Introduction to Rheology

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Contents (overview)

- Motivation, Literature, Journals
- First principles
- Simple models: Maxwell, Voigt, Burger, Carreau, Ostwald - de Waele
- Glossary
- Rheological hardware
- Examples: Dispersions (response and phenomena), Polymer melts, ...
- Fourier-Transformation
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Literature:

Books

Einführung in Rheologie und Rheometrie (also available in English)
Gebhard Schramm, Gebr. Haake GmbH, Karlsruhe
(easy; book to start with)

Das Rheologie Handbuch (also available in English)
Thomas Mezger, Vincentz Verlag, 2000
(easy, covers lots of practical problems, nice hardware section)

Rheology for Chemists, an Introduction
J. W. Goodwin and R. H. Hughes, Royal Society of Chemistry 2000
(easy)

A Handbook of elementary Rheology
Howard A. Barnes, University of Wales, Institute of Non-Newtonian Fluid Mechanics, Aberystwyth 2000, (good overview, very elaborated literature at the end)

The structure and rheology of complex fluids
Ronald G. Larson (Head of society of rheology), Oxford University Press 1999
(more advanced)

Rheology Principles, Measurements and Applications
Ch. W. Macosko, Wiley-VCH 1994
(more advanced)

Engineering Rheology
R. J. Tanner, Oxford University Press 2000
(for mechanical engineers)
**Rheological measurements**

*(Hardware)*

**Rheology: A Historical Perspective**
R. I. Tanner and K. Walters, Elsevier 1998

*(lots about people and phenomena)*

**Journals**

**Journal of Applied Rheology**
http://www.ar.ethz.ch/

*(incl. Jobs!, Hardware guide, reports about upcoming and previous conferences)*

**Rheologica Acta (Springer)**
http://www.springerlink.com/

**Journal of Rheology (The Society of Rheology)**
http://scitation.aip.org/joro/

**Journal of Non-Newtonian fluid mechanics**
http://www.elsevier.com/

**Internet**

[www.rheologie.de](http://www.rheologie.de)
[www.rheology-esr.org](http://www.rheology-esr.org)
[www.rheology.org](http://www.rheology.org)
Definition of the term “Rheology”

Rheology is the science of deformation and flow of matter.

Side conditions:
conservation of energy, conservation of mass, symmetry constraints, incompressibility;

Analysis of:
Deformations: strain (shear), stretch (elongation);
stress (torque); normal forces;

Typical examples of daily live: (⇒ motivation)

1) Brush with paint on a wall

\[ v = 1 \text{ m/s} = 1000 \text{ mm/s} \]
\[ d = 0.2 \text{ mm} \]

What is the relevant quantity?

Assumption: layered structure

\[ \frac{v_i}{d_i} = \text{constant for all } i! \]
\[
\Rightarrow \frac{v_i}{d_i} = \frac{v_n}{d_n} = \frac{v}{d} = \frac{1000 \text{ mm/s}}{0.2 \text{ mm}} = 5000 \frac{1}{\text{s}}
\]

\[
\Rightarrow \text{shear rate } \dot{\gamma} = \frac{v}{d} [1/\text{s}]
\]

Why is this a rate and not a frequency?
Frequency is only used with respect to periodic phenomena, otherwise: rate!
both: [1/s]!

2) Piston in an engine

frequency:
\[
\frac{\omega_1}{2\pi} = 6000 \frac{1}{\text{min}}
\]

(=rpm, rotations per minute)
\[
\frac{\omega_1}{2\pi} = 100 \frac{1}{\text{s}}
\]

stroke \((\text{german: Hub})\):
\[
s = 10 \text{ cm} = 0.1 \text{ m}
\]
\[
\Rightarrow \bar{v} = \frac{\omega_1}{2\pi} \cdot s \cdot 2 = 100 \cdot 0.1 \cdot 2 \left[ \frac{\text{m}}{\text{s}} \right] = 20 \left[ \frac{\text{m}}{\text{s}} \right]
\]
\[
\Rightarrow \bar{v}_1 = \frac{\omega_1}{2\pi} \cdot s = 20 \left[ \frac{\text{m}}{\text{s}} \right]
\]
\[
\Rightarrow \nu_{\text{max}} = (\pi/2)20 \left[ \frac{\text{m}}{\text{s}} \right] \approx 30 \left[ \frac{\text{m}}{\text{s}} \right] \quad \text{why } \pi/2?
\]
\[
d = 20 \mu \text{m} = 20 \cdot 10^{-6} \text{ m}
\]
\[
\Rightarrow \dot{\gamma}_{\text{max}} = \frac{\nu_{\text{max}}}{d} = \frac{30 \text{ m/s}}{20 \cdot 10^{-6} \text{ m}} = 1.5 \cdot 10^6 \left[ \frac{1}{\text{s}} \right]
\]

think about:
- shower lotion
- lipstick
- coating of paper
- extrusion of fibres \((\Rightarrow \text{clothing})\)
unit of $\dot{\gamma}$: $[1/s] = \text{inverse time}$

comparison: $\frac{1}{\dot{\gamma}} \leftrightarrow \lambda_p$

$\dot{\gamma} \cdot \lambda_p$ is a unitless quantity

Why can we assume that Hooke’s law could be correct?

Do we “buy” this law?

Hooke: $F = k \cdot x$

Possible reasons:

a) $F = F_{(x,...)} = F_{(x)}$ (assumption)

Taylor-expansion (Taylor around $x = 0$ $\Rightarrow$ MacLaurin series)

$$F_{(x)} = F_{(x=0)} + \left. \frac{\partial F}{\partial x} \right|_{x=0} \cdot x + \frac{1}{2!} \left. \frac{\partial^2 F}{\partial x^2} \right|_{x=0} \cdot x^2$$

because at equil. linear

at equil. small $x$ nonlinear part

b) Interaction Potential for vibrational (IR) spectroscopy (beside Hooke):

Morse-Potential $U(x)$ (Potential, not force!)

$$\frac{\partial U}{\partial x} = F \leftrightarrow U = \int F \, dx$$
Potential has units of energy!

Morse: $U_{(x)} = A(1 - \exp(-\beta(x - x_0)))^2$

Taylor:

$$e^{-\beta x} = 1 - \beta x + \frac{\beta^2 x^2}{2!} - \frac{\beta^3 x^3}{3!} + ...$$

$$\Rightarrow U_{(x)} = A(1 - (1 - \beta \cdot x + ...))^2 = A(\beta \cdot x + ...)^2 \approx A\beta^2 x^2$$

$$F = \frac{\partial U}{\partial x} = 2A\beta^2 x = k \cdot x$$

a) + b) $\Rightarrow$ no proof, but we “buy” Hooke’s law

exercise: prove Hooke’s law for the finite extendable nonlinear elastic interaction (FENE), frequently used in computer simulation, for $x \approx R_0$

$$U_{(x)} = -A \cdot \ln \left(1 - \left(\frac{x}{R_0}\right)^2\right)$$

Note: $A$: Dissociation energy
Remark:
If we remember typical force-constant from IR (⇒ spectroscopy books)

\[ k = 500 \text{ N/m} \quad (\omega = \sqrt{\frac{k}{m}}) \]

and we remember typical area needed for a chain, e.g. polyethylene:

- orthorhombic
- \( a = 7.5 \text{ Å} \)
- \( b = 5 \text{ Å} \)
- \( c = 2.5 \text{ Å} \)

2 chains per unit cell

\[
\frac{A}{\text{chain}} = \frac{7.5 \cdot 5 \text{ Å}^2}{2} = \frac{37.5 \text{ Å}^2}{2} \approx 20 \text{ Å}^2 = 20 \cdot 10^{-20} \text{ m}^2
\]

Renormalization to area + relative change in length

\[
\frac{F}{A} = \sigma = E \cdot \frac{x}{L} \quad \sigma + E: \text{ unit: pressure [1 Pa = 1 N/m}^2]\]
upper limit:
\[ \frac{F}{A} = \frac{k \cdot x}{A} = \sigma = E \cdot \frac{x}{L} \]
\[ \Rightarrow \frac{k \cdot L}{A} = E = \frac{500 \cdot 10^{20} \cdot 10^{-10}}{20} \left[ \frac{N \cdot m}{m \cdot m^2} \right] = 250 \cdot 10^9 Pa = 250 \text{ GPa} \]
C in unit cell \( \approx 10^{10} \text{ m} \) (one bond)
Tungsten (W): 150 GPa

But:
\[ \begin{array}{c}
\text{bending modes are weaker} \\
\Rightarrow \text{only several GPa}
\end{array} \]

**Hooke for polymers (rubber elasticity)**

Start of chain in coordinate origin, where is end?

\[ W_{(t)} \propto \text{Gauss} \]
\[ W_{(t)} \propto \frac{1}{\sqrt{2\pi} \cdot \sigma} \cdot \exp \left( -\frac{(x - \mu)^2}{2\sigma^2} \right), \text{ here } \mu = 0 \]

Boltzmann:
\[ \Delta S = k \cdot \ln(W) = C + k \cdot \ln(\exp(-x^2)) = C - k \cdot x^2 \]
with \( \Delta G = \Delta H \cdot T \cdot \Delta S \), \( \Delta H = 0 \)
\[ \Delta G = -T \cdot (C - k \cdot x^2) \]

\( \Delta G \): units of energy:
\[ \frac{\partial \Delta G}{\partial x} = F, \text{ (W=\int Fdx) } \Rightarrow F \propto \frac{T \cdot k \cdot x}{2} \text{ (temp. + elongation!)} \]

only needed:
\[ \Delta H \approx 0; \quad W_{(t)} \propto \text{Gauss} \]

See analogy for Gauss in crystallography! \( \Rightarrow \) Debye-Waller factor!
Why can we assume that Newton’s law could be correct?

Newton: \[ \frac{F}{A} = \sigma = \eta \cdot \frac{v}{d} = \eta \cdot \dot{\gamma} \]

Note: In Rheology Newton’s law is associated with \( \sigma = \eta \cdot \dot{\gamma} \),
not with his other law: \( F = m \cdot \ddot{x} = m \cdot a \).

Why not:

\[
\begin{align*}
\frac{F}{A} & \propto x \quad ? \\
F & \propto a, \quad a = \ddot{x} \quad ? \\
F & \propto \sqrt{\dot{\gamma} \frac{\pi}{2} \dot{\gamma}} \quad ?? \\
\text{why?}
\end{align*}
\]

Do we “buy” this?

We need proportionality between viscous force and velocity: \( F_{\text{viscous}} \propto v \)

Remember:

Law from Stokes: \( F = 6\pi \cdot \eta \cdot r \cdot v \) (F: e.g. gravity)

Note: unit of \( \eta \):

\[ \eta = \frac{F}{A} \cdot \frac{v}{d} = \frac{p \cdot d}{v} \left[ \frac{\text{Pa} \cdot \text{m} \cdot \text{s}}{\text{m}} \right] = \eta \left[ \text{Pa} \cdot \text{s} \right], \text{old: Poise}; 1 \text{Pa s} = 10 \text{ P}; 1 \text{ cP} = 1 \text{ mPas} \text{ (Poiseuille)}; \]

Typical values:

- Blood: \( 100 - 4 \text{ mPas} \) (thicker than water!; shear thinning)
- Glycerin
  - \( 0^\circ \text{C} \) : \( 10,000 \text{ mPas} \)
  - \( 20^\circ \text{C} \) : \( 1,400 \text{ mPas} \)
  - \( 60^\circ \text{C} \) : \( 60 \text{ mPas} \)
- Oil, SAE 10
  - \( 30^\circ \text{C} \) : \( 200 \text{ mPas} \)
- \( \text{H}_2\text{O} \): \( 1 \text{ mPas} \) (\( \Leftrightarrow \) memorize!)
- Air: \( 0.02 \text{ mPas} \)
Gedankenexperiment

(⇒ Prof. Sillescu, article Lord Rayleigh 1891! see Appendix A, p. 93-114)

Tube; big mass M; lots of particles with small mass m strike on mass M; M is moved with speed \( v_M \); What force is needed?

For M: \( \Delta l_M = v_M \cdot \Delta t \)
For m: \( \Delta l = v \cdot \Delta t \), same velocity for all small particles!

After time \( \Delta t \):

Average density of particles m: \( \rho = \frac{N}{\Delta l} \), number density, not mass density!

The mass M is hit by the following number of particles during \( \Delta t \):

\[
N^+ + N^- = \frac{1}{2} \cdot \rho \cdot (\Delta l - \Delta l_M) + \frac{1}{2} \cdot \rho \cdot (\Delta l + \Delta l_M) = \rho \cdot \Delta l = N
\]

50:50 probability that particles fly in correct direction

direction of particles

but \( N^- > N^+ \)!!
if we define a clash-rate:

\[ Z = \frac{N}{\Delta t} \quad \Rightarrow \quad \rho = \frac{N \cdot \Delta t}{\Delta l \cdot \Delta t} = \frac{N}{v \cdot \Delta t} = \frac{Z}{v} \quad \Rightarrow \quad Z = \rho \cdot v \]

\[ Z^+ = \frac{1}{2} \rho (v - v_M) = \frac{1}{2} Z \frac{v - v_M}{v} \]

\[ Z^- = \frac{1}{2} \rho (v + v_M) = \frac{1}{2} Z \frac{v + v_M}{v} \]

\[ Z = Z^+ + Z^- = \rho \cdot v \]

each particle transfers elastic impact onto mass M with relative momentum \( \tilde{p} = 2m\vec{v} \)

\[ p^+ = 2m(v - v_M) \]
\[ p^- = -2m(v + v_M) \]

In one time unit \( \Delta t \), this balances the outer force \( F \) needed to push mass M with velocity \( v_M \).

\[ F = Z^+ \cdot p^+ + Z^- \cdot p^- \]

\[ F = \frac{1}{2} Z \frac{v - v_M}{v} \cdot 2m(v - v_M) - \frac{1}{2} Z \frac{v + v_M}{v} \cdot 2m(v + v_M) \]

\[ = \frac{Z \cdot m}{v} \left[(v - v_M)(v - v_M) - (v + v_M)(v + v_M)\right] \]

\[ = \frac{Z \cdot m}{v} \left[v^2 - 2vv_M + v_M^2 - (v^2 + 2vv_M + v_M^2)\right] \]

\[ = \frac{Z \cdot m}{v} (-4vv_M) = -4mZ \cdot v_M \]

\[ \Rightarrow F \propto v_M \]

Friction is proportional to the velocity of the mass M.
Sir Isaac Newton
1642 – 1727

"Newton was the first to formulate a hypothesis regarding the magnitude of the force required to overcome frictional resistance in a viscous fluid."

