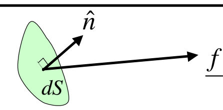
Molecular Forces *(continued)*



How can we write $\underline{f}$ (the force on an arbitrary surface dS) in terms of the quantities Π_{pk}?

$$\underline{f} = f_1\hat{e}_1 + f_2\hat{e}_2 + f_3\hat{e}_3$$

f_1 , the force on dS in 1-direction, can be broken into <u>three</u> parts associated with the three stress components:

$$\Pi_{11}, \Pi_{21}, \Pi_{31}$$

first part:

$$\left(\Pi_{11}\right)\underbrace{\begin{pmatrix} projection\ \ of \\ dA\ onto\ the \\ 1-surface \end{pmatrix}}_{\hat{n}\cdot\hat{e}_1\, dS} = \Pi_{11}\hat{n}\cdot\hat{e}_1\, dS$$

$$\left(\frac{force}{area}\right) \cdot \left(area\right)$$

Molecular Forces *(continued)*

f_1 , the force on dS in 1-direction, is composed of THREE parts:

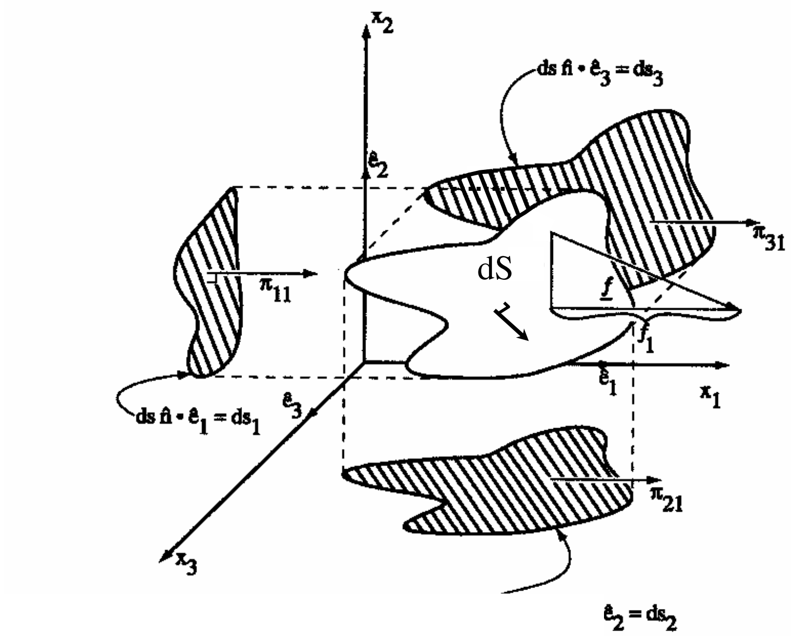
first part:
$$\left(\Pi_{11}\right)\begin{pmatrix} projection\ \ of \\ dA\ onto\ the \\ 1-surface \end{pmatrix} = \Pi_{11}\hat{n}\cdot\hat{e}_1\, dS$$

second part:
$$\left(\Pi_{21}\right)\begin{pmatrix} projection\ \ of \\ dA\ onto\ the \\ 2-surface \end{pmatrix} = \Pi_{21}\hat{n}\cdot\hat{e}_2\, dS$$

third part:
$$\left(\Pi_{31}\right)\begin{pmatrix} projection\ \ of \\ dA\ onto\ the \\ 3-surface \end{pmatrix} = \Pi_{31}\hat{n}\cdot\hat{e}_3\, dS$$

stress on a 2 -surface in the 1-direction

the sum of these three = f_1



Molecular Forces *(continued)*

f_1 , the force in the 1-direction on an arbitrary surface *dS* is composed of THREE parts.

$$f_1 = \Pi_{11}\hat{n}\cdot\hat{e}_1\,dS + \Pi_{21}\hat{n}\cdot\hat{e}_2\,dS + \Pi_{31}\hat{n}\cdot\hat{e}_3\,dS$$

stress — appropriate area

Using the distributive law:

$$\boxed{f_1 = \hat{n}\cdot\left(\Pi_{11}\hat{e}_1 + \Pi_{21}\hat{e}_2 + \Pi_{31}\hat{e}_3\right)dS}$$

