It should be remembered that the metric tensor ν_{ij} and ν^{ij} in a convected coordinate system are related to the metric tensors g_{ij} and g^{ij} in a spatial coordinate system by Eqs. (2.84) and (2.85).

Therefore, we can write the following general rule of coordinate transformation of a second-order tensor:

$$\mathrm{A}_{mn}(\boldsymbol{\xi}, t) = (\partial x^i/\partial \xi^m)(\partial x^j/\partial \xi^n)a_{ij}(\mathbf{x}, t) \tag{2.102}$$

where $A_{mn}(\boldsymbol{\xi}, t)$ and $a_{ij}(\mathbf{x}, t)$ are covariant components of a tensor of second order in convected and fixed coordinate systems, respectively. Then the material derivative of $A_{mn}(\boldsymbol{\xi}, t)$ requires the material derivative of the right-hand side of Eq. (2.102), yielding (see Appendix 2B)

$$\frac{\mathrm{D}A_{mn}}{\mathrm{D}t} = \left(\frac{\partial x^i}{\partial \xi^m}\frac{\partial x^j}{\partial \xi^n}\right)\frac{\mathfrak{d}a_{ij}}{\mathfrak{d}t} \tag{2.103}$$

where

$$\frac{\mathfrak{d}a_{ij}}{\mathfrak{d}t} = \frac{\partial a_{ij}}{\partial t} + v^k\frac{\partial a_{ij}}{\partial x^k} + \frac{\partial v^k}{\partial x^i}a_{kj} + \frac{\partial v^k}{\partial x^j}a_{ik} \tag{2.104}$$

or in direct notation

$$\frac{\mathfrak{d}\mathbf{a}}{\mathfrak{d}t} = \frac{\mathrm{D}\mathbf{a}}{\mathrm{D}t} + (\nabla\mathbf{v})\cdot\mathbf{a} + \mathbf{a}\cdot(\nabla\mathbf{v})^{\mathrm{T}} \tag{2.105}$$

Here, $\mathfrak{d}/\mathfrak{d}t$ is called the "convected derivative" due to Oldroyd (1950), and it is the fixed coordinate equivalent of the material derivative of a second-order tensor referred to in convected coordinates. The physical interpretation of the right-hand side of Eq. (2.104) may be given as follows. The first two terms represent the derivative of tensor a_{ij} with time, with the fixed coordinate held constant (i.e., $\mathrm{D}a_{ij}/\mathrm{D}t$), which may be considered as the time rate of change as seen by an observer in a fixed coordinate system. The third and fourth terms represent the stretching and rotational motions of a material element referred to in a fixed coordinate system. This is because the velocity gradient $\partial v^k/\partial x^i$ (or the velocity gradient tensor $\mathbf{L}$ defined by Eq. (2.59)) may be considered as a sum of the rate of pure stretching and the material derivative of the finite rotation. For this reason, the convected derivative is sometimes referred to as the "codeformational derivative" (Bird et al. 1987).

Similarly, for contravariant components $A^{mn}(\boldsymbol{\xi}, t)$ and $a^{ij}(\mathbf{x}, t)$ of a tensor of second order in convected and fixed coordinate systems, respectively, we have

$$\frac{\mathrm{D}A^{mn}}{\mathrm{D}t} = \left(\frac{\partial \xi^m}{\partial x^i}\frac{\partial \xi^n}{\partial x^j}\right)\frac{\mathfrak{d}a^{ij}}{\mathfrak{d}t} \tag{2.106}$$

where

$$\frac{\mathfrak{d}a^{ij}}{\mathfrak{d}t} = \frac{\partial a^{ij}}{\partial t} + v^k \frac{\partial a^{ij}}{\partial x^k} - \frac{\partial v^i}{\partial x^k} a^{kj} - \frac{\partial v^j}{\partial x^k} a^{ik} \tag{2.107}$$

or in direct notation

$$\frac{\mathfrak{d}\mathbf{a}}{\mathfrak{d}t} = \frac{\mathrm{D}\mathbf{a}}{\mathrm{D}t} - (\nabla\mathbf{v})^{\mathrm{T}} \cdot \mathbf{a} - \mathbf{a} \cdot (\nabla\mathbf{v}) \tag{2.108}$$

In Chapter 3, we show that the contravariant and covariant components, respectively, of the convected derivative of the stress tensor give rise to different expressions for the material functions in steady-state simple shear flow. When compared with experimental data, it turns out that the material functions predicted from the contravariant components of the convected derivative of the stress tensor give rise to a correct trend, while the material functions predicted from the covariant components of the convected derivative of the stress tensor do not.

