives

$$\nabla^2 \mathbf{u} = - \frac{(1 + \nu)(1 - 2\nu)}{E(1 - \nu)} \rho \mathbf{b} \quad (3.31)$$

Equation (3.31) is three independent Poisson's equations. When body force is neglected, the Navier equation is reduced to Laplace equation.

Applications of Navier equation to several elastostatic problems are found in various texts of elasticity such as Sadd (2009) and Landau (1986).

3.1.5 Nonlinear Elasticity

Stress of elastic material is an algebraic function of strain. When deformation is infinitesimal, it is clear that the stress is a function of infinitesimal strain. However, there is no obvious reference to choose a finite strain among various finite strains in nonlinear elasticity. The *principle of material frame-indifference*, which will be explained in Sect. 5, might be helpful for this problem. However, for a while, we assume that appropriate strain measure is $\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T$. For simplicity, we consider only isotropic materials.

Since we are interested in only isotropic material, the learning from Sect. 5.3 gives

$$\mathbf{T} = G_0 \mathbf{I} + G_1 \mathbf{B} + G_2 \mathbf{B}^2 \quad (3.32)$$

where G_0 , G_1 and G_2 are functions of principal invariants of \mathbf{B} . Cauchy elastic materials are the ones whose stress is expressed by Eq. (3.32). It is known that the work done by stress of Eq. (3.32) may depend on deformation path (Ogden 1984).

Consider the stress power shown in Eq. (2.53). We are interested in the condition that allows the stress power to be time derivative of a scalar function. Exploiting properties of trace, we have

$$\text{tr}(\mathbf{T} \cdot \mathbf{L}) = \text{tr}\left(\mathbf{T} \cdot \frac{d\mathbf{F}}{dt} \cdot \mathbf{F}^{-1}\right) = \text{tr}\left(\mathbf{T} \cdot \frac{d\mathbf{V}}{dt} \cdot \mathbf{V}^{-1}\right) = \text{tr}\left(\mathbf{V}^{-1} \cdot \mathbf{T} \cdot \frac{d\mathbf{V}}{dt}\right) \quad (3.33)$$

Here, Eq. (1.46) was used. Consider a scalar-valued function of \mathbf{V} of Eq. (1.15) such that

$$\mathbf{T} = \mathbf{V} \cdot \frac{\partial \Phi}{\partial \mathbf{V}} \quad (3.34)$$

Since \mathbf{V} is symmetric tensor, substitution of Eq. (3.34) into Eq. (3.33) yields

$$\text{tr}(\mathbf{T} \cdot \mathbf{L}) = \frac{\partial \Phi}{\partial \mathbf{V}} : \frac{d\mathbf{V}}{dt} = \frac{d\Phi}{dt} \quad (3.35)$$

Thus, Eq. (3.34) is the condition that the stress power must be material time derivative of a scalar-valued function of \mathbf{V} . If the scalar function of Eq. (3.34) is a function of \mathbf{V} , then it is also a function of $\mathbf{B} = \mathbf{V}^2 = \mathbf{F} \cdot \mathbf{F}^T$. Note that \mathbf{B} is much more convenient than \mathbf{V} because \mathbf{B} does not require complicate polar decomposition. Then, Eq. (3.34) becomes

$$\mathbf{T} = 2\mathbf{B} \cdot \frac{\partial \Phi}{\partial \mathbf{B}} \quad (3.36)$$

Equations (3.34) and (3.36) are known as the constitutive equations of Green elasticity or hyperelasticity.

If material is isotropic, the scalar function Φ must be a function of principal invariants of \mathbf{B} . Then, Eq. (3.36) can be rewritten by

$$\mathbf{T} = 2(I_{\mathbf{B}}\Phi_3 + II_{\mathbf{B}}\Phi_2)\mathbf{I} + 2\Phi_1\mathbf{B} - 2III_{\mathbf{B}}\Phi_2\mathbf{B}^{-1} \quad (3.37)$$

where

$$\Phi_1 = \frac{\partial \Phi}{\partial I_{\mathbf{B}}}; \quad \Phi_2 = \frac{\partial \Phi}{\partial II_{\mathbf{B}}}; \quad \Phi_3 = \frac{\partial \Phi}{\partial III_{\mathbf{B}}} \quad (3.38)$$

If material is incompressible, then it is clear that $III_{\mathbf{B}} = 1$ and Eq. (3.37) becomes

$$\mathbf{T} = -p\mathbf{I} + 2\left(\frac{\partial\Phi}{\partial I_{\mathbf{B}}}\mathbf{B} - \frac{\partial\Phi}{\partial I_{\mathbf{B}^{-1}}}\mathbf{B}^{-1}\right) \quad (3.39)$$

Note that p cannot be determined by constitutive equation because volume is preserved. The pressure p can be determined by boundary condition. The *Cayley–Hamilton theorem* with $III_{\mathbf{B}} = 1$ gives

$$I_{\mathbf{B}} = II_{\mathbf{B}^{-1}}; \quad II_{\mathbf{B}} = I_{\mathbf{B}^{-1}} \quad (3.40)$$

Mechanical behavior of rubber can be approximated to isotropic incompressible elasticity.

3.2 Viscous Fluids

3.2.1 Constitutive Equation of Viscous Fluids

Normal fluids are isotropic. Since stress of viscous fluid is a function of deformation rate, the most general form should be

$$\mathbf{T} = \beta_0\mathbf{I} + \beta_1\mathbf{D} + \beta_2\mathbf{D}^2 \quad (3.41)$$

where β_k are functions of principal invariants of deformation rate tensor \mathbf{D} . The linearization of Eq. (3.41) gives the constitutive equation of *Newtonian fluid*. Although $I_{\mathbf{D}} = \text{tr}(\mathbf{D}) = \nabla \cdot \mathbf{v}$ is a linear function of \mathbf{D} , the other principal invariants are not linear functions of \mathbf{D} . If $\beta_2 \neq 0$, Eq. (3.41) cannot be linearized. Then, Newtonian fluids are obtained from Eq. (3.41) whenever $\beta_2 = 0$, $\beta_2 \equiv 2\eta_s$ is a constant, and β_0 is given by

$$\beta_0 = -p + \eta_b(\nabla \cdot \mathbf{v}) \quad (3.42)$$

Here, pressure p is a function of mass density and temperature, which is given from the equation of state. Viscosities η_b and η_s are called, respectively, bulk and shear viscosities. Finally, the stress of Newtonian fluid is given by

$$\mathbf{T} = -p\mathbf{I} + \eta_b(\nabla \cdot \mathbf{v})\mathbf{I} + 2\eta_s\mathbf{D} \quad (3.43)$$

Note that the deviatoric stress is given by

$$\mathbf{T}' = 2\eta_s \left[\mathbf{D} - \frac{\text{tr}(\mathbf{D})}{3}\mathbf{I} \right] = 2\eta_s\mathbf{D}' \quad (3.44)$$

No flow implies that stress becomes hydrostatic pressure which must be determined by the equation of the state of the fluid. Hence, p in Eq. (3.43) is the pressure of equilibrium thermodynamics. All fluid cannot sustain its shape without a container, and such isotropic term is necessary. The stress without $-p\mathbf{I}$ is called extra stress which is generated by flow. Extra stress is denoted and defined as

$$\mathbf{T}_{\text{ex}} = \mathbf{T} + p\mathbf{I} = \eta_b(\nabla \cdot \mathbf{v})\mathbf{I} + 2\eta_s\mathbf{D} \quad (3.45)$$

Thermodynamic analysis will show that shear viscosity must be positive, while the sum of bulk viscosity and two-thirds of shear viscosity must be positive.

3.2.2 Navier–Stokes Equation

Consider only Newtonian fluids. Substitution of Eq. (3.43) into equation of motion (2.16) yields

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + (\eta_b + \eta_s)\nabla(\nabla \cdot \mathbf{v}) + \eta_s \nabla^2 \mathbf{v} \quad (3.46)$$

Equation (3.46) is called *Navier–Stokes equation* which is actually three nonlinear partial differential equations with four unknown functions. This equation should be solved with continuity equation so that the number of equations is equal to that of unknown functions.

Liquids behave like *incompressible fluid* in moderate conditions. Hence, it is a good approximation that

$$\nabla \cdot \mathbf{v} = 0 \quad (3.47)$$

Application of Eq. (3.47) gives

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \eta_s \nabla^2 \mathbf{v} \quad (3.48)$$

It is the *Navier–Stokes equation* of incompressible fluids. Since the density of incompressible fluid is a constant and the hydrostatic pressure cannot be given from the equation of state, the four equations of Eqs. (3.47) and (3.48) have four unknown functions: three components of velocity and hydrostatic pressure.

Since both Eqs. (3.46) and (3.48) are difficult to be solved exactly, several approximations have been developed. These approximations are based on dimensional analysis because nondimensionalization makes it easier to compare the magnitudes of various quantities such as velocity, density, viscosity, pressure, and gravitation. Consider the following nondimensionalizations:

$$\mathbf{x} = l_c \bar{\mathbf{x}}; \quad \nabla = \frac{1}{l_c} \bar{\nabla}; \quad \mathbf{v} = v_c \bar{\mathbf{v}}; \quad \mathbf{b} = g \bar{\mathbf{b}}; \quad t = t_c \bar{t}; \quad p = p_c \bar{p} \quad (3.49)$$

where bar and subscript c indicate dimensionless quantity and characteristic quantity, respectively. Note that g is the acceleration of gravity. Characteristic quantities are chosen among the quantities to represent the system (Deen 1998). Then, Eq. (3.48) can be rewritten in terms of dimensionless quantities as follows:

$$\text{Re} \left(\frac{1}{\text{St}} \frac{\partial \bar{\mathbf{v}}}{\partial \bar{t}} + \bar{\mathbf{v}} \cdot \bar{\nabla} \cdot \bar{\mathbf{v}} \right) = - \left(\frac{l_c p_c}{\eta_s v_c} \right) \bar{\nabla} \bar{p} + \bar{\nabla}^2 \bar{\mathbf{v}} + \frac{\text{Re}}{\text{Fr}} \bar{\mathbf{b}} \quad (3.50)$$

where dimensionless numbers Re, Sr, and Fr are defined as

$$\text{Re} = \frac{\rho v_c l_c}{\eta_s}; \quad \text{St} = \frac{t_c v_c}{l_c}; \quad \text{Fr} = \frac{v_c^2}{g l_c} \quad (3.51)$$

Note that Re is the *Reynolds number* which represents the ratio of inertial force to viscous force, St is the *Strouhal number* which indicates the ratio of the time intrinsic for flow to the convection time, and Fr is the *Froude number* which corresponds to the ratio of inertial force to gravitational force.

If Sr is much larger than other dimensionless quantities, then the time derivative term can be neglected. Then, the velocity can be considered as the one independent of time. If Re is much smaller than Fr, then the effect of body force can be neglected. The body force is usually neglected in the flow of polymer melts, because their viscosity is much higher.

There are two ways to select the characteristic pressure: *viscous pressure scale* and *inertial pressure scale*. The former is given by

$$p_c = \frac{\eta_s v_c}{l_c} \quad (3.52)$$

and the latter is given by

$$p_c = \rho v_c^2 \quad (3.53)$$

If viscous scale is used, then the incompressible Navier–Stokes equation becomes

$$\frac{\partial \bar{\mathbf{v}}}{\partial \bar{t}} + \text{St} \bar{\mathbf{v}} \cdot \bar{\nabla} \cdot \bar{\mathbf{v}} = - \frac{\text{St}}{\text{Re}} \bar{\nabla} \bar{p} + \frac{\text{St}}{\text{Re}} \bar{\nabla}^2 \bar{\mathbf{v}} + \frac{\text{St}}{\text{Fr}} \bar{\mathbf{b}} \quad (3.54)$$

If the characteristic time t_c is chosen as

$$t_c = \frac{\rho l_c^2}{\eta_s}, \quad (3.55)$$

then we have

$$\text{St} = \text{Re} \quad (3.56)$$

Hence, Eq. (3.54) becomes

$$\frac{\partial \bar{\mathbf{v}}}{\partial t} + \text{Re} \bar{\mathbf{v}} \cdot \bar{\nabla} \cdot \bar{\mathbf{v}} = -\bar{\nabla} \bar{p} + \bar{\nabla}^2 \bar{\mathbf{v}} + \frac{\text{Re}}{\text{Fr}} \bar{\mathbf{b}} \quad (3.57)$$

Taking the limit $\text{Re} \rightarrow 0$, we have

$$\frac{\partial \bar{\mathbf{v}}}{\partial t} = -\bar{\nabla} \bar{p} + \bar{\nabla}^2 \bar{\mathbf{v}} \quad (3.58)$$

This equation is effective for suspensions consisting of tiny particles and incompressible Newtonian fluid. The *Stokes flow* is the flow that Eq. (3.58) is a good approximation. Equation (3.58) is a set of linear partial differential equations because the convection term $\bar{\mathbf{v}} \cdot \bar{\nabla} \bar{\mathbf{v}}$ is removed. Various solution methods for Eq. (3.58) are found in Kim and Karrila (2005).