Force in the 1-direction on an arbitrary surface *dS*

Molecular Forces *(continued)*

The same logic applies in the 2-direction and the 3-direction

$$f_1 = \hat{n}\cdot\left(\Pi_{11}\hat{e}_1 + \Pi_{21}\hat{e}_2 + \Pi_{31}\hat{e}_3\right) dS$$
$$f_2 = \hat{n}\cdot\left(\Pi_{12}\hat{e}_1 + \Pi_{22}\hat{e}_2 + \Pi_{32}\hat{e}_3\right) dS$$
$$f_3 = \hat{n}\cdot\left(\Pi_{13}\hat{e}_1 + \Pi_{23}\hat{e}_2 + \Pi_{33}\hat{e}_3\right) dS$$

Assembling the force vector:

$$\begin{aligned}\underline{f} &= f_1\hat{e}_1 + f_2\hat{e}_2 + f_3\hat{e}_3 \\ &= dS\ \hat{n}\cdot\left(\Pi_{11}\hat{e}_1 + \Pi_{21}\hat{e}_2 + \Pi_{31}\hat{e}_3\right)\hat{e}_1 \\ &\quad + dS\ \hat{n}\cdot\left(\Pi_{12}\hat{e}_1 + \Pi_{22}\hat{e}_2 + \Pi_{32}\hat{e}_3\right)\hat{e}_2 \\ &\quad + dS\ \hat{n}\cdot\left(\Pi_{13}\hat{e}_1 + \Pi_{23}\hat{e}_2 + \Pi_{33}\hat{e}_3\right)\hat{e}_3\end{aligned}$$

Molecular Forces *(continued)*

Assembling the force vector:

$$\begin{aligned}\underline{f} &= f_1\hat{e}_1 + f_2\hat{e}_2 + f_3\hat{e}_3 \\ &= dS\ \hat{n}\cdot\left(\Pi_{11}\hat{e}_1 + \Pi_{21}\hat{e}_2 + \Pi_{31}\hat{e}_3\right)\hat{e}_1 \\ &\quad + dS\ \hat{n}\cdot\left(\Pi_{12}\hat{e}_1 + \Pi_{22}\hat{e}_2 + \Pi_{32}\hat{e}_3\right)\hat{e}_2 \\ &\quad + dS\ \hat{n}\cdot\left(\Pi_{13}\hat{e}_1 + \Pi_{23}\hat{e}_2 + \Pi_{33}\hat{e}_3\right)\hat{e}_3 \\ &= dS\ \hat{n}\cdot\left[\Pi_{11}\hat{e}_1\hat{e}_1 + \Pi_{21}\hat{e}_2\hat{e}_1 + \Pi_{31}\hat{e}_3\hat{e}_1\right. \\ &\quad + \Pi_{12}\hat{e}_1\hat{e}_2 + \Pi_{22}\hat{e}_2\hat{e}_2 + \Pi_{32}\hat{e}_3\hat{e}_2 \\ &\quad \left. + \Pi_{13}\hat{e}_1\hat{e}_3 + \Pi_{23}\hat{e}_2\hat{e}_3 + \Pi_{33}\hat{e}_3\hat{e}_3\right]\end{aligned}$$

linear combination of dyadic products = **tensor**

Molecular Forces *(continued)*

Assembling the force vector:

$$\underline{f} = dS\ \hat{n}\cdot\left[\Pi_{11}\hat{e}_1\hat{e}_1 + \Pi_{21}\hat{e}_2\hat{e}_1 + \Pi_{31}\hat{e}_3\hat{e}_1 + \Pi_{12}\hat{e}_1\hat{e}_2 + \Pi_{22}\hat{e}_2\hat{e}_2 + \Pi_{32}\hat{e}_3\hat{e}_2 + \Pi_{13}\hat{e}_1\hat{e}_3 + \Pi_{23}\hat{e}_2\hat{e}_3 + \Pi_{33}\hat{e}_3\hat{e}_3\right]$$

$$= dS\ \hat{n}\cdot\sum_{p=1}^{3}\sum_{m=1}^{3}\Pi_{pm}\hat{e}_p\hat{e}_m$$

$$= dS\ \hat{n}\cdot\Pi_{pm}\hat{e}_p\hat{e}_m$$

$$\boxed{\underline{f} = dS\ \hat{n}\cdot\underline{\underline{\Pi}}}$$

Total stress tensor (molecular stresses)