Now, we can apply the general rule of transformation to the material derivative of a strain tensor in the convected coordinates, given by Eqs. (2.100) and (2.101). For instance, from Eq. (2.84) we have

$$\frac{\mathrm{D}\nu_{ij}(\boldsymbol{\xi}, t)}{\mathrm{D}t} = \left(\frac{\partial x^m}{\partial \xi^i} \frac{\partial x^n}{\partial \xi^j} \right) \frac{\mathfrak{d}g_{mn}}{\mathfrak{d}t} \tag{2.109}$$

Since the spatial metric $g_{mn}(\mathbf{x})$ is independent of time, it can be easily shown that (Oldroyd 1950)

$$\frac{\mathfrak{d}g_{mn}}{\mathfrak{d}t} = 2d_{mn} \tag{2.110}$$

where d_{mn} are the components of the rate-of-strain tensor $\mathbf{d}$ defined by Eq. (2.60).

It is important to note that there are other types of time derivatives which also transform as a tensor from convected to fixed coordinates. One particular time derivative that has received particular attention by rheologists is the so-called "Jaumann derivative," which was suggested first by Zaremba (1903) and later reformulated by other investigators (DeWitt 1955; Fromm 1947). The Jaumann derivative $\mathcal{D}/\mathcal{D}t$ of a second-order tensor a_{ij} is defined as

$$\frac{\mathcal{D}a_{ij}}{\mathcal{D}t} = \frac{\partial a_{ij}}{\partial t} + v^k \frac{\partial a_{ij}}{\partial x^k} - \omega_{ik}a_{jk} - \omega_{jk}a_{ik} \tag{2.111}$$

or in direct notation[1]

$$\frac{\mathcal{D}\mathbf{a}}{\mathcal{D}t} = \frac{\mathrm{D}\mathbf{a}}{\mathrm{D}t} - (\boldsymbol{\omega} \cdot \mathbf{a}) - (\boldsymbol{\omega} \cdot \mathbf{a})^{\mathrm{T}} \tag{2.112}$$

where $\boldsymbol{\omega}$ is the vorticity tensor defined by Eq. (2.61). The physical interpretation of the right-hand side of Eq. (2.111) may be given as follows. The first two terms represent the material derivative of a_{ij}, similar to the first two terms on the right-hand side of Eq. (2.104). However, the third and fourth terms containing only the vorticity tensor $\boldsymbol{\omega}$ represent the rotational motion of a material element referred to in a fixed coordinate system. For this reason, the Jaumann derivative is sometimes referred to as the "corotational derivative" (Bird et al. 1987). In Chapter 3 we show that the contravariant and covariant components, respectively, of the Jaumann derivative of the stress tensor give rise to identical expressions for the material functions in steady-state simple shear flow, predicting the same trend as that observed experimentally.

2.6 The Description of Stress and Material Functions

Let us consider now the stress tensor, which causes or arises from deformation. In order to give the reason why a second-order tensor is required to describe the stress, a development of Cauchy's law of motion is needed. The physical significance of the stress tensor may be illustrated best by considering the three forces acting on three faces (one force on each face) of a small cube element of fluid, as schematically shown in Figure 2.4. For instance, a force (which is the vector) acting on the face ABCD with an arbitrary direction may be resolved in three component directions: the force acting in the x_1 direction is $T_{11}dx_2dx_3$, the force acting in the x_2 direction is $T_{12}dx_2dx_3$, and the force acting in the x_3 direction is $T_{13}dx_2dx_3$. Similarly, the forces acting on face BCFE are $T_{21}dx_1dx_3$ in the x_1 direction, $T_{22}dx_1dx_3$ in the x_2 direction, $T_{23}dx_1dx_3$