Cf: Principia Mathematica, 1687.
Linear models: Hooke, Newton, Maxwell, Kelvin-Voigt …

incl. oscillatory excitation and response

Hooke – spring

\[
\sigma = G \cdot \gamma \quad \Rightarrow \quad \dot{\sigma} = G \cdot \dot{\gamma}
\]

Newton – dash-pot

\[
\sigma = \eta \cdot \gamma, \quad \dot{\gamma} = \frac{d\gamma}{dt}
\]

Math. def. of linear models:
A linear model is a mathematical description of the relation between stress and strain (respective: strain rate) where only linear terms of \( \gamma \) or \( \dot{\gamma} \) are used. Further more \( G \) and \( \eta \) are constant.

Experimental def.:
Linear response can be assumed if the response (stress, strain, strain rate) is large enough to be detected but still in a regime where \( G \) and \( \eta \) are not affected by the measurement.
The non-linear regime should be avoided for linear response measurements:

Dash-pot (DP) and spring (S) can be arranged in series or in parallel:

\[ G'' \]

rate sweep: \( \eta(\dot{\gamma}) \)

\[ G' \]

strain sweep: \( G'(\gamma_0), G''(\gamma_0) \)

fixed frequency

Dash-pot (DP) and spring (S) can be arranged in series or in parallel:

\[ \sigma_s = \sigma_{DP} \]

viscosity with a bit of elasticity (long term)

\[ \gamma = \gamma_s + \gamma_{DP} \]

\[ \dot{\gamma} = \dot{\gamma}_s + \dot{\gamma}_{DP} \]

Maxwell model (for liquids with some elastic response)

\[ \gamma_s = \gamma_{DP} \]

elasticity with a bit of viscosity (long term)

\[ \sigma = \sigma_s + \sigma_{DP} \]

\[ \sigma = G\gamma + \eta\dot{\gamma} \]

Kelvin-Voigt model (for solids with some viscous response)
Detailed analysis of Maxwell model

\[ \dot{\sigma} = G \cdot \dot{\gamma} \quad \Rightarrow \quad \dot{\gamma}_S = \frac{\dot{\sigma}}{G} \]

\[ \sigma = \eta \cdot \dot{\gamma} \quad \Rightarrow \quad \dot{\gamma}_{DP} = \frac{\sigma}{\eta} \]

\[ \dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \quad (1) \]

1. step-experiment

at time \( t > 0, \dot{\gamma} = 0 \)  (not in the dash-pot, but overall system!)

using (1):

\[ 0 = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \]

\[ \dot{\sigma} = -G_0 \frac{\sigma}{\eta} \]

\[ \frac{d\sigma}{\sigma} = -\frac{G_0}{\eta} dt' \quad \text{(see: first order kinetic, or Lambert-Beer)} \]

\[ \int_{\sigma(0)}^{\sigma(t)} \frac{1}{\sigma} d\sigma = -\frac{G_0}{\eta} \int_0^t dt' \]

\[ \ln(\sigma(t)) - \ln(\sigma(0)) = -\frac{G_0}{\eta} t \]

\[ \ln \frac{\sigma(t)}{\sigma(0)} = -\frac{G_0}{\eta} t \]

relaxation time

\[ \sigma(t) = \sigma(0) \cdot \exp\left(-\frac{G_0}{\eta} t\right) = \sigma(0) \cdot \exp\left(-\frac{t}{\tau}\right); \quad \tau = \frac{\eta}{G} \left[ \frac{\text{Pa} \cdot \text{s}}{\text{Pa}} = \text{s} \right] \]

\[ \sigma(0) = G_0 \cdot \gamma \quad \text{(for short time force is fully in spring)} \]

\[ \sigma(t) = G_0 \cdot \gamma \cdot \exp\left(-\frac{G_0}{\eta} t\right) \quad \Rightarrow \quad \frac{\sigma(t)}{\gamma} = G(t) = G_0 \cdot \exp\left(-\frac{G_0}{\eta} t\right) \]

\[ \lim_{t \to 0} G(t) = G_0 \]

Memory!
Oscillatory response:

**Hooke**

![Graph showing Hooke's law with oscillatory response](image)

distinguish: amplitude $\leftrightarrow$ elongation!

System has $\infty$ memory (⇒ stored energy ⇒ storage modulus $G'$)

**Newton**

![Graph showing Newton's law with oscillatory response](image)

distinguish:

$\omega$ [rad/s] $\leftrightarrow$ $\nu$, $f$ [1/s = Hz]

$\omega = \frac{2\pi}{T} = 2\pi \cdot \nu$

System has no memory (⇒ energy is lost ⇒ loss modulus $G''$)
Maxwell:

\[ \gamma(t) = \gamma_0 \cdot \exp(i \cdot \omega \cdot t) \]
\[ \dot{\gamma} = \gamma_0 \cdot (i \cdot \omega) \cdot \exp(i \cdot \omega \cdot t) = i \cdot \omega \cdot \gamma(t) \]

after initial time we reach dynamic steady state:

\[ \sigma(t) = \sigma_0 \cdot \exp(i \cdot (\omega \cdot t + \delta)) \]
\[ \dot{\sigma} = \sigma_0 \cdot (i \cdot \omega) \cdot \exp(i \cdot (\omega \cdot t + \delta)) = i \cdot \omega \cdot \sigma(t) \]

eq. (1):

\[ \dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \]
\[ i \cdot \omega \cdot \gamma(t) = \frac{i \cdot \omega \cdot \sigma(t)}{G} + \frac{\sigma}{\eta} \]
\[ \frac{G \cdot \gamma(t)}{\sigma(t)} = 1 + \frac{G}{i \cdot \omega \cdot \eta}, \quad \text{def.:} \quad \frac{\gamma(t)}{\sigma(t)} = \frac{1}{G'}(\omega) \]
\[ \frac{G}{G'(\omega)} = 1 + \frac{1}{i \cdot \omega \cdot \tau}, \quad \tau = \frac{\eta}{G} \]
\[ G = 1 + i \cdot \omega \cdot \tau \]
\[ G' = G \cdot \frac{i \cdot \omega \cdot \tau}{1 + i \cdot \omega \cdot \tau} \]
\[ G'' = G' \cdot i \cdot G''(\omega) = G \cdot \frac{i \cdot \omega \cdot \tau \cdot (1 - i \cdot \omega \cdot \tau)}{(1 + i \cdot \omega \cdot \tau) \cdot (1 - i \cdot \omega \cdot \tau)} \]
\[ = G \cdot \frac{\omega^2 \cdot \tau^2 + i \cdot \omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} = G \left( \frac{\omega^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} + i \frac{\omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} \right) \]
\[ \Rightarrow \quad \begin{align*}
G' &= G \cdot \frac{\omega^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} \\
G'' &= G \cdot \frac{\omega \cdot \tau}{1 + \omega^2 \cdot \tau^2}
\end{align*} \]

Note: \((a+b)(a-b)=a^2-b^2\)

Plot:

\[ G', G'' \text{ (linear scale)} \]

Why \(G' = \text{storage?}\)

Why \(G'' = \text{loss?}\)
\[ \lim_{\omega \to 0} G' = \lim_{\omega \to 0} \frac{\omega^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} = \lim_{\omega \to 0} \omega^2 \cdot \tau^2 \propto \omega^2 \]

\[ \approx 1 \]

\[ G' \propto \omega^2 \text{ for small } \omega \]

\[ \lim_{\omega \to 0} G'' = \lim_{\omega \to 0} \frac{\omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} = \lim_{\omega \to 0} \omega \cdot \tau \propto \omega^1 \]

\[ \approx 1 \]

\[ G'' \propto \omega^1 \text{ for small } \omega \]

**trick to memorize:** $G^a \propto \omega^b$, $a + b = 3$

\begin{figure}
\centering
\begin{tikzpicture}
\begin{axis}[
width=\textwidth,
height=\textwidth,
axis lines=left,
xlabel=$\omega \cdot \tau = 1$,
ylabel=log $G$,

domain=1:1000000000000000000,
samples=10000000000000000,

\addplot[smooth,mark=none,black]{\omega^2 \cdot \tau^2} node[above right]{$G'$} node[below right]{$1$};
\addplot[smooth,mark=none,black]{\omega \cdot \tau} node[above right]{$G''$} node[below right]{$2$};
\end{axis}
\end{tikzpicture}
\end{figure}

**Note for “NMR-People”:**

FID: $M \propto \exp\left(-\frac{t}{T_2}\right) \Rightarrow$ Lorentz – shape in $\omega$

\begin{figure}
\centering
\begin{tikzpicture}
\begin{axis}[
width=\textwidth,
height=\textwidth,
axis lines=left,
xlabel=\omega,
ylabel={Re ($\hat{G}'$)},

domain=0:1000000000000000000,
samples=10000000000000000,

\addplot[smooth,mark=none,black]{\frac{\tau}{\omega^2 \cdot \tau^2 + 1}} node[above right]{$G''$};
\addplot[smooth,mark=none,black]{\frac{-\omega \cdot \tau^2}{\omega^2 \cdot \tau^2 + 1}} node[above right]{$G'$};
\end{axis}
\end{tikzpicture}
\end{figure}

Lorentz:

\[
\begin{align*}
\Re(\omega) &= \frac{\tau}{\omega^2 \cdot \tau^2 + 1} \\
\Im(\omega) &= \frac{-\omega \cdot \tau^2}{\omega^2 \cdot \tau^2 + 1}
\end{align*}
\]

Factor $\omega$ missing

in Rheology: $\omega \geq 0$ !!
\( G^{*}_{(\omega \to 0)} = G^{'}_{(\omega \to 0)} = G \)  
(module of spring within Maxwell-element)

width of relaxation spectrum for \( G^{*} \):

\[
G^{*} = G \cdot \frac{\omega \cdot \tau}{\omega^{3} \cdot \tau^{2} + 1}
\]

Set \( \tau \) to \( \tau = 1 \):

\[
G^{*} = G \cdot \frac{\omega}{\omega^{2} + 1}; \quad G = 1
\]

Maximum at:

\[
\frac{dG^{*}_{(\omega)}}{d\omega} = 0 = \frac{1}{\omega^{2} + 1} - \frac{\omega}{(\omega^{2} + 1)^{2}} \cdot 2\omega = 0
\]

\[
\frac{1}{\omega^{2} + 1} = \frac{2\omega^{2}}{(\omega^{2} + 1)^{2}} \cdot (\omega^{2} + 1)
\]

\[
1 = \frac{2\omega^{2}}{\omega^{2} + 1}
\]

\[
\omega^{2} + 1 = 2\omega^{2}
\]

\[
1 = \omega^{2}
\]

\[
\omega = \pm 1 \quad \text{physically meaningful: } \omega = +1
\]

\[
G^{*}_{(\omega=1)} = G \cdot \frac{1}{1+1} = \frac{1}{2} G
\]

**full width at half maximum, \( \omega_{1}, \omega_{2} \)?**

**fwhm**

\[
\frac{1}{G} = \frac{\omega}{\omega^{2} + 1}
\]

\[
\frac{1}{4} \omega^{2} + \frac{1}{4} = \omega
\]

\[
\frac{1}{4} \omega^{2} - \omega + \frac{1}{4} = 0
\]

\[\[\]\]
remember: 

\[ ax^2 + bx + c = 0 \]

\[ x_{1/2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ \omega_{1/2} = \frac{1 \pm \sqrt{1 - 4 \cdot \frac{1}{4} \cdot \frac{1}{4}}}{1/2} \]

\[ = 2 \cdot \left(1 \pm \sqrt{\frac{3}{4}}\right) \]

\[ = 2 \pm \sqrt{3} \]

\[ \omega_1 = 3.732 \]

\[ \omega_2 = 0.268 \]

ratio: \[ \log_{10} \frac{\omega_1}{\omega_2} = 1.14 \]

The full width at half maximum (fwhm) of a single exponential relaxation is 1.14 decades in frequency space.

\[ G^*_{(\omega)} = \frac{\sigma^*}{\gamma} = G'_{(\omega)} + i \cdot G''_{(\omega)} \]

\[ \Rightarrow \sigma^* = G^* \cdot \gamma^*; \quad \gamma = \gamma_0 \cdot \exp(i \cdot \omega \cdot t), \quad \dot{\gamma} = i \omega \cdot \gamma_0 \cdot \exp(i \cdot \omega \cdot t) \]

\[ \Rightarrow \sigma^* = \left[ \frac{G'_{(\omega)} + i \cdot G''_{(\omega)}}{i \omega} \right] \cdot \dot{\gamma} \]

\[ = \eta^* \]

\[ \Rightarrow i \omega \cdot \eta^* = G^* \quad \text{units: [1/s \cdot Pa \cdot s = Pa]} \]