Momentum Balance *(continued)*

$$\begin{pmatrix}\text{rate of increase}\\ \text{of momentum in } V\end{pmatrix} = \begin{pmatrix}\text{net flux of}\\ \text{momentum into } V\end{pmatrix} + \begin{pmatrix}\text{sum of}\\ \text{forces on } V\end{pmatrix}$$

$$\iiint_V \frac{\partial}{\partial t}(\rho\underline{v})\,dV = -\iiint_V \nabla\cdot(\rho\underline{v}\,\underline{v})\,dV + \iiint_V \rho\underline{g}\ dV + \begin{matrix}\text{molecular}\\ \text{forces}\end{matrix}$$

$$\begin{matrix}\text{molecular}\\ \text{forces}\end{matrix} = \iint_S \begin{pmatrix}\text{molecular}\\ \text{forces on}\\ dS\end{pmatrix}$$

$$= -\iint_S \hat{n}\cdot\underline{\underline{\Pi}}\ dS$$

$$= -\iiint_V \nabla\cdot\underline{\underline{\Pi}}\ dV$$

Gauss Divergence Theorem

$$\begin{pmatrix} \text{rate of increase} \\ \text{of momentum in } V \end{pmatrix} = \begin{pmatrix} \text{net flux of} \\ \text{momentum into } V \end{pmatrix} + \begin{pmatrix} \text{sum of} \\ \text{forces on } V \end{pmatrix}$$

$$\iiint_V \frac{\partial}{\partial t}(\rho \underline{v})\, dV = -\iiint_V \nabla \cdot (\rho \underline{v}\,\underline{v})\, dV + \iiint_V \rho \underline{g}\; dV + \begin{matrix} \text{molecular} \\ \text{forces} \end{matrix}$$

$$\begin{matrix} \text{molecular} \\ \text{forces} \end{matrix} = \iint_S \begin{pmatrix} \text{molecular} \\ \text{forces on} \\ dS \end{pmatrix}$$

$$= -\iint_S \hat{n} \cdot \underline{\underline{\Pi}}\; dS$$

$$= -\iiint_V \nabla \cdot \underline{\underline{\Pi}}\; dV$$

Gauss Divergence Theorem

Our choice: positive compression (pressure is positive)

Forces "***on***" versus "***by***" cause a sign change, as does positive "***tension***" versus positive "***compression***"

Final Assembly:

$$\begin{pmatrix} \text{rate of increase} \\ \text{of momentum in } V \end{pmatrix} = \begin{pmatrix} \text{net flux of} \\ \text{momentum into } V \end{pmatrix} + \begin{pmatrix} \text{sum of} \\ \text{forces on } V \end{pmatrix}$$

$$\iiint_V \frac{\partial}{\partial t}(\rho \underline{v})\, dV = -\iiint_V \nabla \cdot (\rho \underline{v}\,\underline{v})\, dV + \iiint_V \rho \underline{g}\; dV - \iiint_V \nabla \cdot \underline{\underline{\Pi}}\; dV$$

$$\iiint_V \left[\frac{\partial \rho \underline{v}}{\partial t} + \nabla \cdot (\rho \underline{v}\,\underline{v}) - \rho \underline{g} + \nabla \cdot \underline{\underline{\Pi}} \right] dV = 0$$

Because V is *arbitrary*, we may conclude:

$$\frac{\partial \rho \underline{v}}{\partial t} + \nabla \cdot (\rho \underline{v}\,\underline{v}) - \rho \underline{g} + \nabla \cdot \underline{\underline{\Pi}} = 0$$

Microscopic momentum balance

Microscopic momentum balance

$$\frac{\partial \rho \underline{v}}{\partial t} + \nabla \cdot (\rho \underline{v}\underline{v}) - \rho \underline{g} + \nabla \cdot \underline{\underline{\Pi}} = 0$$

After some rearrangement:

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v}\right) = -\nabla \cdot \underline{\underline{\Pi}} + \rho \underline{g}$$

$$\rho \frac{D\underline{v}}{Dt} = -\nabla \cdot \underline{\underline{\Pi}} + \rho \underline{g}$$

Equation of Motion

Now, what to do with $\underline{\underline{\Pi}}$?