3.2.3 Viscous Model for Polymer Melts

Since polymer melts have very high viscosity, it is usual to use $\text{Re} = 0$. However, the viscosity of polymer melt is not constant even though the temperature dependence of the viscosity is not considered. Shear viscosity of polymer melt is a function of deformation rate tensor. Since polymer melt is considered as incompressible fluid, the first principal invariant of \mathbf{D} is zero. For simplicity, if the third invariant is neglected, then the viscosity becomes the scalar-valued function of only the second invariant. It is more convenient to use *shear rate* $\dot{\gamma} \geq 0$ defined below rather than the second invariant:

$$\dot{\gamma} = \sqrt{4|II_{\mathbf{D}}|} \quad (3.59)$$

Note that in simple shear flow, deformation rate tensor is usually given by

$$\mathbf{D} = g(\mathbf{a}\mathbf{b} + \mathbf{b}\mathbf{a}) \quad (3.60)$$

where g is a function of position and time, \mathbf{a} is the unit vector along the *flow direction*, and \mathbf{b} is the unit vector in the direction where the magnitude of velocity varies (Tanner 2002). The direction of \mathbf{b} is called *gradient direction*, and the third direction other than \mathbf{a} and \mathbf{b} is called *vorticity direction*. Then, Eq. (3.59) implies that

$$\dot{\gamma} = |g| \quad (3.61)$$

Note that shear flow is the one that satisfies $\mathbf{a} \cdot \mathbf{b} = 0$.

In polymer processing, it is usual to use the following viscous fluid model:

$$\mathbf{T} = -p\mathbf{I} + 2\eta(\dot{\gamma})\mathbf{D} \quad (3.62)$$

with

$$\eta(\dot{\gamma}, T) = \frac{\eta_o(T)}{\{1 + [\eta_o(T)\dot{\gamma}/\sigma_o]^a\}^b} \quad (3.63)$$

Here, the viscosity model (3.63) is called the Carreau–Yasuda model (Bird et al. 1987). The *Carreau–Yasuda model* has four parameters at constant temperature. Note that Eq. (3.63) implies that

$$\lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma}, T) = \eta_o(T) \quad (3.64)$$

Hence, η_o is called the *zero-shear viscosity*. When $\eta_o\dot{\gamma}\sigma_o^{-1} \ll 1$, Eq. (3.62) behaves like the constitutive equation of incompressible Newtonian fluid.

Viscosity of most liquids depends on temperature. The temperature dependence of liquid agrees well, in most cases, with

$$\eta_o(T) = \eta_\infty \exp\left(\frac{T_a}{T}\right) \quad (3.65)$$

where both η_∞ and T_a are positive material parameters. The activation energy of flow is defined by

$$T_a = \frac{E_a}{R} \quad (3.66)$$

where R is the gas constant whose value is about $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Adopting Eq. (3.65), the Carreau–Yasuda model becomes 6-parameter model. One of the most important features of the Carreau–Yasuda model is temperature–shear rate superposition. The plot of $\eta/\eta_o(T)$ against $\dot{\gamma}/\dot{\gamma}_o$ is nearly independent of temperature. Note that

$$\dot{\gamma}_o = \frac{\sigma_o}{\eta_o(T)} \quad (3.67)$$

The zero-shear viscosity of polymer melt is also dependent on molecular weight of polymer. It is known that

$$\frac{\eta_o(M, T)}{\eta_o(M_C, T)} = \begin{cases} \frac{M}{M_C} & \text{for } M \leq M_C \\ \left(\frac{M}{M_C}\right)^{3.4} & \text{for } M \geq M_C \end{cases} \quad (3.68)$$

where M_C and M are, respectively, the *critical molecular weight* and *weight-average molecular weight* (Chap. 4). Hence, we can confirm experimentally the T - M - $\dot{\gamma}$ superposition from the plot of $\eta/\eta_o(T)$ against $\dot{\gamma}/\dot{\gamma}_o$. Since the critical molecular weight depends on kinds of polymers, it can be considered as material constant. Equation (3.68) is nearly independent of molecular weight distribution.

It is difficult to obtain sufficiently many viscosity data for the identification of Eq. (3.63). Hence, the use of the above superposition principle is very effective in the determination of the material parameters. This will be discussed in Part II.

It is difficult to obtain isothermal viscosity data whose shear rates are so wide to identify Eq. (3.63). Usual range of shear rate is $\eta_o\dot{\gamma}\sigma_o^{-1} \gg 1$. In this region of shear rate, Eq. (3.63) is approximated by

$$\eta = \frac{K}{\dot{\gamma}^n} \quad (3.69)$$

This is the two-parameter model called the *power law fluid model*.

It is worthwhile to mention that shear viscosity of polymer melts or polymer solutions is calculated by

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (3.70)$$

where σ is the shear stress measured from steady simple shear flow. There are several methods to measure the shear viscosity of polymeric fluid, which will be discussed in Part III. Since shear stress must not be a decreasing function of shear rate, it is clear that $0 < n < 1$ as well as $0 < ab < 1$. Both Eqs. (3.63) and (3.70) represent that the shear viscosity is a decreasing function of shear rate. Hence, most polymeric fluids are *shear-thinning fluids*.

3.3 Viscoelastic Models

3.3.1 Spring–Dashpot Models

Stress of polymeric materials depends on both strain and strain rate because the materials are viscoelastic. Before the birth of the society of rheology, the materials have been studied and modeled. At that time, solids were considered as linear elastic body (called *Hookean body*) whose stress is linear function of strain, whereas fluids were considered as linear viscous fluid (called Newtonian fluid) whose stress is linear function of strain rate. Since spring can be represented for linear elastic solids and dashpot for linear viscous fluids, it is a natural way to model linear viscoelasticity by the combinations of spring and dashpot.

The *Maxwell model* is a one-dimensional model that a spring and a dashpot are connected in a series. When the modulus of the spring is denoted by $G_M > 0$ and the viscosity of the dashpot by $\eta_M > 0$, the one-dimensional stress σ is given by

$$\sigma = G_M \gamma_e = \eta_M \frac{d\gamma_v}{dt} \quad (3.71)$$

where γ_e is the strain of the spring and γ_v is the strain of the dashpot. Since the two mechanical elements are connected in a series, it is clear that the total strain is given by

$$\gamma = \gamma_e + \gamma_v \quad (3.72)$$

Combining Eqs. (3.71) and (3.72), we have

$$\frac{d\sigma}{dt} + \frac{G_M}{\eta_M} \sigma = G_M \frac{d\gamma}{dt} \quad (3.73)$$

Since the units of G_M and η_M are Pa and Pa-s, respectively, we can define relaxation time such that

$$\lambda_M = \frac{\eta_M}{G_M} \quad (3.74)$$

The general solution of Eq. (3.73) is given by

$$\sigma(t) = \sigma(t_0) \exp\left(-\frac{t-t_0}{\lambda}\right) + \int_{t_0}^t G(t-\tau) \frac{d\gamma}{d\tau} d\tau \quad (3.75)$$

where the relaxation modulus $G(t)$ is defined by

$$G(t) = G_M \exp\left(-\frac{t}{\lambda_M}\right) \quad (3.76)$$

If we know the time when stress is zero, say it is t_0 , Eq. (3.75) becomes simpler:

$$\sigma(t) = \int_{t_0}^t G(t-\tau) \frac{d\gamma}{d\tau} d\tau \quad (3.77)$$

However, because stress of viscoelastic material is determined by deformation history, it is difficult to know when stress is zero. Setting $t_0 \rightarrow -\infty$, Eq. (3.75) becomes independent of initial condition:

$$\sigma(t) = \int_{-\infty}^t G(t-\tau) \frac{d\gamma}{d\tau} d\tau \quad (3.78)$$

Equation (3.78) is valid even if $\sigma(-\infty) \neq 0$.

Equation (3.78) with Eq. (3.76) is the constitutive equation of the Maxwell model. If strain is given by $\gamma(t) = \gamma_o \Theta(t)$ where $\Theta(t)$ is the *unit step function* defined by

$$\Theta(t) = \begin{cases} 1 & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{cases} \quad (3.79)$$

The test by the step strain is called stress relaxation. The derivative of the unit step function is the *Dirac delta function*:

$$\frac{d\Theta}{dt} = \delta(t) \quad (3.80)$$

Then, stress is given by

$$\sigma(t) = G(t)\gamma_o = G_M\gamma_o \exp\left(-\frac{t}{\lambda_M}\right) \quad (3.81)$$

Equation (3.81) implies that stress becomes smaller as time increases. This tendency qualitatively agrees with the experimental results of viscoelastic materials. Only two material parameters G_M and λ_M cannot fit experimental data.

It is interesting that the stress of Eq. (3.81) at $t = -1$ is larger than the stress at $t = 0$. It is ridiculous because strain was zero for $t < 0$. How can we remove this contradiction?

In Eq. (3.78), $t - \tau$ implies the interval between the time at which stress is measured and the time at which strain was given. Hence, $G(t - \tau)$ represents the weight of the effect of deformation given before $t - \tau$. It is a reasonable reasoning that the effects from far past must be smaller than those from near past. This notion is called *fading memory*. The principle of fading memory insists that relaxation modulus must be a decreasing function of time. Furthermore, the stress at present time cannot be affected by the strain which will be given in future. This is called *principle of causality*. If $t - \tau$ is less than zero, then τ is the time of future. The principle of causality insists that $G(t) = 0$ for $t < 0$. Thus, Eq. (3.76) must be replaced by

$$G(t) = G_M e^{-t/\lambda_M} \Theta(t) \quad (3.82)$$

The *Voigt model* (or *Kelvin–Voigt model*) is the one in which spring and dashpot are connected in parallel. Because of parallel connection, both mechanical elements have the same strain. Then, the total stress is given by

$$\sigma = G_V \gamma + \eta_V \frac{d\gamma}{dt} \quad (3.83)$$

This one-dimensional constitutive equation easily gives stress when strain is given. As for stress relaxation test, the stress is easily calculated as follows:

$$\sigma(t) = G_V \gamma_0 \Theta(t) + \eta_V \gamma_0 \delta(t) \quad (3.84)$$

Compared with Eq. (3.81), the stress of the Voigt model does not decrease just as that of elastic material. Only difference from linear elasticity is the last term containing the Dirac delta function. This term is not detectable in any experiment. At any way, Eq. (3.84) implies that the relaxation modulus of the Voigt model is given by

$$G(t) = G_V \Theta(t) + \eta_V \delta(t) \quad (3.85)$$

Equation (3.83) is a linear differential equation of strain. The general solution is given by

$$\gamma(t) = \exp\left(-\frac{t-t_0}{\tau_V}\right) \gamma(t_0) + \int_{t_0}^t \frac{1}{\eta_V} \exp\left(-\frac{t-\tau}{\tau_V}\right) \sigma(\tau) d\tau \quad (3.86)$$

where the *retardation time* of the Voigt model $\tau_V = \eta_V/G_V$. Application of integration by parts gives

$$\gamma(t) = e^{-(t-t_0)/\tau_V} \left[\gamma(t_0) - \frac{\sigma(t_0)}{G_V} \right] + \frac{\sigma(t)}{G_V} - \int_{t_0}^t \frac{1}{G_V} \exp\left(-\frac{t-\tau}{\tau_V}\right) \frac{d\sigma}{d\tau} d\tau \quad (3.87)$$

Just as before, we take $t_0 \rightarrow -\infty$ to remove the effect of initial condition. Then, we have

$$\gamma(t) = \int_{-\infty}^t J(t-\tau) \frac{d\sigma}{d\tau} d\tau \quad (3.88)$$

where $J(t)$ is called *creep compliance* and is given by

$$J(t) = \frac{1 - e^{-t/\tau_V}}{G_V} \Theta(t) \quad (3.89)$$

The unit step function was introduced to Eq. (3.89) because of the principle of causality.

In creep experiment, strain is measured as a function of time under the stress controlled by $\sigma(t) = \sigma_o \Theta(t)$. When creep test is done, the strain of elastic materials does not vary, while the strain of the Voigt model depends on time as follows:

$$\gamma(t) = \sigma_o J(t) \Theta(t) \quad (3.90)$$

As time goes to infinity, strain of Eq. (3.90) approaches to σ_o/G_V which is the strain of the spring of the Voigt model when the spring is exerted by the stress σ_o . This implies that the growth of the creep strain is retarded. Because of this retardation of strain, the characteristic time in Eq. (3.89), τ_V , is called *retardation time*.

Although the Maxwell model and the Voigt model are successful in the description of a few viscoelastic phenomena, the agreement is qualitative, not quantitative. Furthermore, the creep behavior of the Maxwell model and the relaxation behavior of the Voigt model are disappointing. Improvement is expected when more mechanical elements are involved in modeling.