[to memorize: “iong”, i omega \( \eta \) equals G]

\[ \eta^* = \eta' + i \eta'' \]

\[ |\eta^*| = \sqrt{\eta'^2 + \eta''^2} \]

\[ \omega \cdot |\eta^*| = |G^*| \]
Phase lag $\delta$: \[ \tan \delta = \frac{G^*}{G'} \]

Experimental advantage: $G''$, $G'$ extensive quantities
\[ \tan \delta \] intensive quantity

If, e.g. filling factor is “bad”, $G'$ is wrong, $G''$ is also wrong, but $G''/G'$ is still accurate

$\Rightarrow \tan \delta$ is generally very reproducible

\[ \frac{\Delta G' \cdot \Delta G''}{G' \cdot G''} \approx 10\% \] typical error margin for rheological measurements
Chapter 13, The Group is Prepared

1.9 James Clerk Maxwell

Chapter 13, The Group is Prepared
Essay: James Clerk Maxwell (1831–1879)

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Im ersten Teil seines Artikels „On Faraday’s Lines of Force“ (1855–1856) entwickelte Maxwell eine Analogie zwischen den elektrischen und magnetischen Feldlinien und den Stromlinien einer bewegten, inkompressiblen Flüssigkeit. Mit dieser Analogie konnte Maxwell viele Beobachtungen Faradays erklären, und er leitete

James Clerk Maxwell (1831–1879) (American Institute of Physics, AIP, Emilio Segré Visual Archives)


Weiterhin setzte Maxwell voraus, dass das Medium elastisch ist. Auf diese Weise ergeben sich in Maxwells Modell magnetische Felder aus Rotationen innerhalb des Mediums und elektrische Felder aus seiner elastischen Verzerrung. Jeder elastische Stoff überträgt jedoch Wellen. In Maxwells Medium ergab sich die
Wellengeschwindigkeit aus dem Verhältnis von elektrischer zu magnetischer Kraft. Maxwell verwendete die Zahlen für die Konstanten $\varepsilon_0$ und $\mu_0$, die Kohlrusch und Weber als Ergebnis eines Experiments im Jahre 1856 erhalten hatten und setzte sie in die Gleichungen, die aus seinem Modell folgten, ein. Nach genaueren Berechnungen kam er zu dem erstaunlichen Ergebnis, daß die Ausbreitungsgeschwindigkeit gleich der Lichtgeschwindigkeit ist (siehe Abschnitt 29.3).


Without any mathematics: step experiments (step in stress or step in strain)

\[ \gamma(t) = \frac{\sigma}{\eta}, \quad \gamma(t_a) = \frac{\sigma}{G} \]

Kelvin-Voigt model

2nd possibility:
strain step:

\[ \gamma \sim \exp\left(-\frac{t}{\tau}\right) \]

Maxwell - model
More complex models (but still linear models!):

![Graph showing memory behavior](image)

Memory (Gedächtnis)

The memory of the system might be defined for a step strain experiment as follows:

\[
\frac{d\sigma}{\gamma dt} = \frac{dG}{dt}
\]

\[
M_{(t)} = -\frac{dG_{(t)}}{dt}, \text{ minus sign, so that } M_{(t)} \text{ is positive;}
\]

\[
\Rightarrow d\sigma = -M \cdot \gamma dt
\]

\[
\sigma_{(t)} = \int_{0}^{\sigma} d\sigma = -\int_{t'=-\infty}^{t'} M_{(t-t')}\gamma(t') \, dt'
\]

Memory depends only on elapsed time: \( t - t' = s, \ dt' = -ds \)

\[
\sigma_{(0)} = -\int_{0}^{\infty} M_{(t)}\gamma_{(t-s)} \, ds
\]

exchange of limits and: \( dt' = -ds \)
for infinite small motion:
\[ d\sigma = Gd\gamma \]
\[ d\sigma = G \frac{d\gamma}{dt} dt = G\dot{\gamma} dt \]
\[ \sigma = \int_{t_0}^t G_{(t-t')} \dot{\gamma}_{t'} dt', \quad s = t - t' \]
\[ \sigma = \int_0^t G_{(t-t')} dt \]

if we have a modulus function with an exponential memory:

monomodal: \[ G_{(t)} = G_0 \exp\left(-\frac{t}{\tau}\right) \Rightarrow \sigma_{(t)} = \int_{-\infty}^t G_0 \exp\left(-\frac{(t-t')}{\tau}\right) \dot{\gamma}_{t'} dt' \]

Improvement of this model: several relaxation times

**Multimode models**

\[ \Rightarrow G_{(t)} = \sum_{k=1}^N G_k \exp\left(-\frac{t}{\tau_k}\right), \quad N \text{- mode model} \]

\[ \Rightarrow \sigma = \int_{-\infty}^t \sum_{k=1}^N G_k \exp\left(-\frac{t}{\tau_k}\right) \dot{\gamma}_{(t')} dt' \]

picture for multimode Maxwell-model:

Also possible: multimode Kelvin-Voigt (several Kelvin-Voigt models in series);

Under oscillatory shear, a multimode Maxwell-model will respond as follows (see next page)

remember: fwhm for single Maxwell: 1.14 decades \( \Rightarrow \) spacing ?! in \( \omega \)

not uncommon for polymers: 5 – 7 decades relaxation time distribution
To reduce the need of maths for a while, a glossary on important rheological terms is inserted:

**Glossary**

a) Lamellar flow

\[ \gamma = \frac{x}{h} \]
\[ \dot{\gamma} = \frac{1}{h} \frac{dx}{dt} = \frac{1}{h} \cdot v \]

For this model: \( \dot{\gamma} \neq \dot{\gamma}_{(h)} \), in contrast: tube

Shear deformation is equally distributed throughout the sample. For sliding plate geometry: the points of similar elongation amplitude form lamellae.

For high shear rates, generally instabilities can occur (Reynolds number) and the lamellar flow profile is disrupted.

Other possibility: plug-flow (tooth paste!)

---

b) Reynolds number

The Reynolds number describes the ratio between the kinetic energy of a system and the energy lost by viscous flow.

\[ \text{Re} = \frac{E_{\text{kin}}}{E_{\text{viscous}}} \]

For \( \text{Re} > 2000 \) we find transition between lamellar \((F \propto \dot{\gamma})\) and turbulent \((F \propto \dot{\gamma}^2)\) flow!

For a capillary (diameter: circle) we find: \( \text{Re} = \frac{2\pi \cdot v \cdot r \cdot \rho}{\eta} \)

\( r: \) radius, \( \rho: \) density, \( v: \) avg. velocity, \( \eta: \) viscosity
example:
Aorta (main blood vessel close to the heart):

\[ r = 1 \text{ cm} = 0.01 \text{ m} \]
\[ \eta = 4 \text{ mPas} = 0.004 \text{ N/m}^2 \cdot \text{s} ; \quad 1 \text{ N} = 1 \text{ kg} \cdot \text{m} / \text{s}^2 \]
\[ \rho = 1000 \text{ kg/m}^3 \]
\[ v = 0.3 \text{ m/s} \]

\[ \text{Re} = \frac{2 \cdot 10^{-2} \cdot 10^3 \cdot 3 \cdot 10^{-1}}{4 \cdot 10^3} \left[ \frac{\text{m} \cdot \text{s}^2 \cdot \text{m}^2 \cdot \text{kg} \cdot \text{m}}{\text{kg} \cdot \text{m} \cdot \text{s} \cdot \text{m}^2 \cdot \text{s}} \right] = 1500, \text{close to transition: lamellar} \rightarrow \text{turbulent!} \]

c) Cox-Merz-rule

The Cox-Merz-rule is an empirical rule that connects the shear rate dependent viscosity with the absolute value of the frequency dependent complex viscosity, as calculated by:

\[ i \omega \cdot \eta^*_i(a \omega) = G^*(a \omega) \]

via:

\[ \eta_0 = |\eta^*(a \omega)|, \quad a \approx 1 \quad (\text{experimentally}) \]

\[ \Rightarrow \eta_0 = |\eta^*(a \omega)| ; \quad \text{note} : \omega \neq \text{frequency} \nu ; \omega = 2\pi \cdot \nu \]

This rule holds only for rheologically simple materials!

\[ \eta(\dot{\gamma}) = |\eta^*(a \omega)| = \left\{ \frac{G'_{(a \omega)}^2 + G''_{(a \omega)}^2}{\omega} \right\} \]

\[ G'_{(a \omega)} = G \cdot \frac{\omega^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} \]
\[ G''_{(a \omega)} = G \cdot \frac{\omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} \]

e.g. Maxwell-model:
\[
\lim_{\omega \to \infty} \left| \eta^*(\omega) \right| = \lim_{\omega \to \infty} \left| \frac{G^2}{\omega} \right| \propto \left| \frac{\omega^2 \cdot \tau^2}{\omega} \right| = \text{const.} = \eta_0
\]

\[
\lim_{\omega \to \infty} \left| \eta^*(\omega) \right| = \lim_{\omega \to \infty} \left| \frac{G^2}{\omega} \right| \propto \left| \frac{\omega^2 \cdot \tau^2}{\omega} \right| \propto \omega^{-1}
\]

\[
\log\left(\left| \eta^*(\omega) \right| \right)
\]

for single Maxwell-model

d) Lissajous figures

oscillatory shear

\[
\gamma \sim \cos(\omega t), \quad \sigma \sim \sin(\omega t)
\]

vector description of circle

general for ellipse:

\[
\begin{pmatrix}
x(t) \\ y(t)
\end{pmatrix} = \begin{pmatrix}
\cos(\omega t) \\ \cos(\omega t - \delta)
\end{pmatrix}
\]

\[
\tan \frac{\delta}{2} = \frac{b}{a}
\]

phase lag
Linear response: (⇒ ellipse) Contains symmetry elements for Lissajous figure:
2 mirror plains + point symmetry

In case of non-linearity: only point symmetry (⇒ I_{(301)}, I_{(501)}, …)

Note: deviations < 2-3% of sinusoidal response can generally not be seen in Lissajous figures!! ⇒ much less sensitive compared to FT-Rheology (see later)

e) Shear thinning

*(deutsch auch: Strukturviskos), pseudoplastic*

monotonically decaying viscosity flow curves; viscosity as a function of shear rate in steady state, so no implicit memory involved.

To describe shear-rate dependent viscosity, empirical equations with 1, 2, 3, 4 parameters are used, e.g.:

1 parameter: Newton’s law! ⇒ η = η₀

Ostwald-de Waele (example for 2 parameter model)

η = b ⋅ γ⁻ᵃ

a: scaling parameter, shear thinning exponent; a∈[0, 1] : 0 ⇒ Newton

1 ⇒ max. shear thinning exponent
if $a = 1$: $F = \eta \cdot \dot{\gamma} = b \cdot \dot{\gamma}^1 \cdot \dot{\gamma} = b$

force independent of $\dot{\gamma}$, force is constant!

at $\dot{\gamma} = 1 \Rightarrow \eta = b$

**Carreau** (example for 3 parameter model)

$$\eta = \frac{\eta_0}{1 + (\beta \cdot \dot{\gamma})^c}$$

also other def. for Carreau: $\eta = \frac{\eta_0}{1 + \beta \cdot \dot{\gamma}^c}$ (not equal!)

c: scaling parameter $c \in [0, 1]$

$\beta$: pivot point (knee),

if $\dot{\gamma} = \frac{1}{\beta} \Rightarrow \eta = \frac{\eta_0}{1 + \left(\beta \cdot \frac{1}{\beta}\right)^c} = \frac{\eta_0}{1 + 1^c} = \frac{\eta_0}{2}$

**4 parameter models:**

- further parameter needed to: e.g. model the width of the knee as the next parameter

- introduction of “second Newtonian plateau” for high shear rates

- e.g.: $\eta(\dot{\gamma}) = \frac{\eta_0}{(1 + (\beta \cdot \dot{\gamma})^c)^d}$

  where $cd < 1$

  **WHY??**
**Thixotropy**  shear thinning + long memory (⇒ Hysteresis)

A decrease of apparent viscosity under constant shear rate, followed by a gradual recovery when the stress or shear rate is removed. The effect is time dependent.

greek: thixis: shake
trepo: changing

in principle we can have two types of hysteresis:

or:

**Shear thickening** (≠ rheopex ≠ dilatancy)

\[ \eta(\dot{\gamma}_1) > \eta(\dot{\gamma}_2) \text{ for } \dot{\gamma}_1 > \dot{\gamma}_2 \]

**Anti-thixotropy**  shear thickening + memory (⇒ Hysteresis)
or:

Rheopexy
Structure is generated without shear so that viscosity or module increases as a function of time only (not as a result of applied shear).

Dilatancy
Why is wet sand “dry” for a few seconds when we walk barefoot on the beach? ⇒ dilatancy!
Application of shear changes (reduces) level of liquid in packed spheres (granula). This can cause shear thickening.