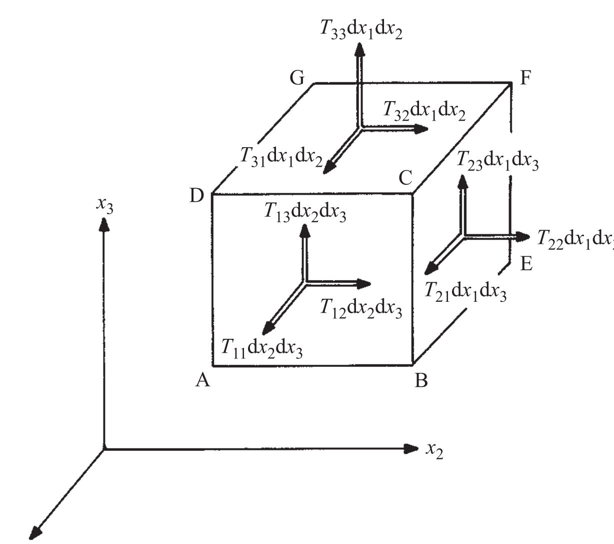

Figure 2.4 Stress components on a cube.

in the x_3 direction. Likewise, the forces acting on face DCFG are $T_{31}\mathrm{d}x_1\mathrm{d}x_2$ in the x_1 direction, $T_{32}\mathrm{d}x_1\mathrm{d}x_2$ in the x_2 direction, and $T_{33}\mathrm{d}x_1\mathrm{d}x_2$ in the x_3 direction.

In dealing with the state of stresses of incompressible fluids under deformation or in flow, the total stress tensor **T** is divided into two parts:

$$\left\| T_{ij} \right\| = \left\| \begin{matrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{matrix} \right\| = \left\| \begin{matrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{matrix} \right\| + \left\| \begin{matrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{matrix} \right\| \tag{2.113}$$

where the component T_{ij} of the stress tensor **T** is the force acting in the x_i direction on unit area of a surface normal to the x_i direction. The components T_{11}, T_{22}, and T_{33} are called normal stresses since they act normally to surfaces, the mixed components T_{12}, T_{13}, and so on, are called shear stresses. In direct notation, Eq. (2.113), using Cartesian coordinates, can be expressed by

$$\mathbf{T} = -p\boldsymbol{\delta} + \boldsymbol{\sigma} \tag{2.114}$$

where the $\boldsymbol{\delta}$ is the unit tensor, $\boldsymbol{\sigma}$ is the deviatoric stress tensor (or the extra stress tensor) that vanishes in the absence of deformation or flow, and p is the isotropic pressure. Note in Eq. (2.113) or Eq. (2.114) that p has a negative sign since it acts in the direction opposite to a normal stress (T_{11}, T_{22}, T_{33}), which by convention is chosen as pointing out of the cube (see Figure 2.4). It should be mentioned that in an incompressible liquid, the state of stress is determined by the strain or strain history only to within an additive isotropic constant, and thus p appearing in Eq. (2.113) or in Eq. (2.114) is the pressure that can be determined within the accuracy of an isotropic term. As is shown in some later chapters (e.g., Chapter 5), only pressure gradient plays a role in describing fluid motion. Thus the isotropic term, $p\boldsymbol{\delta}$ in Eq. (2.114) has no effect on fluid motion, i.e., the addition of an isotropic term of arbitrary magnitude has no consequence to the total stress tensor **T** when a fluid is in motion.