The *standard solid model* is the parallel connection of the Maxwell model with a spring whose modulus is G_1 . Then, the one-dimensional constitutive equation becomes

$$\lambda \frac{d\sigma}{dt} + \sigma = \eta_2 \left(1 + \frac{G_1}{G_2} \right) \frac{d\gamma}{dt} + G_1 \gamma \quad (3.91)$$

where η_2 and G_2 are viscosity and modulus of the Maxwell model, respectively. The differential equation can be replaced again by Eq. (3.78), but the relaxation modulus is given by

$$G(t) = \left[G_1 + G_2 \exp\left(-\frac{t}{\lambda}\right) \right] \Theta(t) \quad (3.92)$$

with

$$\lambda = \frac{\eta_2}{G_2} \quad (3.93)$$

The *Jeffreys model* is the connection of the Voigt model with a dashpot of η_1 in a series. Then, the one-dimensional constitutive equation is given by

$$\frac{d\sigma}{dt} + \frac{G_2}{\eta_1 + \eta_2} \sigma = \frac{\eta_1}{\eta_1 + \eta_2} G_2 \frac{d\gamma}{dt} + \frac{\eta_1 \eta_2}{\eta_1 + \eta_2} \frac{d^2\gamma}{dt^2} \quad (3.94)$$

where η_2 and G_2 are viscosity and modulus of the Voigt model, respectively. The Jeffreys model describes the creep behavior of polymeric fluid well, while the standard solid model describes the relaxation behavior of polymeric solid well. The creep compliance of the Jeffreys model is given by

$$J(t) = \left(\frac{t}{\eta_0} + \frac{1 - e^{-t/\tau}}{G_2} \right) \Theta(t) \quad (3.95)$$

where the retardation time is given by

$$\tau = \frac{\eta_2}{G_2} \quad (3.96)$$

3.3.2 Generalization of One-Dimensional Models

However, these two 3-element models still suffer from quantitative disagreement with experimental data even though a quite large improvement is achieved compared with the 2-element models. The *generalized Maxwell model* is the parallel connection of N different Maxwell elements with a single spring. The generalized Maxwell model gives better fitting of relaxation data as N increases. Similarly, connection of N different Voigt elements and a single dashpot in a series gives better fitting of creep data as N increases. This is called the *generalized Voigt model*. The relaxation modulus of N -mode Maxwell model is given by

$$G(t) = \left(G_\infty + \sum_{k=1}^N G_k e^{-t/\lambda_k} \right) \Theta(t) \quad (3.97)$$

where k th-mode relaxation time is defined as $\lambda_k = \eta_k/G_k$. The N -mode Voigt model has the creep compliance such as

$$J(t) = \left(\frac{t}{\eta_0} + \sum_{k=1}^N \frac{1 - e^{-t/\tau_k}}{G_k} \right) \Theta(t) \quad (3.98)$$

where k th-mode retardation time is defined as $\tau_k = \eta_k/G_k$.

The generalized Maxwell and Voigt models can be generalized further by the introduction of relaxation and retardation spectra. The summation in Eqs. (3.97) and (3.98) is replaced by integration:

$$G(t) = \int_{-\infty}^{\infty} H(\lambda) e^{-t/\lambda} d \log \lambda \quad (3.99)$$

and

$$J(t) = \int_{-\infty}^{\infty} L(\tau) (1 - e^{-t/\tau}) d \log \tau \quad (3.100)$$

Note that these integral equations adopt logarithmic scale to make the *relaxation time spectrum* $H(\lambda)$ have the dimension of modulus and to make the *retardation time spectrum* $L(\tau)$ have the dimension of compliance. The two spectra cannot be measured directly because they are conceptual quantities. We shall show that the relaxation time spectrum is uniquely determined in Part II. Similar approaches can be applied to the uniqueness of retardation time spectrum. Equations (3.99) and (3.100) are the *Fredholm integral equation of the first kind* (Arfken 2001). How to solve this integral equation will be discussed in Part II, too.

From various spring–dashpot models (Tschoegl 1989), we know that all linear viscoelastic models satisfy Eqs. (3.78) and (3.88). The two equations are known as the *Boltzmann superposition principle*. This will be proved in Part II. Then, the modeling of relaxation modulus or creep compliance is more effective than the design of multielement spring–dashpot models. A parsimonious modeling is to model the Laplace transform of creep compliance:

$$\frac{1}{s\tilde{G}(s)} = \frac{1}{\eta_0 s} + \frac{J_1}{[1 + (\tau_1 s)^{\alpha_1}]^{\beta_1}} + \frac{J_2}{[1 + (\tau_2 s)^{\alpha_2}]^{\beta_2}} \quad (3.101)$$

where $\tilde{G}(s)$ is the Laplace transform of relaxation modulus (Marin and Graessley 1977). Equation (3.101) agrees very well with experimental data of polymer melts with narrow molecular weight distribution when $\beta_1 = \beta_2 = 1$. Another parsimonious model is

$$G(t) = G_\infty + G_1 \exp\left(-\left(\frac{t}{\lambda}\right)^\beta\right) \quad (3.102)$$

It is known as *Kohlrausch–Williams–Watts (KWW) equation* (Riande 2000).

An interesting generalization is to apply fractional derivative to spring–dashpot models (Smit and de Vries 1970). Although the spring–dashpot models contain derivatives of integer order, the *fractional models* use *fractional derivative* which is defined as (Bagley and Torvik 1983)

$$\frac{d^\alpha f(t)}{dt^\alpha} = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{f(\tau)}{(t-\tau)^\alpha} d\tau, \quad 0 < \alpha < 1 \quad (3.103)$$

3.3.3 Concept of Internal Variable

Consider the Maxwell model. The strains of the spring and the dashpot cannot be controlled separately. The mechanical work on the model is stored in the spring element. The mechanical work per unit volume done on the Maxwell material is given by

$$dW = \sigma d\gamma = \sigma d\gamma_e + \sigma d\gamma_v \quad (3.104)$$

Hence, we have

$$\frac{dW}{dt} = G_M \gamma_e \frac{d\gamma_e}{dt} + \eta_M \left(\frac{d\gamma_v}{dt} \right)^2 \quad (3.105)$$

Here, we used $\sigma = \sigma_e = \sigma_v$ and $\gamma = \gamma_e + \gamma_v$. When $U_e \equiv \frac{1}{2} G_M \gamma_e^2$, Eq. (3.105) becomes

$$\frac{dU_e}{dt} = G_M \gamma_e \frac{d\gamma_e}{dt}, \quad (3.106)$$

Then, for arbitrary interval of time, we have

$$W \equiv \int_{t_0}^t \frac{dW}{dt} dt' = U_e(\gamma_e(t)) - U_e(\gamma_e(t_0)) + \int_{t_0}^t \eta_M \left(\frac{d\gamma_v}{dt'} \right)^2 dt' \quad (3.107)$$

The last term in the right-hand side of Eq. (3.107) is always positive and an increasing function of time t if viscosity η_M is positive. Meanwhile, the first two terms in the right-hand side represent the difference of a scalar function of strain γ_e . Hence, it can be said that a part of mechanical work done on the Maxwell material is stored. The stored energy can be considered as the increase in the Helmholtz free energy of the material. Then, one may think that the thermodynamics of the Maxwell model cannot be described by the use of only strain and temperature.

It was known that irreversible thermodynamics of viscoelastic materials cannot be described completely by the use of only the state variables of equilibrium thermodynamics and their gradients. Additional state variables needed for viscoelastic materials are called *internal variables* (Coleman and Gurtin 1967; Maugin and Muschik 1994; Muschik 1990). The internal variables were motivated from the internal strain such as spring strain. The irreversible thermodynamics for viscoelasticity will be discussed in Sect. 4.

3.3.4 Generalization of Three-Dimensional Model

Linear mechanical behaviors of materials are observed when deformation is infinitesimal. Then, application of infinitesimal strain and the Boltzmann superposition principle allows us to write

$$\mathbf{T} = \int_{-\infty}^t \mathbf{C}(t - \tau) \frac{d\mathbf{E}}{d\tau} d\tau \quad (3.108)$$

where \mathbf{C} is a fourth-order tensor-valued function of time. If the material is isotropic, the fourth-order tensor, relaxation modulus can be written by

$$\mathbf{C}(t) = [\Lambda(t)\delta_{ik}\delta_{pq} + G(t)(\delta_{ip}\delta_{kq} + \delta_{iq}\delta_{kp})]\mathbf{e}_i\mathbf{e}_k\mathbf{e}_p\mathbf{e}_q \quad (3.109)$$

Since $\Lambda(t)$ the time-dependent version of λ in Eq. (3.3) and $G(t)$ corresponds to time-dependent shear modulus, we can define time-dependent bulk modulus and write

$$\mathbf{T} = \int_{-\infty}^t K(t-\tau) \frac{de_V}{d\tau} d\tau \mathbf{I} + 2 \int_{-\infty}^t G(t-\tau) \frac{d\mathbf{E}'}{d\tau} d\tau \quad (3.110)$$

This is the three-dimensional extension of Eq. (3.78). If we are interested in incompressible viscoelastic fluids, then Eq. (3.110) can be rewritten by

$$\mathbf{T} = -p\mathbf{I} + 2 \int_{-\infty}^t G(t-\tau) \mathbf{D}(\tau) d\tau \quad (3.111)$$

Note that when deformation is infinitesimal, the time derivative of infinitesimal strain is the deformation rate tensor and the deformation rate tensor of incompressible fluid is traceless.

3.3.5 Generalization of Nonlinear Viscoelasticity

One may figure nonlinear version of the Maxwell model such as

$$\lambda_M \frac{d\mathbf{T}'}{dt} + \mathbf{T}' = 2\eta_M \mathbf{D}; \quad (3.112)$$

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}' \quad (3.113)$$

Here, incompressible fluid is assumed. The one-dimensional strain rate is replaced by deformation rate tensor, and the ordinary time derivative is replaced by the material time derivative. Although this extension seems plausible, various problems arise. One of the most important problems is related to the time rate of stress. The use of the material time derivative gives rise to the ambiguity in physical meaning of stress rate. Besides, mechanical behavior of material must be independent of observer. These problems can be solved with the principle of material frame-indifference which will be discussed in Sect. 5.

Applying integration by parts, Eq. (3.78) can be rewritten by

$$\sigma(t) = \int_{-\infty}^t \mu(t - \tau) \dot{\gamma}(\tau) d\tau \quad (3.114)$$

where $\mu(t)$ is called the *memory function* defined as

$$\mu(t) = -\frac{dG}{dt} \geq 0 \quad (3.115)$$

Then, one may want to replace the one-dimensional strain by the finite strain, say $\mathbf{H}(t)$ for convenience:

$$\mathbf{T} = -p\mathbf{I} + \int_{-\infty}^t \mu(t - \tau) \mathbf{H}(\tau) d\tau \quad (3.116)$$

In this approach, we have to determine which strain measure is suitable. Furthermore, we have to investigate whether the principle of material frame-indifference is satisfied by Eq. (3.116).

There are two branches in the development of nonlinear viscoelastic constitutive equations: differential types based on Eq. (3.112) and integral types based on Eq. (3.116). These will be studied in Part III. When boundary value problem is considered, the differential-type constitutive equation is more convenient than the integral-type one in numerical implementation.

Problem 3

[1] From Eq. (3.3), derive

$$e_{ik} = \frac{1}{2G} \left(T_{ik} - \frac{\lambda}{3\lambda + 2G} T_{mm} \delta_{ik} \right) \quad (3.a)$$

[2] Derive Eq. (3.15)

[3] Show that

$$E = \frac{9KG}{3K + G}; \quad \nu = \frac{3K - 2G}{2(3K + G)} \quad (3.b)$$

[4] Consider a spherical shell whose outer and inner radii are R_{out} and R_{in} , respectively. The shell contains a fluid with pressure of p_{in} . The pressure of surroundings is p_{out} . Because of symmetry, it can be assumed that the displacement field is given by

$$\mathbf{u} = u(r)\mathbf{e}_r \quad (3.c)$$

where spherical coordinate system is used. Find displacement field and stress tensor.

- [5] Derive the constitutive equation of linear isotropic body, Eq. (3.11), from that of isotropic hyperelastic body, Eq. (3.36).
- [6] Derive Eq. (3.39) from Eq. (3.37) by the use of the Cayley–Hamilton theorem.
- [7] Derive Eq. (3.42).
- [8] Derive Eq. (3.50).
- [9] Derive Eq. (3.57).
- [10] It is known that

$$s\tilde{G}(s)\Big|_{s=i\omega} = G'(\omega) + iG''(\omega) \quad (3.d)$$

Derive storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ from Eq. (3.101) as for $\beta_1 = \beta_2 = 1$.

- [11] When $\mathbf{H}(\tau) = \mathbf{C}_t(\tau)$ and $\mu(t) = (G_0/\lambda)\exp(-t/\lambda)\Theta(t)$, show that stress of Eq. (3.116) satisfies

$$\mathbf{T}' + \lambda \left(\frac{d\mathbf{T}'}{dt} - \mathbf{L} \cdot \mathbf{T}' - \mathbf{T}' \cdot \mathbf{L}^T \right) = 2G_0\lambda\mathbf{D} \quad (3.e)$$

4 Thermodynamics

4.1 Equilibrium Thermodynamics

We shall not treat theories of equilibrium thermodynamics in detail because this book is not a text of thermodynamics. However, we shall review some features of equilibrium thermodynamics, which are necessary in the development of viscoelastic constitutive equations of polymers. The readers of this book are assumed familiar with the theory of equilibrium thermodynamics provided in sophomore courses such as physical chemistry in departments of chemistry and chemical engineering, thermodynamics in department of mechanical engineering, and thermal physics in department of physics.