Experiment:

Dilatation: Ausweitung

Bingham plastic
(the “evil” in the ketchup bottle!)
(Deutsch: strukturviskose Flüssigkeit mit Fließgrenze = plastisches Fluid)

\[ \sigma = \eta \cdot \dot{\gamma} + \sigma_{yield} \]
\[ \sigma_{yield} = G \cdot \gamma_{yield} \]

\[ \sigma_{yield} \text{ Ketchup } \approx 20 \text{ Pa} \]
Extension of Bingham-model: Herschel-Bulkley

include: powerlaw for viscosity \( \sigma = \sigma_{\text{m}} + k \cdot \dot{\gamma}^n \)

for measurements \( \Rightarrow \) vane rheometer (see later)

Dimensionless groups

Reynolds (already covered), Deborah, Péclet, Taylor

For several phenomena in nature only unitless quantities seem to play the important role:

e.g.:  1) Arrhenius group

\[
k_r = A \cdot \exp \left( \frac{-E_a}{RT} \right)
\]

unitless

if \( E_a << RT \) \( \Rightarrow k_r \approx A \)

if \( E_a >> RT \) \( \Rightarrow k_r << A, \) slow down

2) kinetics

\[
A_{\text{to}} = A_{\text{to}} \cdot \exp(-k_r \cdot t)
\]

\( k_r \cdot t >> 1 \) basically complete reaction

\( k_r \cdot t << 1 \) just started
Deborah number

[book of judges 5.5, song of Deborah: “Even the mountains flowed before the Lord ...”]

remember:

\[ \sigma_{0}\gamma/G = \gamma \exp\left(-\frac{G \cdot t}{\eta}\right) \]

\[ \frac{1}{De} = \frac{G \cdot t}{\eta}, \quad \frac{\eta}{G} = \tau \]

\[ De = \frac{\eta}{G \cdot t} = \frac{\tau}{t} \] \leftarrow internal relaxation time

\[ De \gg 1, \text{ short observation time } \Rightarrow \text{ solid like} \]

\[ De \approx 1, \text{ viscoelastic response} \]

\[ De \ll 1, \text{ long observation time } \Rightarrow \text{ liquid response} \]

if we take:

\[ \frac{1}{t} = \dot{\gamma} \]

under oscillatory shear:

\[ \gamma = \gamma_0 \cdot \cos(\omega \cdot t) \]

\[ \dot{\gamma} = \omega \cdot \gamma_0 \cdot \left(-\sin(\omega \cdot t)\right) \]

\[ De = \dot{\gamma} \cdot \tau \approx \omega \cdot \gamma_0 \cdot \tau \] e.g. longest relaxation time in polymer

Note: Generally Deborah-nr. is not precisely defined \( (\dot{\gamma} = \omega \cdot \gamma_0, \text{ or } \dot{\gamma} = \omega) \), and there is confusion with Weissenberg-nr.: \( Wi \equiv \dot{\gamma} \cdot \tau \)

Weissenberg normally used in the context of: \( \rightarrow \dot{\gamma} = \text{const.}, \text{ steady shear} \)

\( \rightarrow \text{ with respect to normal forces} \)

Pipkin diagram:
Péclet number

Stokes: \( F = 6\pi \cdot \eta \cdot r \cdot v \)
\( F = \xi \cdot v \)

Stokes-Einstein for diffusion coefficient \( D \):
\[
D = \frac{k T}{\xi} = \frac{k T}{6\pi \cdot \eta \cdot r}
\]

Time needed to displace object by distance \( r \):
\[
t = \frac{r^2}{D} = \frac{6\pi \cdot \eta \cdot r \cdot r^2}{k T} = \frac{6\pi \cdot \eta \cdot r^3}{k T}
\]

\[
Pe = t \cdot \dot{\gamma} = \frac{6\pi \cdot \eta \cdot r^3 \cdot \dot{\gamma}}{k T} = \frac{6\pi \cdot r^3 \cdot \sigma}{k T}
\]
\[
\sigma = \eta \cdot \dot{\gamma}
\]

frequently used in context with colloids;

Taylor vortex

moving bob

moving cup

secondary flow
caused by inertia

\( \Omega \)

\( \rho \)

\( \Omega \): angular velocity

\( \rho \): density

\( \Omega \) to Taylor vortices

less sensitive
to Taylor vortices

more sensitive
to Taylor vortices

\[
Ta = \frac{\rho^2 \cdot \Omega^2 \cdot (R_o - R_i)^3 \cdot R_i}{(\eta(\dot{\gamma}))^2} < 3400
\]
Units for $T_a$ (only check, no proof):

$$T_a = \left[ \frac{\text{kg} \cdot \text{m}^4}{\text{m}^6 \cdot \text{s}^2 \cdot \left( \frac{\text{N}}{\text{m}^2 \cdot \text{s}} \right)^2} \right] = \frac{\text{kg} \cdot \text{m}^4}{\text{m}^2 \cdot \text{s}^4 \cdot \text{N}^2} = \left( \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \right) \cdot \frac{1}{\text{N}^2} = 1$$

$\Rightarrow$ unitless quantity

--- END OF GLOSSARY ---
What do we expect for $\eta_{(p,T)}$?

Gases
Mean free path length: $l$

Cross-section: $A = \pi (2r)^2 = 4\pi \cdot r^2$

In physics: $\sigma$ (confusing for rheology)

one particle

\[ \rho = \frac{1}{\Delta V} = \frac{1}{L \cdot A} = \frac{1}{L \cdot 4\pi \cdot r^2} \]

volume

\[ \Rightarrow L = \frac{1}{\rho \cdot A} = \frac{1}{N \cdot 4\pi \cdot r^2} \]

normal conditions (Gas, 1 bar, 300 K):

\[ pV = nRT \Rightarrow 1\text{Mol} \approx 22.4\text{l} \]

\[ \rho = \frac{n}{V} = \frac{6 \cdot 10^{23}}{22.4 \cdot 10^{-3} \text{m}^3} \approx 3 \cdot 10^{25} \text{m}^{-3} \]

\[ A \approx 4\pi \cdot \left(10^{-10}\right)^2 \text{m}^2 \approx 10^{-19} \text{m}^2 \]

\[ r \approx 1\text{Å} \]

\[ \Rightarrow L = \frac{1 \text{m}^3}{3 \cdot 10^{-25} \cdot 10^{-19} \text{m}^2} = \frac{1}{3 \cdot 10^6} \text{m} = \frac{1}{3} \mu\text{m} = 300\text{nm} \]

mean free path length

clash rate:

\[ \frac{1}{\Delta t} \]

\[ v = \frac{L}{\Delta t}, \quad v \approx 330 \frac{\text{m}}{\text{s}} \quad \text{more precise:} \quad \frac{1}{2}mv^2 = \frac{3}{2}RT \]

\[ \Delta t = \frac{L}{v} = \frac{3 \cdot 10^{-6}}{330 \frac{\text{m}}{\text{s}}} = \frac{1}{10^9} \text{s} \]

typical clash rate: \[ \frac{1}{\Delta t} = 10^9 \frac{1}{\text{s}} \]
velocity distribution (Maxwell-Boltzmann)
(see Physical Chemistry books for details)

\[ P(v) dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left( -\frac{mv^2}{2kT} \right) \cdot v^2 dv \]

\[ \bar{v} = \left( \frac{8kT}{\pi \cdot m} \right)^{\frac{1}{2}} = \left( \frac{2.54 kT}{m} \right)^{\frac{1}{2}} \]

simple picture: \( \bar{v} = \left( \frac{3kT}{m} \right)^{\frac{1}{2}} \)

\[ \frac{1}{2} m v^2 = \frac{3}{2} kT \]

note: \( \bar{v}^2 \neq v^2 \), generally true for distributions

1st moment  
2nd moment

model:
L: mean free path length

\[ \begin{align*}
\text{momentum transport if particle leaves layer } x_{i+1} & \text{ to go to layer } x_i : \quad m \cdot L \cdot \left( \frac{dv_s}{dx} \right) \\
\text{Number of particles } n \text{ leaving layer } x_{i+1} & \text{ in unit time in direction } x_i : \\
\text{density of particle } \rho_n & = \frac{N}{V_0} = \frac{N}{A \cdot L} = \frac{N}{A \cdot v \cdot t} \Rightarrow \rho_n \cdot A \cdot v \cdot t = N \\
\text{only half fly in correct direction: } \quad \frac{1}{2} \cdot \rho_n \cdot A \cdot v \cdot t = n = \frac{1}{2} \cdot \rho_n \cdot v = \frac{1}{2} \cdot \frac{N}{V_0} \cdot v
\end{align*} \]
\[ \frac{\Delta p}{\Delta t} = \frac{1}{2} \cdot \frac{N \cdot v \cdot m \cdot L}{V_0} \cdot \left( \frac{dv_s}{dx} \right) \]

In unit time, unit area the following momentum \( p \) is transferred:

This must be equal to the force \( F = \eta \cdot \frac{dv_s}{dx} \)

\[ \Rightarrow \eta = \frac{1}{2} \cdot \frac{N \cdot m \cdot v \cdot L}{V_0} = \frac{1}{2} \cdot \rho \cdot v \cdot L \]

Using: \( L = \frac{V_0}{N \cdot 4\pi \cdot r^2} \)

\[ \Rightarrow \eta = \frac{1}{2} \cdot \frac{N \cdot m \cdot v \cdot V_0}{N \cdot 4\pi \cdot r^2} = \frac{1}{8} \cdot \frac{m \cdot v}{\pi \cdot r^2} \]

Using: \( v \approx \left( \frac{3kT}{m} \right)^{\frac{1}{2}} \)

\[ \eta = \frac{1}{8} \cdot \frac{\sqrt{m} \cdot \sqrt{3kT}}{\pi \cdot r^2} \propto \sqrt{\frac{T}{m}} \]

Viscosity of gases is:
- independent of density!
- therefore independent of pressure! \( \eta_{(p,T)} = \eta_{(T)} \)!
- a function of mass and temp. of particles! \( \eta \propto \sqrt{T} \)!

Viscosity of liquids, temperature dependence

- no shear: Boltzmann distribution for particles making transition from left to right;

Typically 1 vacancy per shell (= 12 neighbours)
\( \approx 5-10\% \) free volume
No shear (density diff. amorphous \( \leftrightarrow \) crystall!)

\[ N = \frac{kT}{h} \cdot \exp \left( -\frac{E^*}{RT} \right), \quad E^* : \text{activation energy} \]
- shear: force on single molecule, typical distance $r$

$$F = \sigma \cdot A = \sigma \cdot r^2$$

apply this force for half distance $r$

$$E = \sigma \cdot r^2 \cdot \frac{r}{2} = \sigma \cdot \frac{r^3}{2} = \frac{\sigma \cdot V_m}{2}$$

$V_m$: average occupied volume per molecule,

$V_M$: volume per N_L molecules

So effective jumps $N$ are jumps to the right $N$ minus jumps to the left $N$

$$(1) \quad N = N_+ - N_- = \frac{k_B \cdot T}{h} \left[ \exp \left( -\frac{E^* - \sigma \cdot V_M}{2 \cdot RT} \right) - \exp \left( -\frac{E^* + \sigma \cdot V_M}{2 \cdot RT} \right) \right]$$

The shear rate is the effective number of jumps in one second divided by layer thickness in unit time:

$$(2) \quad \frac{\nu}{d} = \dot{\gamma} = \frac{r \cdot N}{r} \approx N$$

(2) in (1):

$$\dot{\gamma} = \frac{k_B \cdot T}{h} \cdot \exp \left( -\frac{E^*}{RT} \right) \left[ \exp \left( \frac{\sigma \cdot V_M}{RT} \right) - \exp \left( -\frac{\sigma \cdot V_M}{RT} \right) \right]$$

remember: $\sinh(x) = \left( e^x - e^{-x} \right) / 2$

$$\lim_{x \to 0} \sinh(x) = \lim_{x \to 0} \left[ (e^x - e^{-x}) / 2 \right] = \lim_{x \to 0} \left( (1 + x - 1 + x) / 2 \right) = x$$

$$\Rightarrow \dot{\gamma} = \frac{k_B \cdot T}{h} \cdot \exp \left( -\frac{E^*}{RT} \right) \cdot 2 \cdot \frac{V_M}{RT} \cdot \sigma$$

$$\dot{\gamma} = \frac{1}{\eta} \cdot \sigma \quad \frac{V_M}{R} = \frac{V_m \cdot N_L}{R} = \frac{V_m}{k_B}$$

$$\Rightarrow \eta_{(\nu=0)} = \frac{h}{V_m} \cdot \exp \left( +\frac{E^*}{RT} \right)$$
- Arrhenius for T-dependence
- increase of free volume reduces viscosity (hopping probability ↑)
- $E_a \uparrow \Rightarrow \eta \uparrow$; $E_a \downarrow \Rightarrow \eta \downarrow$
- Pressure dependence via average volume per molecule ⇒ weak p-dependence

Stress-strain tensor and normal forces

(Why might we need a tensorial property?!)”

So far we have used $\vec{v}, \vec{x}$ and $\vec{F}$ as collinear (parallel) vectors
⇒ scalar description
If we would like to extend this, what happens if $\vec{x}$ and $\vec{F}$ are not parallel?

We need a transformation between $\vec{x} \leftrightarrow \vec{F}$.