Special types of states of stress are of particular importance. In a liquid that has been at rest (i.e., there is no deformation of a fluid) for a sufficiently long time, there is no tangential component of stress on any plane of a cube and the normal component of stress is the same for all three planes, each perpendicular to the others. This is the situation where only hydrostatic pressure, $-p$, exists. In such a situation, Eq. (2.113) reduces to

$$\left\| T_{ij} \right\| = \left\| \begin{matrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{matrix} \right\| \tag{2.115}$$

From Eq. (2.115) we can now define pressure as

$$-p = \tfrac{1}{3}(T_{11} + T_{22} + T_{33}) \tag{2.116}$$

Note that Eq. (2.116) can also be obtained from Eq. (2.113) with the assumption, $\sigma_{11} + \sigma_{22} + \sigma_{33} = 0$. Since such an assumption is quite arbitrary, the definition of pressure p given by Eq. (2.116) can be regarded as a somewhat arbitrary one. In fact, in general p is the thermodynamic pressure, which is related to the density ρ and the temperature through a "thermodynamic equations of state," $p = p(\rho, T)$; that is, this is taken to be the same function as that used in thermal equilibrium (Bird et al. 1987).

If we now consider the state of stress in an isotropic material, by definition the material has no preferred directions. In simple shear flow, we have

$$T_{13} = T_{31} = 0; \quad T_{23} = T_{32} = 0; \quad T_{12} = T_{21} \neq 0 \tag{2.117}$$

in which the subscript 1 denotes the direction of flow, the subscript 2 denotes the direction perpendicular to flow, and the subscript 3 denotes the remaining (neutral) direction. It follows therefore from Eq. (2.113) that the most general possible state of stress for an isotropic material in simple shear flow may be represented by

$$\left\| \begin{matrix} T_{11} & T_{12} & 0 \\ T_{12} & T_{22} & 0 \\ 0 & 0 & T_{33} \end{matrix} \right\| = \left\| \begin{matrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{matrix} \right\| + \left\| \begin{matrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{matrix} \right\| \tag{2.118}$$

Note that one cannot measure p and the components of the extra stress tensor $\boldsymbol{\sigma}$ separately during flow of a liquid. Therefore, the absolute value of any one normal component of stress is of no rheological significance. The values of the differences of normal stress components are, however, not altered by the addition of any isotropic pressure (see Eq. (2.118)), and they presumably depend on the rheological properties of the material. It follows, therefore, that there are only three independent stress quantities of rheological significance, namely, one shear component and two differences of normal components:

$$\sigma_{12}; \quad T_{11} - T_{22} = \sigma_{11} - \sigma_{22}; \quad T_{22} - T_{33} = \sigma_{22} - \sigma_{33} \tag{2.119}$$

Note that the normal stress difference $\sigma_{11} - \sigma_{33}$ becomes redundant since we have assumed $\sigma_{11} + \sigma_{22} + \sigma_{33} = 0$ in defining p by Eq. (2.116). In the rheology community, $N_1 = \sigma_{11} - \sigma_{22}$ is referred to as the first normal stress difference and $N_2 = \sigma_{11} - \sigma_{33}$ as the second normal stress difference. It now remains to be discussed how the stress quantities may be related to strain or rate of strain to describe the rheological properties of materials, in particular polymeric materials.

For steady-state shear flow, the components of the stress tensor $\mathbf{T}$ may be expressed in terms of three independent functions:

$$\sigma_{12} = \eta(\dot{\gamma})\dot{\gamma} \quad N_1 = \psi_1(\dot{\gamma})\dot{\gamma}^2 \quad N_2 = \psi_2(\dot{\gamma})\dot{\gamma}^2 \tag{2.120}$$

where $\eta(\dot{\gamma})$ is referred to as the shear-rate dependent viscosity, $\psi_1(\dot{\gamma})$ as the first normal stress difference coefficient, and $\psi_2(\dot{\gamma})$ as the second normal stress difference coefficient. Often, $\eta(\dot{\gamma})$, $\psi_1(\dot{\gamma})$, and $\psi_2(\dot{\gamma})$ are referred to as the "material functions" in steady-state shear flow. Note that N_1 and N_2, or $\psi_1(\dot{\gamma})$ and $\psi_2(\dot{\gamma})$, describe the fluid elasticity, which is elaborated on in Chapter 3.

In the past, numerous investigators have reported measurements of the rheological properties of polymeric liquids. Until now, very few polymeric fluids, if any, which exhibit a constant value of shear viscosity (i.e., $\eta(\dot{\gamma}) = \eta_0$) exhibit measurable values