4.1.1 Thermodynamic Space and Processes

Thermodynamics is a macroscopic science of energy transform. Energy transfer occurs in the form of work and heat. As shown in Sect. 2.3, internal energy can be considered as an invention for the purpose of energy conservation. Energy transfers to a system of materials give rise to the changes in two forms of energy: internal energy and kinetic energy as shown in Eq. (2.53).

Most forms of energy can be related to work. Originally, work is a line integration of force field over the path on which material particle moves. As a simplified example, differential work is given by $dW = \phi d\xi$ where ϕ is a force field and $d\xi$ is the differential of the coordinate that describes the path. Dividing the differential work by dt , we can have the equation of power: $dW/dt = \phi v$ where $v = d\xi/dt$. Then, we can find an analogy from stress power: $\mathbf{T} : \mathbf{D} = T_{ik}D_{ik}$ if we match stress to generalized force and deformation rate to generalized velocity. Then, component-wise form of differential work can be generalized by

$$dW = \sum_{k=1}^N \phi_k d\xi_k \quad (4.1)$$

After kinetic energy is canceled in energy balance equation, the following are left:

$$dU = \sum_{k=1}^N \phi_k d\xi_k + dQ \quad (4.2)$$

where dQ is the differential heat. Equation (4.2) implies that internal energy varies according to the variation of N generalized coordinates and heat. Hence, one may imagine that internal energy is determined by $N + 1$ independent variables.

It is a traditional notion in physics that physical phenomena can be described exactly by variables of finite number. The variables are called state variables. It is believed that a thermodynamic system can be fully identified by a set of state variables. If a system with a given set of values of state variables comes to have different set of values of state variables, then the system is said to experience a thermodynamic process. Then, we can imagine an analogy that a system is equivalent to a point which moves in the thermodynamic space whose coordinates are the state variables. A trajectory of the point (the system) is called *thermodynamic process* or simply process.

The first law of energy conservation gives us a clue that the number of state variables might be $N + 1$. Theory of equilibrium thermodynamics reads that if Eq. (4.2) holds, then only $N + 1$ *state variables* describe the thermodynamic phenomena in equilibrium uniquely. From Eq. (4.2), N generalized coordinates $\{\xi_k\}$ can be chosen as state variables. The other state variable, which is related to heat transfer, could be chosen from the second law of thermodynamics. For a while, we

accept the axiom such that in equilibrium, there are $N + 1$ state variables even though the $N + 1$ th state variables are not obviously known yet.

In thermodynamics, surroundings are the universe except the system. If we are interested in surroundings rather than the system, the surroundings can be considered as a system and then the system can be considered as surroundings. The distinction depends on our interest. The state of surrounding is called external condition.

If external condition maintains constant values, then the state variables of the system approach to certain constant values. Equilibrium state is the state represented by the constant values of state variables. Relaxation time is the characteristic time needed for the completion of the variation of state variables. If external conditions vary from one constant set of values to another constant set of values in a time, say external time, much longer than the relaxation time, then the changes in state variables look like immediate transition from one equilibrium to another equilibrium. If the difference between the two external conditions is infinitesimally small and if the external time is much longer than the relaxation time, then state variables change with maintaining equilibrium. The reverse of the process is believed to restore the states of both the system and its surroundings. Such process is called reversible process. It is expected that reversible process requires extremely slow progress. Hence, reversible process is considered as quasi-static process. Otherwise, a process is called irreversible process.

4.1.2 Existence of Entropy and Absolute Temperature

Consider only reversible processes from a given equilibrium state. Adiabatic process is a process without heat transfer. Then, Eq. (4.2) becomes

$$dU - \sum_{k=1}^N \phi_k d\xi_k = 0 \quad (4.3)$$

We can consider a thermodynamic space which is constructed by $\{\xi_k\}$ and U . Then, Eq. (4.3) represents a curve in the thermodynamic space. It is natural to adopt U as the $N + 1$ th coordinate. For a given state denoted by $\mathbf{x}_0 = (U^{(0)}, \xi_1^{(0)}, \dots, \xi_N^{(0)})$, there are infinitely many adiabatic curves passing the state \mathbf{x}_0 . Analogy of state variables to coordinates in thermodynamic space allows us to rewrite Eq. (4.3) as follows:

$$\mathbf{n} \cdot d\mathbf{x} = 0 \quad (4.4)$$

where

$$\mathbf{n} = (\eta, \eta\phi_1, \eta\phi_2, \dots, \eta\phi_N) \quad (4.5)$$

and

$$d\mathbf{x} = (dU, d\xi_1, d\xi_2, \dots, d\xi_N) \quad (4.6)$$

Note that η is a function of the state variables. We can imagine a surface element whose points satisfy Eq. (4.4). Then, the vector \mathbf{n} is perpendicular to the surface element. The surface element can be expressed by a function:

$$f(\mathbf{x}) = f(U, \xi_1, \xi_2, \dots, \xi_N) = \sigma \quad (4.7)$$

The variable σ can be determined by the substitution of \mathbf{x}_0 into Eq. (4.4). Adiabatic surface is the surface represented by Eq. (4.7). Consider the notions of coordinate system in Sect. 3. Then, two adjacent adiabatic surfaces must be parallel to each other because of the parallelism of coordinate. Note that all adiabatic curves passing \mathbf{x}_0 cannot meet any point on adjacent adiabatic surface. Then, we can take σ as a new thermodynamic coordinate whenever N coordinates are taken on adiabatic surface. Furthermore, we can take σ in order to satisfy

$$\left(\frac{\partial \sigma}{\partial U} \right)_{\{\xi_k\}} > 0 \quad (4.8)$$

Then, we can find a function such that

$$U = U(\sigma, \xi_1, \xi_2, \dots, \xi_N) \quad (4.9)$$

We define

$$\tau = \left(\frac{\partial U}{\partial \sigma} \right)_{\{\xi_k\}} > 0 \quad (4.10)$$

The inequality holds because of Eq. (4.8). Note that adiabatic process implies $d\sigma = 0$ because of the definition of σ . Then, the total differential of internal energy is given by

$$dU = \sum_{k=1}^N \phi_k d\xi_k + \tau d\sigma \quad (4.11)$$

Comparison of Eq. (4.11) with Eq. (4.2) gives

$$dQ = \tau d\sigma \quad (4.12)$$

It must be noted that Eq. (4.12) holds whenever the process is reversible because Eq. (4.12) was derived from the assumption that only reversible processes are considered. Now, it is the time to find the physical meanings of σ and τ .

Consider a system which is the union of two subsystems 1 and 2. As for the two subsystems, we can define τ_k and σ_k with $k = 1$ and 2 . Then, we can also define $\phi_k^{(1)}$ and $\xi_k^{(1)}$ for the subsystem 1 and $\phi_k^{(2)}$ and $\xi_k^{(2)}$ for the subsystem 2. The differential heat must satisfy

$$dQ = dQ_1 + dQ_2 \quad (4.13)$$

where dQ_1 and dQ_2 are the differential heats given to subsystems 1 and 2, respectively. Then, the definitions of σ and τ give

$$dQ = \tau d\sigma = \tau_1 d\sigma_1 + \tau_2 d\sigma_2 \quad (4.14)$$

This differential equation means

$$\sigma = \sigma(\sigma_1, \sigma_2) \quad (4.15)$$

Note that σ_1 depends on $\{\xi_k^{(1)}\}$ but is independent of $\{\xi_k^{(2)}\}$. Similarly, σ_2 depends on $\{\xi_k^{(2)}\}$ but is independent of $\{\xi_k^{(1)}\}$. Equation (4.14) gives

$$\left(\frac{\partial \sigma}{\partial \sigma_1} \right)_{\sigma_2} = \frac{\tau_1}{\tau} = f_1(\sigma_1, \sigma_2); \quad \left(\frac{\partial \sigma}{\partial \sigma_1} \right)_{\sigma_2} = \frac{\tau_1}{\tau} = f_1(\sigma_1, \sigma_2) \quad (4.16)$$

Then, we have

$$\tau = \frac{\tau_1}{f_1(\sigma_1, \sigma_2)} = \frac{\tau_2}{f_2(\sigma_1, \sigma_2)} \quad (4.17)$$

We have empirical temperature scale such as Celsius or Fahrenheit scales. Since σ is related to heat, it is reasonable that σ , σ_1 , and σ_2 depend on empirical temperature T' . Then, we can rewrite Eq. (4.15) as follows:

$$\sigma = \sigma\left(T', \left\{ \xi_k^{(1)} \right\}, \left\{ \xi_k^{(2)} \right\}\right) \quad (4.18)$$

When the two subsystems are in thermal equilibrium, we can write

$$\tau_1 = \tau_1(T', \sigma_1); \quad \tau_2 = \tau_2(T', \sigma_2) \quad (4.19)$$

It is assumed that the functional relations of the subsystems must hold for the total system. Then, we have

$$\tau = \tau(T', \sigma_1, \sigma_2) = \tau(T', \sigma(\sigma_1, \sigma_2)) \quad (4.20)$$

Then, Eq. (4.16) gives

$$f_1(\sigma_1 \sigma_2) = \frac{\tau_1(T', \sigma_1)}{\tau(T', \sigma)}; \quad f_2(\sigma_1 \sigma_2) = \frac{\tau_2(T', \sigma_1)}{\tau(T', \sigma)} \quad (4.21)$$

It is possible to eliminate T' dependence whenever there exists a function of the empirical temperature $T(T')$ such that

$$\tau_1 = T(T')\psi_1(\sigma_1); \quad \tau_2 = T(T')\psi_2(\sigma_2); \quad \tau = T(T')\psi(\sigma) \quad (4.22)$$

Consider a monotonically increasing function of σ , say $\psi(\sigma)$. Then, we can invent

$$S = \psi(\sigma); \quad T = \frac{d\sigma}{dS} \tau \quad (4.23)$$

Then, it is clear that

$$dQ = \tau d\sigma = T dS \quad (4.24)$$

From Eq. (4.10), we know that τ , τ_1 , and τ_2 are positive. Hence, we can assume that $\psi(\sigma) > 0$, $\psi_1(\sigma_1) > 0$, and $\psi_2(\sigma_2) > 0$. Then, we have

$$\tau_1 d\sigma_1 = T(T') dS_1; \quad \tau_2 d\sigma_2 = T(T') dS_2; \quad \tau d\sigma = T(T') dS \quad (4.25)$$

where

$$\frac{dS_1}{d\sigma_1} = \psi_1(\sigma_1); \quad \frac{dS_2}{d\sigma_2} = \psi_2(\sigma_2); \quad \frac{dS}{d\sigma} = \psi(\sigma) \quad (4.26)$$

Application of Eq. (4.25) to Eq. (4.14) gives

$$dS = dS_1 + dS_2 \quad (4.27)$$

If we scale T to make correspondence to ideal gas temperature, then T becomes the absolute temperature and S can be defined as entropy. However, Eq. (4.27) does not imply

$$S = S_1 + S_2 \quad (4.28)$$

If any system has the same entropy at $T = 0$, which is the third law of equilibrium thermodynamics, then Eq. (4.28) holds. Equation (4.28) implies that entropy is an

extensive quantity. Extensive quantity satisfies the definition of the homogenous function of the first order:

$$S(\lambda U, \lambda \xi_1, \lambda \xi_2, \dots, \lambda \xi_N) = \lambda S(U, \xi_1, \xi_2, \dots, \xi_N) \quad (4.29)$$

for any positive real number λ .

The second law is an empirical law. We have derived S and T from the analogy of state variables to coordinates. The parallelism of coordinates implies that near a given state, there must be infinitely many states which cannot be connected to the given state through any adiabatic curve. This is called *inaccessible statement of Caratheodory*. The approach introduced above was developed by C. Caratheodory (Ma 1985). Although the way of Caratheodory shows the existence of entropy in a generalized manner, it is far from the empirical notion, the maximization of entropy.

4.1.3 Clausius Inequality

Originally, the Clausius inequality was derived from the Carnot engine. Refer (Huang 1963) for the detail of the inequality. The inequality states that

$$\oint_C \frac{dQ}{T} \leq 0 \quad (4.30)$$

where the integral symbol represents a cycling process irrespective of reversibility. This is called the *Clausius inequality*. In Huang (1963), any cyclic process is assumed to be decomposed to tiny cyclic processes consisting of isothermal and adiabatic processes in thermodynamic space. Then, it is questionable what the absolute temperature T is in an irreversible process. From the original derivation of Clausius, the temperature T must be the one of the heat reservoirs. A number of theoretical problems are involved in the inequality. Hence, Callen took the following axioms on entropy (Callen 1985):

[1] Entropy is a concave function of state variables

$$S = S(U, \xi_1, \xi_2, \dots, \xi_N) \quad (4.31)$$

[2] Partial derivative of entropy with respect to internal energy is positive

$$\left(\frac{\partial S}{\partial U} \right)_{\{\xi_k\}} > 0 \quad (4.32)$$

[3] Entropy is a positively homogeneous function of degree 1 as shown in Eq. (4.29).