This transformation should:
1. transform a vector into a vector
2. transform a plane into a plane
3. have a fixed origin in both systems

1-3 define an affine coordination transformation. This transformation is linear if the new system $\vec{y} = (y_1, y_2, y_3)$ is generated out of the old system $\vec{x} = (x_1, x_2, x_3)$ by a linear set of equations:
\[y_1 = a_{11} \cdot x_1 + a_{12} \cdot x_2 + a_{13} \cdot x_3\]
\[y_2 = a_{21} \cdot x_1 + a_{22} \cdot x_2 + a_{23} \cdot x_3\]
\[y_3 = a_{31} \cdot x_1 + a_{32} \cdot x_2 + a_{33} \cdot x_3\]

if we introduce matrix (3 by 3 matrix, second rank tensor)
\[
\mathbf{A} = \begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix},
\]
we can write: \[\vec{y} = \mathbf{A} \cdot \vec{x}\]

Example for a simple rotation of a vector \(\vec{x}\) in 2 dimensions:

Rotation around origin by angle \(\varphi\)
in math. positive sense (counterclockwise)

\[\vec{x} = \begin{pmatrix}
\cos \alpha \\
\sin \alpha
\end{pmatrix}, \quad \vec{y} = \begin{pmatrix}
\cos (\alpha + \varphi) \\
\sin (\alpha + \varphi)
\end{pmatrix}\]

use of addition theorems:
\[
\cos (\alpha + \varphi) = \text{Re}(e^{i(\alpha+\varphi)}) = \text{Re}(e^{i\alpha} \cdot e^{i\varphi}) = \text{Re}((\cos \alpha + i \cdot \sin \alpha)(\cos \varphi + i \cdot \sin \varphi))
\]
\[
= \text{Re}(\cos \alpha \cdot \cos \varphi - \sin \alpha \cdot \sin \varphi + i \cdot (...))
\]
\[
= \cos \alpha \cdot \cos \varphi - \sin \alpha \cdot \sin \varphi
\]

analogue for the sine (using the imaginary part):
\[
\sin (\alpha + \varphi) = ... = \cos \alpha \cdot \sin \varphi + \sin \alpha \cdot \cos \varphi
\]

\[\Rightarrow \vec{y} = \begin{pmatrix}
\cos (\alpha + \varphi) \\
\sin (\alpha + \varphi)
\end{pmatrix} = \begin{pmatrix}
\cos \varphi & -\sin \varphi \\
\sin \varphi & \cos \varphi
\end{pmatrix} \cdot \begin{pmatrix}
\cos \alpha \\
\sin \alpha
\end{pmatrix} = \mathbf{A} \cdot \vec{x}\]
Definition of the extra stress tensor (right handed system!)

This results in the following extra stress tensor:

\[
\tau = \begin{pmatrix}
\tau_{11} & \tau_{12} & \tau_{13} \\
\tau_{21} & \tau_{22} & \tau_{23} \\
\tau_{31} & \tau_{32} & \tau_{33}
\end{pmatrix}
\]

The stress-tensor \( \sigma \) is the sum of the extra stress tensor plus the hydrostatic pressure. The hydrostatic pressure acts equally along the \( \tau_{11}, \tau_{22}, \) and \( \tau_{33} \) components.

\[
\sigma = -p \cdot \bar{E} + \bar{\tau}, \quad p: \text{pressure}, \quad \bar{E}: \text{unit tensor} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

Properties of the extra stress tensor

- The tensor is symmetric (like many in quantum mechanics, see e.g. Fermi’s golden rule):
  \[
  \tau_{ij} = \tau_{ji},
  \]
  \( \Rightarrow \) reduction from 9 variables to 6 variables

- forces that pull have positive prefactor
- forces that push have negative prefactor

The tensor has properties that are invariant under transformation of coordinates:

1\textsuperscript{st} invariant: Trace of the tensor \( \bar{A} \)

\[
I_1 = \text{tr} \bar{A} = \sum_{i=1}^{3} a_{ii} = a_{11} + a_{22} + a_{33}
\]

indices \( \tau_{ij} : \)

i: the force acts on a plane that is normal to the basis vector \( i \)

j: the force acts in the direction of the basis vector \( j \)
(see also quantum mechanic books \( \mathbb{1} = \sum_{i=1}^{\infty} |\alpha_i\rangle \langle \alpha_i| \))

\[ I_2 = \frac{1}{2} \left[ \text{tr} (\overline{A})^2 - \text{tr} (\overline{A}) \right] \]

\[ I_3 = \det \overline{A} = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \]

Due to the first invariant \( \tau_{11} + \tau_{22} + \tau_{33} = 0 \) the trace of the extra stress tensor has only two variables. \( \Rightarrow \begin{cases} N_1 = \tau_{11} - \tau_{22} \\ N_2 = \tau_{22} - \tau_{33} \end{cases} \) normal stress differences

What do normal stress differences mean?

- assume shear stress along \( \tau_{21} \)

\( \tau_{22} : \) force that pushes plates apart
\( \tau_{33} : \) force that pushes material into plate-plate geometry
\( N_1 = \tau_{11} - \tau_{22} : \) first normal stress difference, generally positive
\( N_2 = \tau_{22} - \tau_{33} : \) second normal stress difference, generally negative \( |N_1| > |N_2| \)

to memorize: \( N_a = \tau_{aa} - \tau_{a+1, a+1} \)
What do we expect for $N_{1,2}(\dot{\gamma}, \gamma_0)$?

- $N_{1,2}$ should only be a function of $\dot{\gamma}$ due to kinetic nature of the phenomenon, e.g.:

$$N_{1,2} = a + b \cdot \dot{\gamma} + c \cdot \dot{\gamma}^2 + ... \quad a, b, c : \text{constant}$$

- if we do not apply a shear rate $N_{1,2}$ should be 0 $\Rightarrow a = 0$
- if we apply a shear rate, the force $N_{1,2}$ should be independent of the direction

$$\Rightarrow N_{1,2}(\dot{\gamma}) = N_{1,2}(\dot{\gamma})$$

$$\Rightarrow \text{even function with respect to } \dot{\gamma}^n$$

We expect equation like: \( N_{1,2} = c \cdot \dot{\gamma}^2 \) as first approximation

$$\dot{\psi}_1 = \frac{N_1}{\dot{\gamma}^2} = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}^2}$$

$$\dot{\psi}_2 = \frac{N_2}{\dot{\gamma}^2} = \frac{\tau_{22} - \tau_{33}}{\dot{\gamma}^2}$$

$\dot{\psi}_1$ : first normal stress coefficient

$\dot{\psi}_2$ : second normal stress coefficient

$\dot{\psi}_1$ : generally positive, $|\dot{\psi}_1| > |\dot{\psi}_2|$ (typical factor: 10);

$N_1$ can be as high or even higher than $\tau_{12}$!

$\dot{\psi}_2$ : generally small and negative

$\dot{\psi}_1 + \dot{\psi}_2$ can be measured separately using both:

\[
\begin{align*}
\dot{\gamma} & \quad \text{N}_1 \\
\text{cone-plate} & \quad \& \\
\text{Information: } N_1
\end{align*}
\]

\[
\begin{align*}
\dot{\gamma} & \quad \text{N}_1 + N_2 \\
\text{plate-plate} & \\
\text{Information: superposition } N_1 \text{ and } N_2
\end{align*}
\]
Typical examples for extra stress tensor:

a) ideal viscous fluid

\[
\tau = \begin{pmatrix}
0 & \tau_{12} & 0 \\
\tau_{21} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

\[\tau_{12} = \tau_{21}\]

b) viscoelastic liquid

\[
\bar{\tau} = \begin{pmatrix}
\tau_{11} & \tau_{12} & 0 \\
\tau_{21} & \tau_{22} & 0 \\
0 & 0 & \tau_{33}
\end{pmatrix}
\]

5 unknowns

\[\tau_{12} = \tau_{21}, \quad \tau_{11} + \tau_{22} + \tau_{33} = 0\]

3 degrees of freedom \(\Rightarrow \eta, \psi_1, \psi_2\)

The first normal stress coefficient can be estimated using:

\[
\lim_{\omega \to 0} \psi_1(\dot{\gamma}) = \frac{2 \cdot G'(\omega)}{\omega^2} \quad \text{for } \dot{\gamma} = \omega
\]

Phenomena where we can directly “see” normal forces

a) Rod-climbing

Parabola, \(f(r) \propto r^2\)

centrifugal forces
(e.g. water)

**Newtonian** fluid

leading term, \(f(r) \propto -r^4\)

\(f(R, r, \psi_1, \psi_2, \rho, \omega, \ldots)\)

**Non-Newtonian** fluid

climbing effect is called

**Weissenberg effect**
b) Secondary flow for rotating disc

Newtonian fluid
Non-Newtonian fluid

centrifugal forces

up!

see: cover page
book: Tanner
Newton or not?

c) Extrudate swell

Newtonian fluid
Non-Newtonian fluid

parabola
die swell

\[ \Rightarrow \text{film blowing} \]
(e.g. plastic bags)
New chapter:

**Possible measurements (for oscillatory rheometers) and hardware**

1) Detection of onset of non-linearity at fixed frequency

![Graph showing log G vs log γ₀](image)

- a: Problem: torque too low, hard to get sensitivity
- b: onset of non-linearity, but: depends on accuracy of detection!
- c: in filled materials sometimes an overshoot in $G''$ is detected: Payne-effect

**(name!): not pain**

Typical values:
- Polymer melts: $γ₀ < 0.05 – 0.3$
- Solutions: $γ₀ < 0.1 – 1$
- Cross-linked rubber: $γ₀ ≈ 0.01$

$⇒$ we know linear regime for a fixed frequency ($\dot{γ}_{\text{max}} = γ₀ \cdot 2\pi \cdot ω₁$)

We can assume:
- Linear if $ω₂ < ω₁$
- Perhaps non-linear if $ω₂ > ω₁$

2) Measurement of $G'$, $G''$ at $T = \text{const.}$, $ω$: variable, $γ₀$: parameter

![Graph showing log G vs log ω](image)

Frequency dependent module

$⇒$ distribution of relaxation times
e.g. via Multimode-Maxwell models

$⇒$ see section about polymers (later)

(reptation, rubber plateau, TTS)
Typical range: $10^2 < \omega < 60$,
dynamic range: 4 decades of hardware due to mechanical device!

$\gamma(t) = \gamma_0 \cdot \sin(\omega \cdot t)$
$\dot{\gamma} = \gamma_0 \cdot \omega \cdot \cos(\omega \cdot t)$
$\dot{\gamma}_{\text{max}} = \gamma_0 \cdot \omega$

$\Rightarrow$ adjust $\gamma_0$ every 1 - 2 decades for best performance

3) Temperature dependent measurement

$\gamma_0$: fixed but parameter, $T$: variable, $\omega$: fixed

Instrument for this: DMTA, (Dynamic mechanical thermo analyser)
cheap due to limited $\omega$-range
(sometimes also E-module measurements)
4) Shear rate dependent viscosity

![Graph showing log(\eta) vs. log(\dot{\gamma})](image)

- asymptotic behaviour ⇒ in principle no linear regime!
- experimental linear regime
- e.g. 10% reduction relative to \( \eta_0 \)

Fit with: 1 - 4 parameter model (see before)

Hardware:

**Couette geometry**

preferentially: static bob, moving cup (because of Taylor vortices!)
inside moving: Searle-type, outside moving: Couette-type

Mooney-Ewart

e.g. 10% reduction relative to \( \eta_0 \)

Haake-type

Air bubble ⇒ low friction at lower end

for low viscosity materials, e.g. water
To prevent evaporation of water:

If plate-geometries are used:

Dodecane, C\textsubscript{12}H\textsubscript{26} or saturated H\textsubscript{2}O vapor

Area \( \propto r_0^2 \)

Torque at infinitesimal area:

\[ \Delta N = \Delta \mathbf{F} \times \mathbf{r} \Rightarrow \Delta N \propto r^1 \]

\( \Rightarrow \) total torque \( N \propto r_0^3 \)

e.g. change from 50 mm plate-plate geometry to 8 mm plate-plate geometry: torque reduction by

\[ \left( \frac{50}{8} \right)^3 \approx 244 \Rightarrow 2.5 \text{ decades reduction} \]

\( N \propto r_0^3 \)

typical values for \( \alpha \): 0.02 - 0.1 rad

\( \Rightarrow 1.14 - 5.73^\circ \Rightarrow \) very small!