Now, what to do with $\underline{\underline{\Pi}}$? Pressure is part of it.

Pressure

definition: An isotropic force/area of molecular origin. Pressure is the same on any surface drawn through a point and acts normally to the chosen surface.

$$pressure = p\,\underline{\underline{I}} = p\,\hat{e}_1\hat{e}_1 + p\,\hat{e}_2\hat{e}_2 + p\,\hat{e}_3\hat{e}_3 = \begin{pmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{pmatrix}_{123}$$

Test: what is the force on a surface with unit normal $\hat{n}$?

Momentum Balance *(continued)* Polymer Rheology

back to our question,

Now, what to do with $\underline{\underline{\Pi}}$?

Pressure is part of it.

There are other, nonisotropic stresses

Extra Molecular Stresses

definition: The extra stresses are the molecular stresses that are not isotropic

$$\underline{\underline{\tau}} \equiv \underline{\underline{\Pi}} - p\,\underline{\underline{I}}$$

Extra stress tensor, i.e. everything complicated in molecular deformation

Now, what to do with $\underline{\underline{\tau}}$?

This becomes the central question of rheological study

Momentum Balance *(continued)* Polymer Rheology

Constitutive equations for Stress

- are tensor equations
- relate the velocity field to the stresses generated by molecular forces
- are based on observations (empirical) or are based on molecular models (theoretical)
- are typically found by trial-and-error
- are justified by how well they work for a system of interest
- are observed to be symmetric

$$\underline{\underline{\tau}} = f(\nabla \underline{v}, \textit{material properties})$$

Observation: the stress tensor is symmetric

Microscopic momentum balance

$$\rho\left(\frac{\partial \underline{v}}{\partial t}+\underline{v}\cdot\nabla\underline{v}\right)=-\nabla\cdot\underline{\underline{\Pi}}+\rho\underline{g}$$

Equation of Motion

In terms of the extra stress tensor:

$$\rho\left(\frac{\partial \underline{v}}{\partial t}+\underline{v}\cdot\nabla\underline{v}\right)=-\nabla p-\nabla\cdot\underline{\underline{\tau}}+\rho\underline{g}$$

Equation of Motion

Newtonian Constitutive equation

$$\underline{\underline{\tau}}=-\mu\left(\nabla\underline{v}+\left(\nabla\underline{v}\right)^T\right)$$

- for incompressible fluids (see text for compressible fluids)
- is empirical
- may be justified for some systems with molecular modeling calculations

How is the Newtonian Constitutive equation related to Newton's Law of Viscosity?

$$\underline{\underline{\tau}} = -\mu\left(\nabla \underline{v} + (\nabla \underline{v})^T\right)$$

- incompressible fluids

$$\tau_{21} = -\mu \frac{\partial v_1}{\partial x_2}$$

- incompressible fluids
- rectilinear flow (straight lines)
- no variation in x_3-direction

Back to the momentum balance . . .

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v}\right) = -\nabla p - \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$

Equation of Motion

$$\underline{\underline{\tau}} = -\mu\left(\nabla \underline{v} + (\nabla \underline{v})^T\right)$$

We can incorporate the Newtonian constitutive equation into the momentum balance to obtain a momentum-balance equation that is specific to incompressible, Newtonian fluids

Navier-Stokes Equation

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v}\cdot\nabla\underline{v}\right) = -\nabla p + \mu\nabla^2\underline{v} + \rho\underline{g}$$

- incompressible fluids
- Newtonian fluids