Concave function implies that for any two states \mathbf{x}_1 and \mathbf{x}_2 ,

$$S(t\mathbf{x}_1 + (1-t)\mathbf{x}_2) \geq tS(\mathbf{x}_1) + (1-t)S(\mathbf{x}_2) \quad (4.33)$$

where t is any real number in the interval of $0 \leq t \leq 1$. Then, it can be proved that the internal energy U is a positively homogeneous function of degree 1 and ϕ_k and T are positively homogeneous functions of degree 0. Equivalently, temperature and generalized forces are intensive properties. Concavity of entropy results in convexity of internal energy, too.

4.1.4 Thermodynamic Potentials

Although equilibrium thermodynamics started from imperfect foundation, axiomatic unification of equilibrium thermodynamics agrees well with experimental results. Any counter example has not been found. This makes beginners feel much difficulty in understanding thermodynamics. Hence, we adopt the result of the Clausius inequality:

$$dS \geq \frac{dQ}{T} \quad (4.34)$$

Equation (4.2) illustrates that $T^{-1}dQ = T^{-1}(dU - dW)$. Then, Eqs. (4.2) and (4.34) give the following inequalities:

$$dS \geq \frac{dU}{T} - \sum_{k=1}^N \frac{\phi_k}{T} d\xi_k; \quad (4.35a)$$

$$dU \leq TdS + \sum_{k=1}^N \phi_k d\xi_k; \quad (4.35b)$$

$$dH \equiv d\left(U - \sum_{k=1}^N \phi_k \xi_k\right) \leq TdS - \sum_{k=1}^N \xi_k d\phi_k; \quad (4.35c)$$

$$dF \equiv d(U - TS) \leq -SdT + \sum_{k=1}^N \phi_k d\xi_k; \quad (4.35d)$$

$$dG \equiv d(H - TS) \leq -SdT - \sum_{k=1}^N \xi_k d\phi_k \quad (4.35e)$$

Here, H is the *enthalpy*, F is the *Helmholtz free energy*, and G is the *Gibbs free energy*. The equalities of Eqs. (4.35a) hold whenever the process is reversible.

Equations (4.35a) illustrate that the Helmholtz free energy is a state function of system temperature and mechanical coordinates $\{\xi_k\}$, while the internal energy is a state function of entropy and mechanical coordinates. This is the result from *Legendre transform* (McQuarrie 2000).

Furthermore, spontaneous process occurs in the direction to the decrease of system's Helmholtz energy under the constraint of fixed temperature and mechanical coordinates. Similar analysis can be done for the internal energy, the enthalpy, and the Gibbs free energy. Hence, U , H , F , and G can play the role of entropy, the indicator of spontaneous process under the corresponding constraints.

These thermodynamic functions are called thermodynamic potential because important thermodynamic properties are obtained from the partial derivatives of them as shown in Eq. (4.35a). Entropy can be obtained from the partial derivatives of free energies:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\{\xi_k\}} = -\left(\frac{\partial G}{\partial T}\right)_{\{\phi_k\}} \quad (4.36)$$

Here, it must be noted that the two partial differentiations with respect to temperature are different because different state variables are fixed in the partial derivatives: F for mechanical coordinate and G for generalized forces.

4.2 Classical Irreversible Thermodynamics

4.2.1 Basic Assumptions

Classical irreversible thermodynamics (CIT) is based on local equilibrium hypothesis, which means every material particles can be considered as a tiny system in equilibrium (De Groot 1984). This does not mean the equilibrium of the whole system. Although all material particles are in equilibrium, each material particle may have different states. Each equilibrium state is assumed to be fully described by state variables such as strain and internal energy. For isotropic fluids, thermodynamic space consists of specific volume (volume per unit mass) and internal energy. Therefore, classical irreversible thermodynamics is founded on the same thermodynamic space of equilibrium thermodynamics.

It was known that classical irreversible thermodynamics is successful in describing the mechanical phenomena involving classical constitutive equations such as the Fourier conduction law, viscous fluids, and elastic solids. Since stress of viscous fluid is independent of current strain except volume change, the thermodynamic state of viscous fluids can be identified by internal energy and specific volume.

The specific volume can be replaced by density because $\bar{v} = \rho^{-1}$. Then, each material particle is assumed to have entropy field such that

$$s = \tilde{s}(\tilde{\mathbf{x}}, t) = s(u, \rho) \quad (\text{for fluid}) \quad (4.37)$$

and

$$s = s(u, \mathbf{B}) \quad (\text{for solid}) \quad (4.38)$$

Note that deformation gradient \mathbf{F} contains both pure deformation and rigid body motion of rotation, while $\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T$ or $\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F}$ represents only pure deformation. Hence, it is reasonable that \mathbf{B} (or \mathbf{C}) is more appropriate than \mathbf{F} as a thermodynamic state variable. Fundamentally, the use of \mathbf{B} (or \mathbf{C}) is supported by the principle of material frame-indifference, which will be discussed in Sect. 5.

We start from fluid. The local equilibrium hypothesis gives

$$ds = \frac{\partial s}{\partial u} du + \frac{\partial s}{\partial \rho} d\rho \quad (4.39)$$

Note that since thermodynamic space is given by (u, ρ) , we do not use the notation of Eq. (4.36) for convenience if there is no confusion. The total differentials in Eq. (4.39) are assumed to be replaced by material time derivative. Hence, Eq. (4.39) can be rewritten by

$$\frac{ds}{dt} = \frac{\partial s}{\partial u} \frac{du}{dt} + \frac{\partial s}{\partial \rho} \frac{d\rho}{dt} \quad (4.40)$$

From the equilibrium thermodynamics, we know that

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V} \right)_U = \frac{p}{T} \quad (4.41)$$

Then, local equilibrium hypothesis leads to the use of

$$\frac{\partial s}{\partial u} = \frac{1}{T}; \quad \frac{\partial s}{\partial \rho} = \frac{p}{\rho^2 T} \quad (4.42)$$

Since both internal energy per unit mass u and mass density ρ are fields, the use of Eqs. (2.5) and (2.53) gives

$$\rho \frac{ds}{dt} = (-\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D}) \frac{1}{T} - (\nabla \cdot \mathbf{v}) \frac{p}{T} \quad (4.43)$$

where Eq. (4.42) was used. The main purpose of the local equilibrium hypothesis is to derive an inequality in terms of field variables, which represents the second law. The inequality is called the Clausius–Duhem inequality.

As for solid, we can take thermodynamic space as the pair of internal energy and deformation gradient. Then, similar procedure leads to

$$\rho \frac{ds}{dt} = (-\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D}) \frac{1}{T} + \rho \frac{\partial s}{\partial \mathbf{B}} : \frac{d\mathbf{B}}{dt} \quad (4.44)$$

4.2.2 Entropy Balance Equation

In order to rewrite the Clausius inequality in terms of field variables, we define entropy production S_{irr} such that

$$dS = \frac{dQ}{T} + dS_{\text{irr}} \quad (4.45)$$

Compared with the Clausius inequality Eq. (4.34), it is clear that for any thermodynamic process,

$$dS_{\text{irr}} \geq 0 \quad (4.46)$$

The equality holds if and only if the thermodynamic process is reversible.

We consider an arbitrary region Ω of a continuum, and the entropy of the region is assumed to be calculated by

$$S = \iiint_{\Omega} \rho s \, dV \quad (4.47)$$

Similarly, we define *entropy production* per unit mass as

$$S_{\text{irr}} = \iiint_{\Omega} \rho s_{\text{irr}} \, dV \quad (4.48)$$

Then, the differential heat term in Eq. (4.45) can be generalized as follows:

$$\frac{dS}{dt} = \frac{dS_{\text{irr}}}{dt} - \iint_{\partial\Omega} \frac{1}{T} \mathbf{q} \cdot d\mathbf{a} + \iiint_{\Omega} \frac{\rho r}{T} \, dV \quad (4.49)$$

Differential form of Eq. (4.49) is obtained by the substitution of Eqs. (4.47) and (4.48) into Eq. (4.49) and application of the Reynolds transport theorem:

$$\rho \frac{ds}{dt} = -\nabla \cdot \left(\frac{\mathbf{q}}{T} \right) + \frac{\rho r}{T} + \rho \frac{ds_{\text{irr}}}{dt} \quad (4.50)$$

Note that the first two terms in the right-hand side of Eq. (4.50) correspond to dQ/T of Eq. (4.34), which can be interpreted as the entropy transfer by heat transfer. On the other hand, the last term is the entropy production because it was introduced to make the Clausius inequality be the entropy balance equation. In order to emphasize this correspondence, we introduce the notation such that

$$\nabla \cdot \mathbf{j}_s = \nabla \cdot \left(\frac{\mathbf{q}}{T} \right) - \frac{\rho r}{T} \quad (4.51)$$

Here, \mathbf{j}_s is defined as the entropy flux which consists of two fluxes such that

$$\mathbf{j}_s = \frac{\mathbf{q}}{T} + \mathbf{j}_{\text{rad}} \quad (4.52)$$

where

$$\nabla \cdot \mathbf{j}_{\text{rad}} = -\frac{\rho r}{T} \quad (4.53)$$

Although the vector field \mathbf{j}_{rad} may not be determined uniquely from the given density, temperature, and r , it must not give rise to any significant problem because we will always use \mathbf{j}_{rad} only through its divergence.

With the help of Eq. (4.50), the Clausius inequality in Eq. (4.46) can be rewritten by

$$\rho \frac{ds_{\text{irr}}}{dt} = \rho \frac{ds}{dt} + \nabla \cdot \mathbf{j}_s \geq 0 \quad (4.54)$$

Equation (4.54) is called the *Clausius–Duhem inequality*. Since the entropy production is the source term from the flux formalism of balance equation, the second law is the positiveness of entropy source.

4.2.3 Application of Entropy Balance

If Eq. (4.43) is substituted to Eq. (4.54), then this inequality can be written in terms of measurable field variables

$$\rho \frac{ds_{\text{irr}}}{dt} = \frac{1}{T} (\mathbf{T} : \mathbf{D} - \nabla \cdot \mathbf{q} + \rho r) - (\nabla \cdot \mathbf{v}) \frac{p}{T} + \nabla \cdot \mathbf{j}_s \geq 0 \quad (4.55)$$

Stress can be decomposed into isotropic and deviatoric parts as follows:

$$\mathbf{T} = \mathbf{T}' + \frac{\text{tr}(\mathbf{T})}{3} \mathbf{I} \quad (4.56)$$

Note that $\text{tr}(\mathbf{T}') = 0$. Then, we know that

$$\mathbf{T} : \mathbf{D} = \mathbf{T}' : \mathbf{D} + \frac{1}{3} \text{tr}(\mathbf{T}) \text{tr}(\mathbf{D}) \quad (4.57)$$

Since $\text{tr}(\mathbf{D}) = \nabla \cdot \mathbf{v}$, application of Eq. (4.57) to Eq. (4.55) gives the Clausius inequality such that

$$\rho T \frac{ds_{\text{irr}}}{dt} = \mathbf{T}' : \mathbf{D}' + (\nabla \cdot \mathbf{v}) \left[\frac{\text{tr}(\mathbf{T})}{3} + p \right] - \frac{\mathbf{q} \cdot \nabla T}{T} \geq 0 \quad (4.58)$$

Note that the following identity is used in Eq. (4.58):

$$\mathbf{T}' : \mathbf{D} = \mathbf{T}' : \left[\mathbf{D}' + \frac{1}{3} \text{tr}(\mathbf{D}) \mathbf{I} \right] = \mathbf{T}' : \mathbf{D}' \quad (4.59)$$

Since ∇T , \mathbf{D}' , and $\text{tr}(\mathbf{D}) = \nabla \cdot \mathbf{v}$ can be given independently, it is obvious that

$$\mathbf{T}' : \mathbf{D}' \geq 0 \quad (4.60)$$

$$(\nabla \cdot \mathbf{v}) \left[\frac{\text{tr}(\mathbf{T})}{3} + p \right] \geq 0 \quad (4.61)$$

and

$$-\frac{\mathbf{q} \cdot \nabla T}{T} \geq 0 \quad (4.62)$$

The constitutive equation of Newtonian fluid is given by Eq. (3.43). Application of Eq. (3.43) to Eqs. (4.60) and (4.61) results in thermodynamic constraints on the phenomenological constitutive equation:

$$\eta_s > 0; \eta_b > -\frac{2}{3} \eta_s \quad (4.63)$$

Assuming that heat conduction follows the Fourier law Eq. (2.40), Eq. (4.62) gives

$$\kappa > 0 \quad (4.64)$$

These results illustrate that the constitutive equations of Newtonian fluid and Fourier conduction law agree with the second law if the material constants satisfy Eqs. (4.63) and (4.64).