Advantage of plate-plate (cone-plate) vs. Couette:

- less sample volume (e.g. 0.1ml vs. 10ml)

Disadvantage of plate-plate:

- leakage (low viscosity material)
- less area \( \Rightarrow \) less sensitivity for low viscosity materials
- heterogeneity of shear rate
5) Creep experiment

\[ G(\gamma_0, t) \text{ measured} \]

Wagner-Ansatz (Manfred Wagner, Prof. in Berlin):

\[ G(\gamma, t) = G(t) \cdot h(\gamma) \]

1. \( \lim_{\gamma \to 0} h(\gamma) = 1 \), linear response

2. decreasing strictly monotonic as a function of time, \( \lim_{\gamma \to \infty} h(\gamma) = 0 \)

**typical examples:**

\[ h(\gamma) = \exp(-n \cdot \gamma), \text{ e.g. } n \approx 0.18 \text{ for PE - melt} \]

\[ h(\gamma) = f_1 \cdot \exp(-n_1 \cdot \gamma) + f_2 \cdot \exp(-n_2 \cdot \gamma), \quad f_1 + f_2 = 1 \]

\[ h(\gamma) = \frac{1}{1 + a \cdot \gamma^2} \quad \text{Doi-theory} \]
**Hardware**

Stress and strain rheometer, typical types of construction:

- **Stress-rheometer**, stress is given, strain measured
  - strain is measured via optical encoder
  - controlled stress is imposed

- **Strain-rheometer (A)**, strain is given, stress measured
  - nominal actual value comparison, feedback loop

- **Strain-rheometer (B)**, ARES-type
  - magnetic suspension, seal + normal forces
  - stress detection
  - force rebalance transducer (FRT)
  - e.g. our ARES: 2K FRT N1
    - (2K = 2000 gcm, N1 = normal forces can be measured)

Sample:
- ball (cheap) or air bearing (expensive); for normal forces air bearing needed
- feedback: “stand still”
Typical hardware specifications (ARES)

**Magnets, transducer:** Al Ni Co - alloy 0.01% / °C

**Magnets, motor:** Nd (Neodym) 0.1% / °C

(compare: Cu: 0.39% / °C)

**Optical encoder:** 30,000 lines + interpolation

0.08·10⁻⁶ radian resolution = 8·10⁻⁸ rad

\[ \frac{8 \times 10^{-8}}{1 \text{ km}} = 0.08 \text{ mm} \]

Alternative: capacitive encoding:

\[ C \propto \frac{1}{d} \quad \omega_{LC} = \frac{1}{\sqrt{LC}} \]

**Dynamic range of transducers:**

newest: 1K FRT N1 (Rheometrics, also Haake)

\[ \frac{N_{\text{max}}}{N_{\text{min}}} = 10^6 , \text{ e.g. } 10^{-1}\text{Nm to } 10^{-7}\text{Nm} ! \]

**Typical prices (2002):**

Stress rheometer: 15k – 40k € (Haake, Bohlin, TA, Rheometrics, …)

ARES (strain): 60k – 100k € (3 types of motors, diff. types of temp. control, 7 diff. transducers, …)

+ cooling (N₂): 10k €

+ dielectric option: 30k €

+ birefringence, dichroism option: 30k €

⇒ up to 180k €

Geometry: 1.5 – 3k €
Typical pathway of a signal from the torque transducer to $G', G''$

Torque transducer:

![Diagram of signal pathway](image)

ADC: discrete in time (⇒ dwell-time) and in intensity (k-bit ADC, $2^k$ slots)
Typical acoustic ADC’s: $16 \text{ bit} = 2^{16} = 65,536 \implies \text{dynamic range: } 1:65,536$

(remark: limit for S/N in FT-Rheology!)

dwell-time: $10\mu s$, sampling rate: $100 \text{ kHz}$

$\implies 10^5 \cdot 6.55 \cdot 10^4 = 6.55 \cdot 10^9 \text{ decisions per second}$

Vane rheometer

(\textit{German: Schaufel, Flügelrad})

useful for determination of yield stress

($\implies$ Bingham fluid) in concentrated

suspensions, greases or food (yoghurt!);

especially if the history of loading should be avoided.

Approximation:

\[
T_m = 2\pi \cdot R_v \left[ \frac{L_v}{R_v} + \frac{2}{3} \right] \cdot \sigma_y
\]

\(T_m\): torque maximum

\(\sigma_y\): yield stress
Melt-flow index

cheap + robust version of a capillary rheometer (see later)
- uncontrolled, non-homogeneous flow
- relative measurement ("index")

typical parameters:
\[ T = 190^\circ C \]
\[ M = 2.16 \text{ kg} \]  
\[ \Rightarrow \text{pressure } \approx 3 \cdot 10^5 \text{ Pa} \]
MFI: flow of polymer in [g] per 10 min
\[ \Rightarrow \text{rough measure of average } M_W \]

Capillary rheometer (⇒ high shear rates)

Model system for e.g. polymer extrusion process
(see also: melt-flow index)

important shear rates:

[Diagram showing different types of shear rates]

- oscillatory / vibrational
- rotational
- elongational
- capillary
- processing
Set-up:

Constant force or constant velocity

\[ \frac{dx}{dt} = v(t) = \dot{\varepsilon} \cdot x_1, \quad \dot{\varepsilon} : \text{stretch rate} \]

Dominantly viscous properties of the material are determined, pressure loss at entrance can be corrected \( \Rightarrow \) “Bagley-Correction”

Information: \( m(t), d, p_n, ..., p_l \) for different \( T, M, v, d, L \)

Elongational rheology, viscosity

Important for: fibre spinning, blow moulding, flat film extrusion, film blowing
If specimen is stretched with constant rate $\dot{\varepsilon}$

$$\frac{dx}{x_1 \cdot dt} = \dot{\varepsilon}$$

$$\int_{x_0}^{x} \frac{1}{x} dx = \int_{0}^{t} \dot{\varepsilon} dt; \quad \dot{\varepsilon} = \text{const.}$$

$$\ln \frac{L}{L_0} = \dot{\varepsilon} \cdot t$$

Hencky-strain, sample length $L \propto e^t$!

[Hencky worked for many years in Mainz-Gustavsburg!]

See Appendix B, p. 115 - 123]

tensile viscosity: $\eta^t = \frac{\sigma_E}{\dot{\varepsilon}}$

without proof: $\lim_{\varepsilon \to 0} \frac{\eta_E}{\eta_0} = 3$ for simple liquids

Trouton’s ratio

experimental apparatus:

A  

B

sample

thickness + elongation monitored via camera

Prof. Meissner  
Zürich  
ex BASF

Prof. Münstedt  
Erlangen  
ex BASF

oil: + compensates gravity  
+ temp. control  
- can act as plasticizer in the sample
Figure 17.5 Tensile Stress Growth data for LDPE [48]. Reprinted by permission of Steinkopf-Verlag, Darmstadt.
Rheology on two specific examples: polymers and dispersions

Polymers

End-to-end distance $\bar{R}$, bond length $b$, N monomers

$$\bar{R} = \sum_{i=1}^{n} \bar{r}_i$$

Gauß:

$$R = \sqrt{\langle R^2 \rangle} = b \cdot \sqrt{N} \Rightarrow R^2 = b^2 \cdot N$$

contour length: $L = N \cdot b$ (“odometer”)

e.g. high Mw-PE, $N = 100,000$, $b = 1.5$ Å

contour length $15 \, \mu$m (in principle visible!), $R = 47$ nm

simplified model:  

$$R_g = \frac{R}{\sqrt{6}}$$

Reptation theory

basic idea:

one-dimensional stochastic process

of chain along contour (reptate: reptile)

simplified

tube with diameter $d$ and other chains are static,

typical distance of other chains: $s \approx d$

typical $d \approx 30 - 80$ Å

one-dimensional Fick-equation, for chain distribution probability

$$\frac{\partial P}{\partial t} = D_{1d} \frac{\partial^2 P}{\partial x^2}$$
Solution for $P(x, t)$: Gauß-statistics

$$P(x, t) = \frac{1}{\sqrt{4\pi \cdot D_{1d} \cdot t}} \cdot \exp \left( -\frac{x^2}{4 \cdot D_{1d} \cdot t} \right)$$

Gauß: $\sigma^2 = r^2 = 2nDt$

$n$: dimensionality

Mean square displacement (⇒ second moment)

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 P(x, t) dx = 2D_{1d} \cdot t$$

If we assume stochastic friction coefficient $\xi'$, where this friction coefficient $\xi'$ is proportional to $N$, therefore also $M$

$$\xi' = \xi \cdot N \quad \xi$: friction per monomer unit

Using the Einstein-relation for the 1-d. diffusion:

$$D_{1d} = \frac{kT}{\xi'} = \frac{kT}{\xi \cdot N} \propto M^{-1}$$

The time $\lambda$ needed to diffuse along $L$ will allow a fully different conformation, so that all memory of the other chains (static) is erased ⇒

$$L^2 = \lambda \cdot 2D_{1d}$$

$$\lambda = \frac{L^2}{2D_{1d}} \propto \frac{M^2}{M^{-1}} = M^3$$

$$\lambda \propto M^3$$

The self-diffusion coefficient $D_s$ is given by the time $t$ to move the center of mass by a typical coil diameter $R$ (3-dimensional problem!).

$$\langle r^2 \rangle = 2nDt, \quad n: \text{dimensionality, here } 3$$

$$D_s = \frac{R^2}{6 \cdot \lambda} \propto \frac{M}{M^3} = M^{-2}$$

$$D_s \propto M^{-2}$$
assuming a Maxwell-model:

\[
\lambda = \frac{\eta}{G} \\
\eta = \lambda \cdot G \quad \text{with} \\
\lambda \propto M^3 \\
G \propto M^0 \quad \text{molecular weight independent given by temporary entanglements,}
\]

“mesh-length”

\[\eta_{\text{Polymer}} \propto M^3, \text{DeGennes 1971, exp.: } \eta_{\text{Polymer}} \propto M^{3.4} \]

for non-entangled: \( \eta_{\text{Polymer}} \propto M^1 \) friction of polymer-contour

Rule of thumb for flexible monomers with 2 carbons per polymer backbone (so not true for PPP, poly-paraphenylene ⇒ persistence length)

\( \Rightarrow n_c \approx 100 - 200 \) monomers

contourlength between entanglements: \( 150 \cdot 3 \text{Å} = 45 \text{ nm, } R_c \approx \sqrt{n} \cdot 3 \text{Å} \approx 3 - 4 \text{ nm} \)

examples, \( M_c \):

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>828 g/mol</td>
</tr>
<tr>
<td>PS</td>
<td>13 kg/mol</td>
</tr>
<tr>
<td>PDMS</td>
<td>12.3 kg/mol</td>
</tr>
<tr>
<td>PIB</td>
<td>7.3 kg/mol</td>
</tr>
<tr>
<td>PMMA</td>
<td>10 kg/mol</td>
</tr>
<tr>
<td>1,4 PBd</td>
<td>1.8 kg/mol</td>
</tr>
<tr>
<td>1,4 PI</td>
<td>5.4 kg/mol</td>
</tr>
</tbody>
</table>

might differ depending on lit. sources
Typical shape for $G'(\omega)$, $G''(\omega)$ for monodisperse linear polymer melts

related length scales:
- $R_g$, 10-50 nm
- $5 - 10$ nm
- $2 - 3$ nm

related time scales:
- $\tau_d$: disengagement
- $\tau_R$: Rouse time
- $\tau_e$: entanglement
- $\tau_s$: segmental motion

Zone I:
- $G' \propto \omega^2$
- $G'' \propto \omega^1$

flow-zone, viscosity and the dissipation dominates response

length scale probed $\approx R_g$

longest relaxation time: $\omega \cdot \tau = 1$ for $\tan \delta = 1$

(Maxwell-model) or
Zone II: (rubber-plateau)

After $G'$ exceeds $G''$, $G'$ levels off. Response is dominated by elastic spring ($G'!$) of physically cross linked entanglements (see motivation for Hooke-solid!). Maximum of relative elastic response is reached for $\tan \delta = \text{Minimum}$, corresponding $G'_p$ ($p$: plateau).

length scale probed:

It is possible to calculate from $G'_p$ the entanglement molecular weight:

$$M_e = \frac{\rho \cdot R \cdot T}{G'_p}$$

$\rho$: density

$R$: Gas constant 

$T$: temperature

Assuming typical values for a polymer melt:

$\rho = 1,000 \text{ kg/m}^3$, $R = 8.3 \text{ J/(mol K)}$, $T = 450 \text{ K}$, $M_e \approx 150 \cdot 70 \text{ g/mol} = 10.5 \text{ kg/mol}$

$$G'_p = \frac{1,000 \cdot 8.3 \cdot 450}{10.5} \left[ \frac{\text{kg} \cdot \text{J} \cdot \text{mol}}{\text{m}^3 \cdot \text{mol} \cdot \text{K} \cdot \text{kg}} \right] = 1 \text{ J} = 1 \text{ Nm}$$

$$G'_p = 3.5 \cdot 10^5 \left[ \frac{\text{Nm}}{\text{m}^2} = \text{Pa} \right]$$

typical plateau value: $10^5$-$10^6 \text{ Pa}$  

(⇒ memorize!)

(high $T_g$ + low $M_e$ ⇒ increase in rubber plateau modulus)

⇒ for higher cross link density in chemical cross linked systems we expect higher modules

⇒ $M_n$ does not affect $G'_p$, but $\eta \propto M_n^{-3}$, $\lambda \propto M_n^{-3}$; so increase in molecular weight by factor 10 ⇒ $10^3$ shift in $\omega$ for plateau length;
5.3 Specific Relaxation Processes and Flow Behavior

Subsequently, there often follows a power law

\[ E(t) \sim t^{-\nu} \]  \hspace{1cm} (5.98)

Experimentally it is indicated by a linear range in the center, when using a log-log plot. Typical values of the exponent are \( \nu \approx 0.5 \).

Figure 5.15 presents, as a third example, results of dynamic-mechanical measurements. They were obtained for a series of monodisperse polystyrenes, i.e. fractions with sharp molecular weights. The curves depict the frequency dependence of the storage shear modulus, \( G'(\omega) \). As we note, the order of appearance of the viscous flow and the \( \alpha \)-process is reversed when compared to the time dependent measurements. The flow-dominated long-time behavior emerges first at low frequencies, whereas an investigation of the rubber-glass transition requires measurements at the high frequency end. The plateau appears in between. Its width varies systematically with the molecular weight, as already mentioned and discussed. There is no plateau at all for the sample with the lowest molar mass (\( M = 8.9 \cdot 10^3 \)), but after its first appearance, it widens progressively with further increasing molecular weight.

Low Frequency Properties of Polymer Melts

Also of interest, in Fig. 5.15, is the finding that the shapes of curves in the terminal region remain similar to each other for all molecular weights. More specifically, within the limit of low frequencies, a constant slope emerges,
Zone III:

G” exceeds again G’.

Strong increase as a function of frequency.

Transition zone towards glass plateau;

Zone IV: (glass plateau)

High torque and high frequency regime, experimentally difficult to obtain.

e.g. small sample diameter (≈ 5 mm), use of TTS (see later)

Length scale probed in dimension of typical length scale of polymer glasses, e.g. 2-3 nm.

Shear rate dependent viscosity (or measured by $\eta(\dot{\gamma}) = |\eta^*(\omega)|$, Cox-Merz), typical shape:

$$\eta_0 \propto M_a^{3.4}$$

$\dot{\gamma} \cdot \lambda \approx 1$

$\lambda$: longest relaxation time

$\dot{\gamma}$: shear rate

$\omega$: angular frequency

$G'$: storage modulus

$G”$: loss modulus

$M_n$: number average molecular weight

$M_2$: second moment of molecular weight distribution

$\log G’$ versus $\log \omega$

$\log G”$ versus $\log \omega$

$3$ decades

$M_{n2} \approx 10 \cdot M_{n1}$

Typical slope for linear polymers: - 0.8 ± 0.1
Time-Temperature-Superposition (TTS) and the Williams-Landel-Ferry (WLF) equation

Assumption:
The internal mobility of a polymer is monotonically (+ continuously) changed via the temperature. The changes keep the ratio (not the difference!) between the different relaxation time distributions and relative strength. This is related to the concept of the “internal clock” that is only affected by the temperature (McKenna). Obviously this assumption must fail if phase transitions (e.g. first order: crystallisation, second order: glass transition or T\textsubscript{ODT}) are involved. If we set a reference temperature T\textsubscript{2}, where we know or have measured G'(\omega(T_2)), G''(\omega(T_2)), we can predict G'(\omega(T_1)), G''(\omega(T_1)).

Maths:
Modification of Arrhenius law ⇒ Vogel-Fulcher equation:

\[ \eta(T) = \eta_0 \cdot \exp\left(\frac{E_a}{R(T - T_{VF})}\right) \]

note: E\textsubscript{a} for flow of linear polymer melts \(\approx 25-30\) KJ/mol (typical value)
no information about T\textsubscript{VF} yet, except:
- if T\textsubscript{VF} = 0 ⇒ Arrhenius
- if T = T\textsubscript{VF} ⇒ singularity in \(\eta\)

therefore we expect:
\[ \frac{T_{VF}}{T} << 1 \]

for typical temperatures \(T \approx 300-500\) K, because it is only a correction!

b) fixed difference of T\textsubscript{VF} relative to T\textsubscript{g} due to the assumption of similar mobility of different polymers at T\textsubscript{g}; using (1):

\[ \frac{\eta(T_1)}{\eta(T_2)} = \frac{\eta_1}{\eta_2} ; \ T_1 > T_2, \ T_2 : \text{ref. temp.} \]

\[ \frac{\eta_1}{\eta_2} = \frac{\omega_2}{\omega_1} ; \ \eta \propto \tau \propto \frac{1}{\omega} ; \ \tau = \frac{\eta}{G} \] Maxwell

\(\omega\): characteristic “frequency” of motion
\[ \eta_2 = f \cdot \eta_T(T_1) \]

\( \eta_2 \): fixed value at reference temperature \( T_2 \) (not defined yet)

\[ \log \frac{\omega_2}{\omega_1} = \log(f) + \frac{E_a}{R(T_1 - T_{Vf})} \cdot \log(e) \]

\( =: -C_1 \) (no units!) 0.434

\[ \frac{E_a \cdot \log(e)}{R} = +C_1 \cdot C_2 \];  \( C_2 \) : unit of temp.!

\( T_{Vf} := T_2 - C_2 \); choice of \( T_2 \) will change \( C_1 \) and \( C_2 \)!

\[ \log \frac{\omega_2}{\omega_1} = -C_1 + \frac{C_1 \cdot C_2}{T_1 - (T_2 - C_2)} = \frac{-C_1 \cdot (T_1 - T_2)}{C_2 + (T_1 - T_2)} \]

only diff. to ref. \( T_2 \) important!

\[ \log \frac{\omega_2}{\omega_1} : = \log a_T = \frac{-C_1 \cdot (T_1 - T_2)}{C_2 + (T_1 - T_2)} \quad \text{WLF-equation} \]

shift factor

If we choose the reference temperature as \( T_2 = T_g \) (other choices also possible!):

\[ \log \frac{\omega(T_g)}{\omega_1} = \frac{-C_1 \cdot (T_1 - T_g)}{C_2 + (T_1 - T_g)} \]

For these conditions (\( T_2 = T_g \)) and for typical polymers it is found:

\( C_1 \approx 17.4 \quad C_2 \approx 51.6 \text{ K} \)

\( C_1 \approx 7.6 \quad C_2 \approx 100 \text{ K} \quad \text{for } T_2 = T_g + 50 \text{ K} \); rem.: \( C_1 \cdot C_2 \approx \text{const. (\( \approx 900 \text{ K} \))} \)

apparent activation energy: \[ E_a = \frac{C_1 \cdot C_2 \cdot R}{\log(e)} \approx 17.5 \text{ kJ/mol } \quad \left( \text{for } \frac{1}{T} \to 0 \right) \]
If we assume \( \omega(T_g) \approx 0.1 \text{ rad/s} \approx 0.01 \text{ Hz} \) as the typical jump rate (motion) at the glass transition temperature for a spatial entity of several monomer units (e.g. \( \approx 100 \)) \( \Rightarrow \alpha\)-relaxation. We do not look at side chain motion \( \Rightarrow \beta\)-relaxation (typically pure Arrhenius) or \(-\text{CH}_3 \Rightarrow 10^{12} \text{ Hz} \) (at room temperature)

\[
\lim_{T \to T_g} \left( \log \frac{\omega}{\omega_\infty} \right) = \frac{-17.4 \cdot (T - T_g)}{51.6 + (T - T_g)} \approx \frac{-17.4 \cdot T}{51.6 + T} \approx -17.4
\]

\( \Rightarrow C_1 \) is related to prefactor

\[
\frac{0.1}{\omega_\infty} = 10^{-17.4} \quad \omega_\infty = 10^{16.4} ; \quad \frac{\omega}{2\pi} = \nu \quad \nu_\infty = 10^{15.6}
\]

further: \( T_{VF} = T_2 - C_2 \) \( \quad T_2 = T_g \)

\( T_{VF} = T_g - 51.6 \text{ K} \)
so: $T_m > T_g > T_{VF}$

rule of thumb for polymers:

$$\frac{T_g}{T_m} = \frac{2}{3}$$

(in Kelvin!, absolute energy scale)

$$T_g - C_2 = T_{VF} \quad (C_2 \approx 50 \text{ K})$$

$$\log a_T = \log \frac{0.1}{\omega(T)} = \frac{17.4 \cdot \Delta T}{51.6 + \Delta T}$$

$T_2 = T_g$:

<table>
<thead>
<tr>
<th>$\Delta T$</th>
<th>$a_T$</th>
<th>$\omega(T)$ [rad/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>$10^{-1.5}$</td>
<td>3.5</td>
</tr>
<tr>
<td>10</td>
<td>$10^{-2.8}$</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>$10^{-4.8}$</td>
<td>$7 \cdot 10^3$</td>
</tr>
<tr>
<td>30</td>
<td>$10^{-6.4}$</td>
<td>$2.5 \cdot 10^5$</td>
</tr>
<tr>
<td>50</td>
<td>$10^{-8.6}$</td>
<td>$3.6 \cdot 10^7$</td>
</tr>
<tr>
<td>100</td>
<td>$10^{-11.5}$</td>
<td>$3 \cdot 10^{10}$</td>
</tr>
</tbody>
</table>

3 deg $\approx$ 1 decade change in mobility, close to $T_g$

15 deg $\approx$ 1 decade change

don’t take this table to literally!
Glossary: (to relax from maths for a second)

Boger fluid: To study the relaxation of high $M_n$ polymers (e.g. normal forces, $G'$, $G''$) the very long relaxation times are shifted to more “practical” values via low $M_n$ solvents.

Dispersions

**Definition:** lat.: dispersio, fragmentation
A system built of several phases where one is a continuous and at least one more phase is fine fragmented within the continuous phase. If the size of the dispersed phase is $< 0.2 \, \mu m$ (visibility!) they might be classified as colloids or colloidal dispersions.

<table>
<thead>
<tr>
<th>continuous phase</th>
<th>dispersed phase</th>
<th>name</th>
<th>example</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>solid</td>
<td>vitreosol</td>
<td>ruby glass</td>
</tr>
<tr>
<td>solid</td>
<td>liquid</td>
<td>solid emulsion</td>
<td>butter</td>
</tr>
<tr>
<td>solid</td>
<td>gas</td>
<td>solid foam</td>
<td>pumic-stone ($Bims$)</td>
</tr>
<tr>
<td>liquid</td>
<td>solid</td>
<td>colloidal sol</td>
<td>dispersion of Au, S in H$_2$O</td>
</tr>
<tr>
<td>liquid</td>
<td>liquid</td>
<td>emulsion</td>
<td>milk, pharmaceutic or cosmetic emulsion</td>
</tr>
<tr>
<td>liquid</td>
<td>gas</td>
<td>foam</td>
<td>soap-foam</td>
</tr>
<tr>
<td>gas</td>
<td>solid</td>
<td>smoke</td>
<td>NH$_4$Cl, carbon black smoke</td>
</tr>
<tr>
<td>gas</td>
<td>liquid</td>
<td>fog, mist</td>
<td>natural mist</td>
</tr>
<tr>
<td>gas</td>
<td>gas</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

why?!
Zero-shear viscosity as a function of solid content:

Einstein 1906: (see Appendix C, p. 124-144 for original work)

\[ \eta = \eta_s (1 + 2.5 \cdot \varphi) \quad \text{for } \varphi < 0.1 \]

\( \eta_s \) : viscosity solvent
\( \varphi \) : volume fraction

lit.: A. Einstein, Ann. Physik, 1906, 10, 289
1911, 34, 591

General behaviour for higher concentrations:

\[ \eta = \eta_s (1 + 2.5 \cdot \varphi + O(\varphi^2) + ...) \]

\( O(\varphi^2) \): not defined yet

Intrinsic viscosity (relative change of viscosity normalised to solvent viscosity):

\[ [\eta] = \frac{\eta(\varphi) - \eta_s}{\eta_s} \]

\( \lim_{\varphi \to 0} [\eta] = 2.5 \), Einstein coefficient

Extension of Einstein, \( O(\varphi^5) \Rightarrow \text{Batchelor (1977)} \)

shear \( \frac{\eta}{\eta_s} = 1 + 2.5 \cdot \varphi + 6.2 \cdot \varphi^2 + O(\varphi^3) \)

extension \( \frac{\eta'}{\eta_s} = 1 + 2.5 \cdot \varphi + 7.6 \cdot \varphi^2 + O(\varphi^3) \)

shear + extension already anisotropic!

Shear can deform liquid particles to prolate or oblate shape if surface tension, mobility and shear rate are sufficient (e.g. blood):

In both cases: aspect ratio: \( \frac{a}{c} \neq 1 \)
High aspect ratio ⇒ more excluded volume (see liquid crystals: Onsager theory)

Zero-shear viscosity as a function of volume fraction (no information about $\eta(\dot{\gamma})$) for higher fractions:

$$\eta = \eta_s + 2.5 \cdot \eta_s \cdot \varphi \left( \frac{d}{d\varphi} \right)$$

(1)  \[ d\eta = 2.5 \cdot \eta_s \cdot d\varphi \]

At certain volume fraction the addition of $d\varphi$ leads to an increase in $d\eta$ that is expected to be:

$$d\eta = 2.5 \cdot \eta(\varphi) \cdot d\varphi$$

$$\int_{\eta_s}^{\eta} d\eta = 2.5 \int_0^{\varphi} d\varphi$$

$$\Rightarrow \ln \frac{\eta}{\eta_s} = 2.5 \cdot [\varphi - 0]$$

$$\eta = \eta_s \cdot \exp(2.5 \cdot \varphi) \quad \text{Ball, Richmond} \quad 1980$$

Taylor:

$$\eta = \eta_s \cdot \left( 1 + \frac{5}{2} \cdot \varphi + \frac{25}{2!4} \cdot \varphi^2 + \ldots \right)$$

too low increase in $\varphi^2$!