Now, turn to the case of solid. Substitution of Eq. (4.44) into Eq. (4.51) yields

$$\rho T \frac{ds_{\text{irr}}}{dt} = -\frac{\mathbf{q} \cdot \nabla T}{T} + \left(\mathbf{T} + 2T\mathbf{B} \cdot \rho \frac{\partial s}{\partial \mathbf{B}} \right) : \mathbf{D} \quad (4.65)$$

Here, the following identity was used:

$$\frac{d\mathbf{B}}{dt} = \mathbf{L} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{L}^T \quad (4.66)$$

Since \mathbf{D} and ∇T can be given independently, Eq. (4.65) implies that

$$\mathbf{T} = -2T\mathbf{B} \cdot \rho \frac{\partial s}{\partial \mathbf{B}} \quad (4.67)$$

and Eq. (4.62). Equation (4.67) implies that if entropy as a function of u and \mathbf{B} is known, then the Cauchy stress can be obtained by the gradient of entropy with respect to \mathbf{B} .

It is noteworthy that $\partial s / \partial \mathbf{B}$ of Eq. (4.67) is made of partial derivatives at fixed internal energy. Experiment at a fixed internal energy is extremely difficult to be implemented, whereas experiment at constant temperature is practical.

4.2.4 The Clausius–Duhem Inequality in Terms of Free Energy

As shown in Eq. (4.35a), the Clausius inequality can be rewritten in terms of Helmholtz free energy. We define

$$F = \iiint_{\Omega} \rho f \, dV \quad (4.68)$$

and

$$f = u - Ts \quad (4.69)$$

Then, it is not difficult to show that f is a function of temperature and mass density for fluids. Similarly, as for solid, f is a function of temperature and deformation gradient. Hence, we have

$$f = \begin{cases} f(T, \rho) & \text{for fluid} \\ f(T, \mathbf{B}) & \text{for solid} \end{cases} \quad (4.70)$$

and the Clausius inequality is given by

$$\rho T \frac{ds_{\text{irr}}}{dt} = -\frac{\mathbf{q} \cdot \nabla T}{T} + \mathbf{T}' : \mathbf{D}' + (\nabla \cdot \mathbf{v}) \left[p + \frac{\text{tr}(\mathbf{T})}{3} \right] \geq 0; \quad (4.71)$$

$$\rho T \frac{ds_{\text{irr}}}{dt} = \left(\mathbf{T} - 2\mathbf{B} \cdot \rho \frac{\partial f}{\partial \mathbf{B}} \right) : \mathbf{D} - \frac{\mathbf{q} \cdot \nabla T}{T} \geq 0 \quad (4.72)$$

Note that Eq. (4.71) is identical to Eq. (4.58). Because of the independence of \mathbf{D} and $\nabla \theta$, Eq. (4.72) is split into two inequalities and we have

$$\mathbf{T} = 2\mathbf{B} \cdot \rho \frac{\partial f}{\partial \mathbf{B}} \quad (4.73)$$

Note that $\partial f / \partial \mathbf{B}$ is made of the partial derivatives at constant temperature, while $\partial s / \partial \mathbf{B}$ of Eq. (4.67) consists of those at constant internal energy. Therefore, we have

$$\left(\frac{\partial f}{\partial \mathbf{B}} \right)_T = -T \left(\frac{\partial s}{\partial \mathbf{B}} \right)_u \quad (4.74)$$

It is worthy to compare Eq. (4.73) with the constitutive equation of hyperelasticity, as in Eq. (3.36). The strain energy function $\Phi(\mathbf{B}, T)$ is easily identified by $\rho f(\mathbf{B}, T)$ for incompressible elastic materials. As for compressible elastic body, the determination of free energy from strain energy function needs some carefulness. It is reasonable to assume that mass density of homogeneous material is constant at the reference configuration. Then, we have

$$\frac{\partial \rho f}{\partial \mathbf{B}} = \sqrt{\det(\mathbf{B})} \frac{\partial \Phi}{\partial \mathbf{B}} \quad (4.75)$$

where Eq. (2.a) and $\det(\mathbf{F}) = \sqrt{\det(\mathbf{B})}$ were used. Then, Eq. (4.75) provides free energy from an experimentally determined strain free energy.

4.3 Theory of Internal Variables

4.3.1 General Theory

When thermodynamic state space is identical to that of equilibrium thermodynamics, it is difficult to describe the irreversible thermodynamics of viscoelastic material. Although the *rational thermodynamics* is constructed to describe

viscoelasticity by introducing the principle of fading memory, it is known that the rational thermodynamics suffers from a few problems (Jou 1996). In order to overcome the demerits of the rational thermodynamics, it is necessary to extend the thermodynamic space of state variables. *Extended irreversible thermodynamics* is to adopt the thermodynamic space as the union of the equilibrium thermodynamic space and fluxes. However, this extended thermodynamic space is not convenient in the development of viscoelastic constitutive equations. The other extended thermodynamic space can be constructed by introducing *internal variables*.

Consider linear viscoelastic models made of spring and dashpot. As an example, consider the Maxwell model. The total strain is the sum of strains of spring and dashpot. It can be said that both strains of spring and dashpot are internal strain or internal variables. In the principle of the model, if a spring strain is given, then dashpot strain is determined by the difference between the total strain and the spring strain and vice versa. However, it is not possible to determine both internal strains independently by any experiment. Furthermore, it is impossible to control the internal variables, while the total strain is both measurable and controllable. As for further information of internal variable, refer to Coleman and Gurtin (1967), Valanis (1971), and Maugin (1999).

Here, we consider a generalization of internal variables more than the internal strains of spring–dashpot models. According to Maugin (1999), internal variables may be measureable but cannot be controlled. This means that we cannot design any experiment to make the internal variables have desired values at will. Thermodynamic theory of internal variables provides a way to restrict the forms of the evolution equations (or kinetic equations) of internal variables as well as any needed constitutive equations. Basic assumptions of the thermodynamics of internal variables are listed below:

- [1] Thermodynamic space consists of the state variables of equilibrium thermodynamics and the internal variables of finite number.
- [2] Each internal variable has its own evolution equation.
- [3] Thermodynamic potentials such as free energies are function of state variables mentioned in [1].
- [4] Internal variables are measurable but not controllable.

For simplicity, consider the case that internal variable is a second-order tensor \mathbf{X} . Then, the thermodynamic space is given by $(u, \mathbf{B}, \mathbf{X}, \nabla T)$ for solid. According to Coleman and Gurtin (1967), it is not necessary to use local equilibrium hypothesis in the identification of

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u} \right)_{\mathbf{B}, \mathbf{X}, \nabla T} \quad (4.76)$$

However, the use of the local equilibrium hypothesis does not give rise to significant difference. The use of $(T, \mathbf{B}, \mathbf{X}, \nabla T)$ is more convenient than that of $(u, \mathbf{B}, \mathbf{X}, \nabla T)$. Then, principle of equipresence (Jou 1996; Truesdell 2004) gives

$$f = f(T, \mathbf{B}, \mathbf{X}, \nabla T); \quad (4.77)$$

$$s = s(T, \mathbf{B}, \mathbf{X}, \nabla T); \quad (4.78)$$

$$\mathbf{T} = \mathbf{T}(T, \mathbf{B}, \mathbf{X}, \nabla T); \quad (4.79)$$

$$\mathbf{q} = \mathbf{q}(T, \mathbf{B}, \mathbf{X}, \nabla T); \quad (4.80)$$

$$\frac{d\mathbf{X}}{dt} = \mathbf{G}(T, \mathbf{B}, \mathbf{X}, \nabla T); \quad (4.81)$$

Then, the material time derivative of free energy is given by

$$\frac{df}{dt} = \frac{du}{dt} - s \frac{dT}{dt} - T \frac{ds}{dt} = \frac{\partial f}{\partial T} \frac{dT}{dt} + \frac{\partial f}{\partial \mathbf{B}} : \frac{d\mathbf{B}}{dt} + \frac{\partial f}{\partial \mathbf{X}} : \frac{d\mathbf{X}}{dt} \quad (4.82)$$

With the help of Eq. (2.53), we have

$$\rho T \frac{ds_{\text{irr}}}{dt} = - \frac{\mathbf{q} \cdot \nabla T}{T} + \mathbf{T} : \mathbf{D} - \rho \left(\frac{df}{dt} \right)_T \geq 0 \quad (4.83)$$

where

$$\rho \left(\frac{df}{dt} \right)_T = \left(2\rho \mathbf{B} \cdot \frac{\partial f}{\partial \mathbf{B}} \right) : \mathbf{D} + \rho \frac{\partial f}{\partial \mathbf{X}} : \mathbf{G} \quad (4.84)$$

Smart mathematical trick of Coleman and Gurtin (1967) gives

$$\mathbf{T} = 2\rho \mathbf{B} \cdot \frac{\partial f}{\partial \mathbf{B}}, \quad (4.85)$$

$$s = - \frac{\partial f}{\partial T}, \quad (4.86)$$

$$\frac{\partial f}{\partial \nabla T} = \mathbf{0}, \quad (4.87)$$

and

$$\rho \frac{\partial f}{\partial \mathbf{X}} : \mathbf{G} + \frac{\mathbf{q} \cdot \nabla T}{T} \leq 0 \quad (4.88)$$

From Eq. (4.87), it is obvious that free energy, entropy, and stress are independent of temperature gradient (Coleman and Gurtin 1967). Then, constitutive theory is to specify the structures of functions such as $f(T, \mathbf{B}, \mathbf{X})$, $\mathbf{G}(T, \mathbf{B}, \mathbf{X}, \nabla T)$, and $\mathbf{q}(T, \mathbf{B}, \mathbf{X}, \nabla T)$. Equations (4.83) and (4.86) play the role of constraints of the functions.

4.3.2 Application to One-Dimensional Model

Consider the Maxwell model. This intuitive model implicitly says that $G_M > 0$ and $\eta_M > 0$. We shall show that these inequalities hold because of the second law. It is natural that free energy is related to energy storage. Then, one may think of free energy as a function of elastic strain such that

$$f = \frac{G_M}{2} \gamma_e^2 + f_o(T) = \frac{G_M}{2} (\gamma - \gamma_v)^2 + f_o(T) \quad (4.89)$$

where G_M is considered as a function of temperature. There are two cases of thermodynamic space: (T, γ, γ_e) and (T, γ, γ_v) .

As for isothermal deformation, we know that $\nabla T = \mathbf{0}$. Then, the second law of Eq. (4.83) becomes

$$\sigma \frac{d\gamma}{dt} - G_M \gamma_e \frac{d\gamma_e}{dt} \geq 0 \quad (4.90)$$

or

$$\sigma \frac{d\gamma}{dt} - G_M (\gamma - \gamma_v) \left(\frac{d\gamma}{dt} - \frac{d\gamma_v}{dt} \right) \geq 0 \quad (4.91)$$

One may suggest one of the simplest evolution equations of internal variable as

$$\frac{d\gamma_v}{dt} = \frac{\gamma_e}{\lambda_M} = \frac{\gamma - \gamma_v}{\lambda_M} \quad (4.92)$$

Equation (4.92) is identical to

$$\frac{d\gamma_e}{dt} = \frac{d\gamma}{dt} - \frac{\gamma_e}{\lambda_M} \quad (4.93)$$

because $\gamma_e = \gamma - \gamma_v$.

Substitution of Eq. (4.93) into Eq. (4.90) gives

$$(\sigma - G_M \gamma_e) \frac{d\gamma}{dt} + \frac{G_M}{\lambda} \gamma_e^2 \geq 0 \quad (4.94)$$

Since $d\gamma/dt$ and γ_e can be given independently, it can be concluded that

$$\sigma = G_M \gamma_e \quad (4.95)$$

and

$$\frac{G_M}{\lambda_M} > 0 \quad (4.96)$$

The same results are obtained by the substitution of Eq. (4.92) into Eq. (4.91).

One-dimensional version of Eq. (4.88) is given by

$$G_M(\gamma - \gamma_v) \frac{d\gamma_v}{dt} \leq 0 \quad (4.97)$$

Substitution of Eq. (4.92) into Eq. (4.97) gives

$$-\frac{G_M}{\lambda_M}(\gamma - \gamma_v)^2 \leq 0 \quad (4.98)$$

Then, we obtain Eq. (4.96) again.

4.3.3 Temperature Equation

Energy balance equation, Eq. (2.53), is not convenient to predict temperature field because it does not contain time derivative of temperature. From equilibrium thermodynamics, we know that specific heat capacity at constant volume is given by

$$c_v = -T \frac{\partial^2 f}{\partial T^2} \quad (4.99)$$

We can consider entropy as a function of temperature, strain, and internal variables: $s = s(T, \mathbf{B}, \mathbf{X})$. Then, we have

$$\begin{aligned} \frac{ds}{dt} &= \frac{c_v}{T} \frac{dT}{dt} + \left(\frac{\partial s}{\partial \mathbf{B}} \right)_{T, \mathbf{X}} : \frac{d\mathbf{B}}{dt} + \left(\frac{\partial s}{\partial \mathbf{X}} \right)_{T, \mathbf{B}} : \frac{d\mathbf{X}}{dt} \\ &= \frac{c_v}{T} \frac{dT}{dt} - \left[\frac{\partial}{\partial \mathbf{B}} \left(\frac{\partial f}{\partial T} \right)_{\mathbf{B}, \mathbf{X}} \right]_{T, \mathbf{X}} : \frac{d\mathbf{B}}{dt} - \left[\frac{\partial}{\partial \mathbf{X}} \left(\frac{\partial f}{\partial T} \right)_{\mathbf{B}, \mathbf{X}} \right]_{T\mathbf{B}} : \frac{d\mathbf{X}}{dt} \end{aligned} \quad (4.100)$$

Here, Eqs. (4.86) and (4.97) were used. The last two terms of Eq. (4.98) can be rewritten by

$$\left[\frac{\partial}{\partial T} \left(\frac{df}{dt} \right)_T \right]_{\mathbf{B}, \mathbf{X}} = \left[\frac{\partial}{\partial \mathbf{B}} \left(\frac{\partial f}{\partial T} \right)_{\mathbf{B}, \mathbf{X}} \right]_{T, \mathbf{X}} : \frac{d\mathbf{B}}{dt} + \left[\frac{\partial}{\partial \mathbf{X}} \left(\frac{\partial f}{\partial T} \right)_{\mathbf{B}, \mathbf{X}} \right]_{T\mathbf{B}} : \frac{d\mathbf{X}}{dt} \quad (4.101)$$

Then, we can write simply

$$\frac{ds}{dt} = \frac{c_v}{T} \frac{dT}{dt} - \frac{\partial}{\partial T} \left(\frac{df}{dt} \right)_T \quad (4.102)$$

With the help of Eqs. (4.51), (4.53), and (4.83), Eq. (4.102) can be rewritten by

$$\rho c_v \frac{dT}{dt} = -\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} + \rho T^2 \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\frac{df}{dt} \right)_T \right] \quad (4.103)$$

If f is known as a function of state variables and if the evolution equations of both \mathbf{B} and internal variable \mathbf{X} , then Eq. (4.103) allows us to calculate temperature field.

The first and second terms in the right-hand side of Eq. (4.103) represent heat transfer, and the third term indicates stress power. It can be shown that the last term is the rate of internal energy at constant temperature (see Problem [1]). Hence, Eq. (4.103) becomes

$$\rho c_v \frac{dT}{dt} = -\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} - \rho \left(\frac{du}{dt} \right)_T \quad (4.104)$$

The stress power can be interpreted as the effect of mechanical work on deformation of material. The last term of Eq. (4.104) can be interpreted as the rate of energy storage in the material. Hence, the last two terms imply that temperature is altered by the part of mechanical work, which is obtained by excluding the kinetic energy and energy storage in the material from the total mechanical work.

Problem 4

- [1] In equilibrium thermodynamics, the following equation is known as the Gibbs–Helmholtz equation:

$$U = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_v; \quad (4.a)$$

$$H = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_p \quad (4.b)$$

Derive Eqs. (4.a) and (4.b).

- [2] The van der Waals equation is an empirical equation of state such that

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (4.c)$$

where R is the gas constant, \bar{V} is the molar volume, and a and b are material parameters. Derive the Helmholtz free energy from Eq. (4.c). Note that the Helmholtz free energy of ideal gas can be derived by $p\bar{V} = RT$ as follows:

$$F^{IG}(\bar{V}, T, n) = -nRT \log(T^{3/2}\bar{V}) + nc^{IG}T \quad (4.d)$$

where n is the mole number of molecules and c^{IG} is the integration constant. Eq. (4.d) was derived by the integration of

$$p = -\left(\frac{\partial F^{IG}}{\partial \bar{V}}\right)_{T,n} \quad (4.e)$$

[3] Derive Eqs. (4.58) and (4.65)

[4] Derive Eqs. (4.72) and (4.83).

[5] Derive Eqs. (4.103) and (4.104).

5 Principle of Constitutive Equation

5.1 Upper-Convective Maxwell Model

In Sect. 3, it was mentioned that the material time derivative of stress is not appropriate. Consider that we are interested in the generalization of the one-dimensional Maxwell model. One may imagine that every material particle is assigned to identical Maxwell model but different orientation. Here, the orientation of the Maxwell model implies the principal axis of the stress. As shown in Fig. 2, the Maxwell element flows along the path of the corresponding material particle.

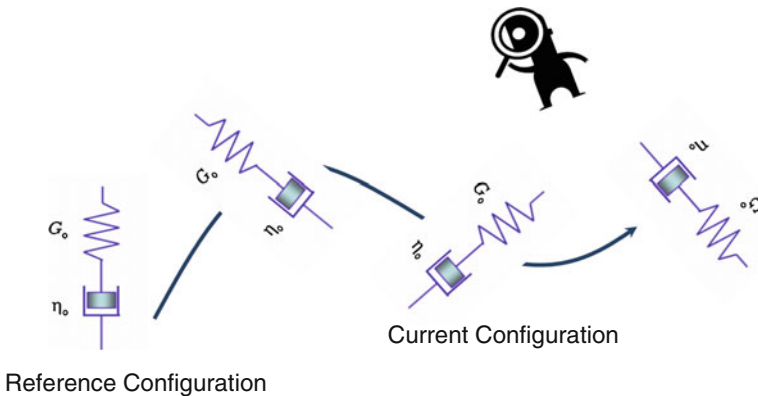


Fig. 2 Convection of Maxwell element in flow

The convective motion of the Maxwell element includes translation, rotation, and pure deformation.

However, the observer cannot see the motion in detail. The observer can detect only the stress field as a function of time in a fixed frame of coordinate system. The stress observed at time of t can be written by

$$\mathbf{T}(t) = T_{ik}(t) \mathbf{e}_i \mathbf{e}_k \quad (5.1)$$

where the base vectors $\{\mathbf{e}_i\}$ are those of the fixed frame of coordinate. If the stress is expressed in terms of the basis imbedded in the convective motion of material particles, which must be aligned in the orientation of the Maxwell model, then we have

$$\mathbf{T}(t) = \tilde{T}^{ik}(t) \mathbf{g}_i(t) \mathbf{g}_k(t) \quad (5.2)$$

where $\{\mathbf{g}^i\}$ are the basis imbedded in the flow. The material time derivative of the stress tensor is given by

$$\frac{d\mathbf{T}}{dt} = \frac{dT_{ik}}{dt} \mathbf{e}_i \mathbf{e}_k = \frac{d\tilde{T}^{ik}}{dt} \mathbf{g}_i \mathbf{g}_k + \tilde{T}^{ik} \frac{d\mathbf{g}_i}{dt} \mathbf{g}_k + \tilde{T}^{ik} \mathbf{g}_i \frac{d\mathbf{g}_k}{dt} \quad (5.3)$$

However, the origin of the stress is the extension of the Maxwell element. Hence, the Maxwell model must be

$$\lambda_M \frac{d\tilde{T}^{ik}}{dt} \mathbf{g}_i \mathbf{g}_k + \tilde{T}^{ik} \mathbf{g}_i \mathbf{g}_k = 2\eta_M \mathbf{D} \quad (5.4)$$

This is the correct three-dimensional extension of the Maxwell model. We have to find the basis $\{\mathbf{g}^i\}$ at each time for using Eq. (5.4), which is not convenient. We need a translation of the component-wise time derivative in terms of easily measurable field quantities. In order to do that, we have to know how to construct the convective basis $\{\mathbf{g}^i\}$ from the orthonormal basis $\{\mathbf{e}_i\}$.

The motion of material particles, Eq. (1.1), can be interpreted as a coordinate transform. The covariant base vector of the reference configuration is given by

$$\tilde{\mathbf{g}}_i = \frac{\partial \tilde{\mathbf{x}}}{\partial \tilde{x}_i} \quad (5.5)$$

Then, the covariant base vector of the current configuration is given by

$$\mathbf{g}_i = \frac{\partial \mathbf{x}}{\partial \tilde{x}_i} = \mathbf{F} \cdot \tilde{\mathbf{g}}_i \quad (5.6)$$

As for contravariant basis, we know that

$$\tilde{\mathbf{g}}_i \cdot \tilde{\mathbf{g}}^k = \mathbf{g}_i \cdot \mathbf{g}^k = \delta_i^k \quad (5.7)$$

Hence, it is obvious that

$$\mathbf{F} = \mathbf{g}_k \tilde{\mathbf{g}}^k; \quad (5.8a)$$

$$\mathbf{F}^{-1} = \tilde{\mathbf{g}}_k \mathbf{g}^k \quad (5.8b)$$

With the help of Eq. (5.8a), we obtain

$$\mathbf{g}^k = \mathbf{F}^{-T} \cdot \tilde{\mathbf{g}}^k \quad (5.9)$$

For simplicity, take the Cartesian coordinate system of the observer as the coordinate system of the reference coordinate system. This simplification gives

$$\tilde{\mathbf{g}}_i = \tilde{\mathbf{g}}^i = \mathbf{e}_i, \quad (5.10)$$

$$\mathbf{g}_i = \mathbf{F} \cdot \mathbf{e}_i, \quad (5.11)$$

and

$$\mathbf{g}^i = \mathbf{F}^{-T} \cdot \mathbf{e}_i \quad (5.12)$$

From Eq. (5.3), application of Eq. (5.11) gives

$$\overset{\nabla}{\mathbf{T}} \equiv \frac{d\tilde{T}^{ik}}{dt} \mathbf{g}_i \mathbf{g}_k = \frac{d\mathbf{T}}{dt} - \mathbf{L} \cdot \mathbf{T} - \mathbf{T} \cdot \mathbf{L}^T \quad (5.13)$$

Equation (5.13) is the definition of the *upper-convective time derivative*, and the modified Maxwell model of Eq. (5.4) is called the *upper-convective Maxwell model (UCM)*:

$$\lambda_M \overset{\nabla}{\mathbf{T}} + \mathbf{T} = 2\eta_M \mathbf{D} \quad (5.14)$$

This is a three-dimensional extension of the Maxwell model. However, this extension is not general but is a model-based extension. We need more general principle for constitutive model which is not based on a particular model.

It is noteworthy that the process of reasoning the UCM exploits the notion that the constitutive equation must be independent of the observer. We need to know how differently various tensorial quantities are recognized by different observers.

5.2 Principle of Material Frame Indifference

5.2.1 Change of Observer

Consider two observers: The observer 1 is fixed, while the observer 2 moves with translation and rotation as shown in Fig. 3. The two observers are assumed to share the same coordinate system when they see the reference configuration. For simplicity, we consider only Cartesian coordinate system. Since the motion of the observer 2 is that of rigid body, the origin of the observer 2 can be described by a vector-valued function $\mathbf{c}(t)$, while the basis of observer 2 can be described by

$$\mathbf{u}_i(t) = \mathbf{Q}(t) \cdot \mathbf{e}_i \quad (5.15)$$

where $\mathbf{Q}(t) = Q_{mn} \mathbf{e}_m \mathbf{e}_n$ is an orthogonal tensor which has the initial condition of $\mathbf{Q}(t=0) = \mathbf{I}$ and $\{\mathbf{e}_i\}$ are the basis of the observer 1.

A material particle is seen as \mathbf{x} by the observer 1, while the same material particle is seen as \mathbf{x}^* by the observer 2. Then, we have

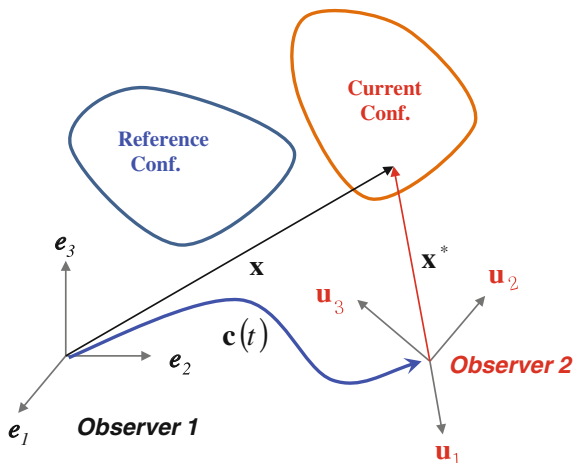
$$\mathbf{x}^* = \mathbf{x} - \mathbf{c}(t) \quad (5.16)$$

The same material particle has different coordinates depending on the observers as follows:

$$\text{Observer 1} \quad x_i = \mathbf{e}_i \cdot \mathbf{x} \quad (5.17)$$

$$\text{Observer 2} \quad x_i^* = \mathbf{u}_i \cdot \mathbf{x}^* \quad (5.18)$$

Fig. 3 Two observers



With the help of Eqs. (5.5) and (5.16), we can find the relation between the two coordinates

$$x_i^* = Q_{ki}x_k + \bar{c}_i \quad (5.19)$$

Here, we introduced $\bar{c}_i = -Q_{ki}c_k$ for the simplification of notation. Equation (5.19) can be rewritten by

$$\mathbf{x}^* = \mathbf{Q}^T \cdot \mathbf{x} + \bar{\mathbf{c}} \quad (5.20)$$

Note that both x_k and x_i^* are real-valued functions of material coordinates and time. Here, we introduced the asterisk symbol in order to denote the tensorial quantity recognized by the observer 2. Since the component of deformation gradient tensor is seen by the observer 1 as $F_{ik} = \partial x_i / \partial \tilde{x}_k$, that of deformation gradient tensor seen by the observer 2 is

$$F_{ik}^* = \frac{\partial x_i^*}{\partial \tilde{x}_k} = Q_{mi} \frac{\partial x_m}{\partial \tilde{x}_k} = Q_{mi} F_{mk} \quad (5.21)$$

Here, Eq. (5.19) was used. Note that $\mathbf{F}^* = F_{ik}^* \mathbf{e}_i \mathbf{e}_k$. Equation (5.21) can be rewritten by

$$\mathbf{F}^* = \mathbf{Q}^T \cdot \mathbf{F} \quad (5.22)$$

From Eq. (5.22), we obtain the following:

$$\mathbf{B}^* = \mathbf{Q}^T \cdot \mathbf{B} \cdot \mathbf{Q}; \quad (5.23)$$

$$\mathbf{C}^* = \mathbf{C} \quad (5.24)$$

From Eq. (5.19), we can calculate the velocity as follows:

$$\begin{aligned} \mathbf{v}^* &= \frac{d}{dt} x_i^* \mathbf{e}_i = \left(\frac{dQ_{ki}}{dt} x_k + Q_{ki} v_k + \frac{d\bar{c}_i}{dt} \right) \mathbf{e}_i \\ &= \frac{d\mathbf{Q}^T}{dt} \cdot \mathbf{x} + \mathbf{Q}^T \cdot \mathbf{v} + \frac{d\bar{\mathbf{c}}}{dt} \end{aligned} \quad (5.25)$$

Differentiation of \mathbf{v}^* with respect to \mathbf{x}^* gives

$$\mathbf{L}^* = \mathbf{Q}^T \cdot \mathbf{L} \cdot \mathbf{Q} + \mathbf{Q}^T \cdot \frac{d\mathbf{Q}}{dt} \quad (5.26)$$

Then, we also have

$$\mathbf{D}^* = \mathbf{Q}^T \cdot \mathbf{D} \cdot \mathbf{Q} \quad (5.27)$$

Because of the identity such that

$$\frac{d\mathbf{I}}{dt} = \mathbf{Q}^T \cdot \frac{d\mathbf{Q}}{dt} + \frac{d\mathbf{Q}^T}{dt} \cdot \mathbf{Q} = \mathbf{0} \quad (5.28)$$

As for spin tensor, we have

$$\mathbf{W}^* = \mathbf{Q}^T \cdot \mathbf{W} \cdot \mathbf{Q} + \mathbf{Q}^T \cdot \frac{d\mathbf{Q}}{dt} \quad (5.29)$$

Infinitesimal difference of \mathbf{x}^* is given by $d\mathbf{x}^* = \mathbf{x}^*(\tilde{\mathbf{x}} + d\tilde{\mathbf{x}}, t) - \mathbf{x}^*(\tilde{\mathbf{x}}, t)$. Then, Eq. (5.20) gives

$$d\mathbf{x}^* = \mathbf{Q}^T \cdot d\mathbf{x} = \mathbf{Q}^T \cdot \mathbf{F} \cdot d\tilde{\mathbf{x}} = \mathbf{F}^* \cdot d\tilde{\mathbf{x}} \quad (5.30)$$

If two arbitrary vectors \mathbf{u} and \mathbf{w} follow $\mathbf{u}^* = \mathbf{Q}^T \cdot \mathbf{u}$ and $\mathbf{w}^* = \mathbf{Q}^T \cdot \mathbf{w}$, then it is obvious that

$$\mathbf{u}^* \times \mathbf{w}^* = \mathbf{Q}^T \cdot (\mathbf{u} \times \mathbf{w}) \quad (5.31)$$

and

$$\mathbf{u}^* \mathbf{w}^* = \mathbf{Q}^T \cdot (\mathbf{u} \mathbf{w}) \cdot \mathbf{Q} \quad (5.32)$$

Furthermore, if a tensor \mathbf{A} obeys $\mathbf{A}^* = \mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q}$, then we know that when $\mathbf{w} = \mathbf{A} \cdot \mathbf{u}$,

$$\mathbf{A}^* \cdot \mathbf{u}^* = \mathbf{Q}^T \cdot (\mathbf{A} \cdot \mathbf{u}) = \mathbf{w}^* \quad (5.33)$$

With the help of Eqs. (1.33), (5.30), and (5.31), the differential area element satisfies the following identity:

$$d\mathbf{a}^* = \mathbf{Q}^T \cdot d\mathbf{a} \quad (5.34)$$

Since the stress vector issuing from a material point, it is obvious that $\mathbf{t}^* = \mathbf{Q}^T \cdot \mathbf{t}$. Then, Eq. (5.33) leads to

$$\mathbf{t}^o = \mathbf{T}^* \cdot d\mathbf{a}^* \quad (5.35)$$

and

$$\mathbf{T}^* = \mathbf{Q}^T \cdot \mathbf{T} \cdot \mathbf{Q} \quad (5.36)$$

5.2.2 Objective Vector and Tensor

So far, we discussed the consequences of the change of observers. Some vectors follow the relation $\mathbf{u}^* = \mathbf{Q}^T \cdot \mathbf{u}$, while others do not. Similarly, some tensors follow the relation $\mathbf{A}^* = \mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q}$, while others do not. The *Eulerian objective vectors and tensors* are defined as the ones such that

$$\mathbf{u}^* = \mathbf{Q}^T(t) \cdot \mathbf{u} \quad (5.37)$$

and

$$\mathbf{A}^* = \mathbf{Q}^T(t) \cdot \mathbf{A} \cdot \mathbf{Q}(t) \quad (5.38)$$

Meanwhile, right Cauchy–Green tensor \mathbf{C} and Piola–Kirchhoff stress of the 2nd kind are invariant for the change of observer. Note that

$$(\mathbf{F}^{-1})^* = \mathbf{F}^{-1} \cdot \mathbf{Q}(t); \quad (\mathbf{F}^{-T})^* = \mathbf{Q}^T(t) \cdot \mathbf{F}^{-T} \quad (5.39)$$

Equation (5.39) immediately gives

$$\begin{aligned} \tilde{\mathbf{T}}^* &= \det(\mathbf{F}^*) (\mathbf{F}^{-1})^* \cdot \mathbf{T}^* \cdot (\mathbf{F}^{-T})^* \\ &= \det(\mathbf{F}) \mathbf{F}^{-1} \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot \mathbf{T} \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot \mathbf{F}^{-T} \\ &= \tilde{\mathbf{T}} \end{aligned} \quad (5.40)$$

We define *Lagrangian objective tensors* as $\mathbf{A}^* = \mathbf{A}$.

The definition of relative deformation gradient tensor, Eq. (1.59), implies that

$$\mathbf{F}_t(\tau) = \mathbf{F}(\tau) \cdot \mathbf{F}^{-1}(t) \quad (5.41)$$

The use of Eq. (5.22) gives

$$\mathbf{F}_t^*(\tau) = \mathbf{Q}^T(\tau) \cdot \mathbf{F}_t(\tau) \cdot \mathbf{Q}(t) \quad (5.42)$$

Consequently, Eq. (1.66) gives

$$\mathbf{B}_t^*(\tau) = \mathbf{Q}^T(\tau) \cdot \mathbf{B}_t(\tau) \cdot \mathbf{Q}(\tau) \quad (5.43)$$

and

$$\mathbf{C}_t^*(\tau) = \mathbf{Q}^T(t) \cdot \mathbf{C}_t(\tau) \cdot \mathbf{Q}(t) \quad (5.44)$$

In summary, the objective tensors are Cauchy stress tensor \mathbf{T} , left Cauchy–Green tensor \mathbf{B} , right relative Cauchy–Green tensor $\mathbf{C}_t(\tau)$, relative finger tensor $\mathbf{C}_t^{-1}(\tau)$, and deformation rate tensor \mathbf{D} . It is obvious that the identity tensor \mathbf{I} is both Eulerian and Lagrangian objective tensors.

5.2.3 Principle of Material Frame Indifference

Several classical constitutive equations are introduced in Sect. 3. Since Cauchy stress is an Eulerian objective tensor, the formulation of stress tensor, constitutive equation, must obey the transform rule of Eulerian objective tensor. Since \mathbf{I} , \mathbf{B} , and \mathbf{D} are Eulerian objective tensors, it is obvious that the constitutive equations of Newtonian fluid and hyperelasticity follow the transform rule. The *principle of material frame-indifference* states that constitutive formulation must follow the transform rule (Truesdell and Noll 2004). If Piola–Kirchhoff stress of the 2nd kind is considered, then the formulation must consist of Lagrangian objective terms.

As for upper-convective Maxwell model, it obeys the principle of material frame-indifference. To show this, we have to show that the upper-convective time derivative satisfies

$$\overset{\nabla}{\mathbf{T}}^* = \mathbf{Q}^T(t) \cdot \overset{\nabla}{\mathbf{T}} \cdot \mathbf{Q}(t) \quad (5.45)$$

Note that

$$\frac{d}{dt}(\mathbf{Q}^T \cdot \mathbf{T} \cdot \mathbf{Q}) = \mathbf{Q}^T \cdot \frac{d\mathbf{T}}{dt} \cdot \mathbf{Q} + \frac{d\mathbf{Q}^T}{dt} \cdot \mathbf{T} \cdot \mathbf{Q} + \mathbf{Q}^T \cdot \mathbf{T} \cdot \frac{d\mathbf{Q}}{dt} \quad (5.46)$$

and

$$(\mathbf{L} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{L})^* = \mathbf{Q}^T \cdot (\mathbf{L} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{L}) \cdot \mathbf{Q} - \frac{d\mathbf{Q}^T}{dt} \cdot \mathbf{T} \cdot \mathbf{Q} - \mathbf{Q}^T \cdot \mathbf{T} \cdot \frac{d\mathbf{Q}}{dt} \quad (5.47)$$

Here, we used

$$\frac{d\mathbf{Q}}{dt} = -\mathbf{Q} \cdot \frac{d\mathbf{Q}^T}{dt} \cdot \mathbf{Q}; \quad \frac{d\mathbf{Q}^T}{dt} = -\mathbf{Q}^T \cdot \frac{d\mathbf{Q}}{dt} \cdot \mathbf{Q}^T \quad (5.48)$$

Equation (5.45) is immediately obtained by the application of Eqs. (5.46) and (5.47) to the definition of the upper-convective time derivative. Hence, the UCM

model follows the principle of material frame-indifference. Such constitutive model is called objective constitutive equation.

Note that *objective time derivatives* obey Eq. (5.45). It is known that the following time derivatives are also objective:

$$\overset{\Delta}{\mathbf{T}} \equiv \frac{d\mathbf{T}}{dt} + \mathbf{L}^T \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{L} \quad (5.49)$$

and

$$\overset{\circ}{\mathbf{T}} \equiv \frac{d\mathbf{T}}{dt} - \mathbf{W} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{W} \quad (5.50)$$

Equation (5.49) is the *lower-convective time derivative*, and Eq. (5.50) is the *Jaumann time derivative*. Object time derivatives satisfy the principle of material frame-indifference.

Problem 5

- [1] Derive Eqs. (2.a) and (2.b).
- [2] Derive Eq. (5.14).
- [3] Derive Eq. (5.26).
- [4] Derive Eq. (5.39).
- [5] Derive Eq. (5.46).
- [6] Show that the lower-convective time derivative and the Jaumann time derivative are objective.
- [7] Show that

$$\mathbf{R}^* = \mathbf{Q}^T \cdot \mathbf{R}; \quad (5.a)$$

$$\mathbf{U}^* = \mathbf{U}; \quad (5.b)$$

$$\mathbf{V}^* = \mathbf{Q}^T \cdot \mathbf{V} \cdot \mathbf{Q} \quad (5.c)$$

- [8] Show that for any tensor field,

$$\overset{\circ}{\mathbf{A}} = \frac{1}{2} \left(\overset{\nabla}{\mathbf{A}} + \overset{\Delta}{\mathbf{A}} \right) \quad (5.d)$$

- [9] Consider a vector field obeying

$$\frac{d\mathbf{u}}{dt} = \mathbf{L} \cdot \mathbf{u} - \zeta \mathbf{D} \cdot \mathbf{u} \quad (5.e)$$

where ζ is a positive constant. Then, derive that

$$\nabla \mathbf{G} + \zeta(\mathbf{D} \cdot \mathbf{G} + \mathbf{G} \cdot \mathbf{D}) = \mathbf{0} \quad (5.f)$$

where $\mathbf{G} = \mathbf{u}\mathbf{u}$.

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Cho, K.S.

2016, XIV, 612 p. 91 illus., 83 illus. in color., Hardcover

ISBN: 978-94-017-7562-5