Other idea:

Addition of small amount of particles $d\varphi$ to the volume fraction $(1-\varphi)$ of remaining fluid, raises volume fraction by:

$$\frac{d\varphi}{1-\varphi}$$

in analogy to (1):

$$d\eta = \frac{5}{2} \cdot \frac{d\varphi}{1-\varphi} \cdot \eta$$

$$\frac{d\eta}{\eta} = \frac{5}{2} \cdot \frac{d\varphi}{1-\varphi}$$

$$\ln \frac{\eta}{\eta_s} = \left[ \ln \left( \frac{1}{1-\varphi} \right)^{2.5} \right]_{\varphi'=0}^{\varphi' = \varphi} = \ln \left( \frac{1}{1-\varphi} \right)^{2.5} - \ln 1^{2.5}$$

$$\frac{\eta}{\eta_s} = \left( \frac{1}{1-\varphi} \right)^{2.5} = (1-\varphi)^{-2.5}, \text{ singularity at } \varphi = 1 \Rightarrow \text{not physical}$$
If we assume a maximum filling fraction $\varphi_m$, we find:

$$\frac{\eta}{\eta_s} = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-2.5\varphi_m}, \quad \text{Krieger-Dougherty (1959)}$$

Maximum filling factor (⇒ crystallography, inorganic chemistry), examples:

- **Simple cubic, sc** $\varphi_m = 0.52$
- **Hexagonal packed sheet** $\varphi_m = 0.605$
  (colloids high shear rates)
- **random close packing** $\varphi_m = 0.637$
- **body-centered cubic, bcc** $\varphi_m = 0.68$
- **face-centered cubic (fcc) / hexagonal close packing** $\varphi_m = 0.74$
  Max. possible value for monodisperse!
Best theoretical equation for $\eta(\varphi)$:

$$\frac{\eta}{\eta_s} = \frac{9 \left( \frac{\varphi}{\varphi_m} \right)^{\frac{1}{3}}}{8 \left( 1 - \left( \frac{\varphi}{\varphi_m} \right)^{\frac{1}{3}} \right)}$$

Frankel and Acrivos, with $\varphi_m \approx 0.62 - 0.64$

Experimental:

$$\frac{\eta}{\eta_s} = 1 + 2.5 \cdot \varphi + 10.05 \cdot \varphi^2 + 2.7 \cdot 10^{-3} \cdot \exp(16.6 \cdot \varphi)$$

Zero-shear-(rate)-viscosity can drastically be influenced by multimodal distribution:

- e.g. $r_1 : r_2 = 5 : 1$

$$\eta_{\text{pure2}}(\varphi) = \frac{1}{50} \cdot \eta_{\text{(50:50)!}}$$

$\varphi_{\text{total}} = 60\%$

$$\eta_{\text{pure2,60\%}}(\varphi) = \eta_{\text{(60\%2,15\%1)}}$$

15\% increase in solid content, same viscosity

Picture:

- filling of voids

Viscosity as a function of shear-rate for colloids:

- $\eta_0$, 1st Newtonian plateau
- $\gamma_c$: critical shear stress
- 2nd Newtonian plateau
- Shear thickening, layered structure
Scaling-law behaviour (+2-Newton) can be described by:

- Ostwald de Waele \[ \eta(\dot{\gamma}) = A \cdot \dot{\gamma}^{-B} , \quad B \in [0,1] \]

- e.g. Ellis-model, using the Péclet-number as universal parameter
  \[
  \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + b \cdot (Pe)^p},
  \quad Pe = \frac{6 \cdot \sigma \cdot r^3}{kT} = \frac{\eta_k \cdot \dot{\gamma} \cdot r^3}{kT}
  \]

The critical shear-rate can be estimated for a 0.50 = \( \varphi \) mixture:

\[
d^2 \cdot \dot{\gamma}_c \approx 10^7 \frac{\text{nm}^2}{\text{s}} ; \quad d [\text{nm}] , \dot{\gamma}_c [1/\text{s}]
\]

\[
\begin{align*}
\dot{\gamma}_c [1/\text{s}] & = 10^5 \quad \text{e.g.: } d = 100 \text{ nm, } \dot{\gamma}_c \approx 10^3 1/\text{s} \\
10^4 & \quad 10^3 \quad 10^2 \quad 10^1 \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \\
10^1 & \quad 10^2 & \quad 10^3 & \quad 10^4 & \quad 10^5 & \text{particle diameter [nm]}
\end{align*}
\]

Understanding of related forces \( F(x) \) and potentials (\( \cong \) energies) \( \int Fdx = V(x) \) for colloidal particles:

\[
V_{\text{total}} = V_{\text{van-der-Waals}} + V_{\text{electrostatic}} + V_{\text{depletion}} + V_{\text{steric}}
\]

DLVO-theory

DLVO: Derjaguin – Landau – Verwey – Overbeek (1941 + 1948)
Van-der-Waals:

Attractive force between atoms, molecules and particles caused by induced electrical dipols of electron cloud.

Permanent dipol interaction $V(r) \propto \frac{1}{r^3}$,

induced $V(r) \propto \left(\frac{1}{r^3}\right)^2 = -\frac{1}{r^6}$, minus prefactor, because attractive!

For two quadratic surfaces with side length $L$ one finds:

$$V(r) = -\frac{A}{12\pi r^2} \cdot L^2$$

$A$: Hamaker constant [energy]; typical value: $0.4 - 4 \cdot 10^{-19}$ J

For Lennard-Jones potential, also short range repulsion ($\Rightarrow V(r) \propto +f(r)$), for hard spheres, one typically finds:

$$V(r) \propto -a \frac{1}{r^6} + b \frac{1}{r^{12}}$$

$V_{\text{electrostatic}}$:

$$F(r) = \frac{q_1 \cdot q_2}{4\pi \varepsilon_0 \varepsilon_r r^2}$$

Coulomb

$1^{st}$ - Maxwell-equation: $\nabla E = \frac{\rho}{\varepsilon_0 \varepsilon_r}$, $\rho$: charge density

$$E = -\nabla V_e$$, $V_e$: electric potential ($F = \vec{E} \cdot q$; $W = V_e \cdot q$)

in spherical coordinates:

(1) $\Delta V = \frac{1}{r} \frac{d^2}{dr^2} (r \cdot V_e) = -\frac{1}{\varepsilon_0 \varepsilon_r} \cdot \rho$
Approximation of $\rho$ via a Boltzmann-distribution of screened Coulomb potential (single ions):

$$\rho(r) = \rho_0 \cdot \exp\left(-\frac{q \cdot V_e(r)}{kT}\right) \approx \rho_0 \left(1 - \frac{q \cdot V_e(r)}{kT}\right)$$

$$\Rightarrow \rho_{\text{eff}} = \rho_0 \cdot \frac{q \cdot V_e}{kT} \propto V_e$$

using (1)

$$\Delta V_e = \frac{1}{r} \frac{d^2}{dr^2} (r \cdot V_e) = \chi^2 \cdot V_e$$

Eigenvalue problem

(⇒ Quantum mechanics $\hat{H} \cdot \psi = E \cdot \psi$)

solution:

$$V_e(r) = \frac{q}{4\pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r} \cdot \exp(-\chi \cdot r)$$

no screening screened potential, screening length $1/\chi$: Debye length

$$\rho(r) = -\frac{\exp(\chi^2)}{4\pi \cdot r} \cdot \exp(-\chi \cdot r)$$

$1/\chi$ : equivalent to Bohr-radius in H-atom, first Laguerre polynom

$$r_D = \frac{1}{\chi} = \frac{0.304}{\sqrt{c}} \text{ [nm]}$$

for 1:1 electrolyte, c in mol/litre

$c = 1 \text{ mol/l} \Rightarrow r_D = 3 \text{ Å}$

$c = 0.01 \text{ mol/l} \Rightarrow r_D = 30 \text{ Å}$

**Bjerrum length:**

What is the distance $l_b$, where the electrostatic energy of ion is equivalent $kT$?? (“electrostatic yardstick”)
\[ W = \int F dx \]

\[ kT = \int_{-\infty}^{1} \frac{e^e}{4\pi \varepsilon_0 \varepsilon_r x^2} dx, \quad RT = 2.4 \text{ KJ/mol}, \quad \varepsilon_r = 80 \]

\[ \Rightarrow l_b = 7 \text{ Å} \]

for distances smaller 7 Å ⇒ Manning condensation, opposite charges bound to each other

In case of identical spheres at constant surface potential \( \psi_0 \), radius \( a \) of spheres:

\[ V_c = \frac{4\pi \varepsilon_a^2 \psi_0^2}{r} \cdot \exp(-\chi \cdot r) \quad \text{for } \chi \cdot a < 5 \]

\[ V_c = 2\pi \varepsilon_a a \psi_0^2 \cdot \left[ \ln(1 + \exp(-\chi \cdot r)) \right] \quad \text{for } \chi \cdot a > 5 \]

\( V_{\text{depletion}} \):

In bimodal systems with large size difference, e.g. polymeric solution plus particle, polymer does not bind to particle. Potential caused by osmotic pressure.

\[ V_d \propto -\Pi, \quad \Pi: \text{osmotic pressure} \]
$V_{\text{steric}}$:

non charged surfactants or polymers

Influenced by:
- number of chains per area
- layer thickness ($M_n$)
- solvent quality
- anchor strength

systems: e.g. block copolymers (5 - 50% as anchor)

triblocks: bridging $\Rightarrow$ flocculation (e.g. sewage water treatment)
Fig. 12.12. Schematic energy versus distance profiles of DLVO interaction. (a) Surfaces repel strongly; small colloidal particles remain ‘stable’. (b) Surfaces come into stable equilibrium at secondary minimum if it is deep enough; colloids remain ‘kinetically’ stable. (c) Surfaces come into secondary minimum; colloids coagulate slowly. (d) The ‘critical coagulation concentration’. Surfaces may remain in secondary minimum or adhere; colloids coagulate rapidly. (e) Surfaces and colloids coalesce rapidly.
Fourier-Transform-spectroscopy

[Joseph Baron de Fourier (1768-1830), mathematician and physicist]

In the past (in ESR till today): CW (continuous wave)
excite with single frequency
measure the resonance
change frequency

FT: all signals are acquired simultaneously (“multiplex advantage”)

In words:
A Fourier transform analyses the corresponding frequencies of a given timesignal with respect to amplitude, frequency and phase (i.e. full information).
Note:
This method is of special importance in NMR, IR, X-ray, neutrons, QM, ... and Rheology!

Math:
\[
F(\omega) = \int_{-\infty}^{\infty} f(t) \cdot \exp(-i \cdot \omega \cdot t) \, dt
\]
complex! complex (can be separated in \( \cos + \sin \))
real + imaginary part or magnitude + phase

This operation is reversible! (one-to-one)
\[
f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \cdot \exp(+i \cdot \omega \cdot t) \, d\omega
\]

In NMR we use a single-sided, complex, discrete Fast-Fourier transform (FFT) (special algorithm (“butterfly-algorithm”), which needs \( 2^N \) datapoints)

Problem of discretisation (ADC, analogue digital converter)

Signals are not distinguishable!
Nyquist-frequency (cp. solid state-modes, Einstein, Debye model)

Frequency regime in which the signal can be assigned \textit{unambiguously} (= spectral width, SW):
\[
SW = \frac{1}{2 \cdot DW}
\]
Some important mathematical relations

1) FT is linear
\[ a \cdot f(t) + b \cdot g(t) \Leftrightarrow a \cdot F(\omega) + b \cdot G(\omega) \]
i.e. the different signals can be detected independently!
("proof": \[ \int (A + B)C = \int AC + \int BC \], linearity of the integral)

2) The point in time \( t = 0 \) is proportional to the whole integral of the absorptive spectrum.
Proof:
\[ f(t) = \int_{-\infty}^{\infty} F(\omega) \cdot \exp(+i \cdot \omega \cdot t) \, d\omega \]
\[ f(t = 0) = \int_{-\infty}^{+\infty} F(\omega) \cdot \exp(+i \cdot \omega \cdot 0) \, d\omega = \int_{-\infty}^{+\infty} F(\omega) \, d\omega \]

3) Timesignal and spectrum are inverse to each other with respect to the full width at half maximum. (units: s, 1/s !)
Heisenberg’s uncertainty principle:
\[ \Delta t \cdot \Delta E \geq h \]
\[ \Delta E = h \cdot \Delta \nu \]
\[ \Delta t \cdot \Delta \nu \geq 1 \]
4) important Fourier-pairs:

a) exponential $\xrightarrow{\text{FT}}$ Lorentzian

$\exp(-t/\tau)$ (cp. Relaxation etc.)

$$\int_{0}^{\infty} \exp\left(-\frac{t}{\tau}\right) \cdot \exp\left(-i \cdot \omega \cdot t\right) dt = \int_{0}^{\infty} \exp\left(-\left(i \cdot \omega + \frac{1}{\tau}\right) \cdot t\right) dt$$

$$= \left[ -\frac{1}{i \cdot \omega + \frac{1}{\tau}} \cdot \exp\left(-\left(i \cdot \omega + \frac{1}{\tau}\right) \cdot t\right) \right]_{0}^{\infty} = \frac{1}{i \cdot \omega + \frac{1}{\tau}} \cdot \frac{1}{\tau}$$

$$= \frac{1}{\tau \cdot \omega^2 + \frac{1}{\tau^2}} - i \cdot \frac{\omega}{\omega^2 + \frac{1}{\tau^2}}$$

real part imaginary part
absorptive dispersive

Magnitude: $\sqrt{\text{Re}^2 + \text{Im}^2} \Rightarrow \text{“broader feet”}$

(cp. single slit diffraction pattern)

b) box $\xrightarrow{\text{FT}}$ sinc

$$\text{FT}$$

cp. single slit diffraction pattern

q-vector
proof:

\[ \int_{-\infty}^{\infty} \exp(-i \cdot \omega \cdot t) dt = \left[ \frac{-1}{i \cdot \omega} \cdot \exp(-i \cdot \omega \cdot t) \right]_{-\infty}^{\infty} \]

\[ = \frac{-1}{i \cdot \omega} \cdot (\exp(-i \cdot \omega \cdot t_0) - \exp(i \cdot \omega \cdot t_0)) \]

\[ = \frac{-1}{i \cdot \omega} \cdot (\cos(\omega \cdot t_0) - i \cdot \sin(\omega \cdot t_0) - (\cos(\omega \cdot t_0) + i \cdot \sin(\omega \cdot t_0))) \]

\[ = \frac{-1}{i \cdot \omega} \cdot 2 \cdot (-i \cdot \sin(\omega \cdot t_0)) = \frac{2 \sin(\omega \cdot t_0)}{\omega} \cdot \sin(\omega) \]

remark: \( \exp(i \cdot \omega \cdot t) = \cos(\omega \cdot t) + i \cdot \sin(\omega \cdot t); \quad \exp(i \cdot \pi) + 1 = 0 \) (Euler)

c) Gaussian \( \xrightarrow{\text{FT}} \) Gaussian (without proof)

\[ \int_{-\infty}^{+\infty} \exp \left( -\frac{t^2}{2 \sigma^2_t} \right) \cdot \exp(-i \cdot \omega \cdot t) = \sqrt{2\pi} \cdot \sigma_t \cdot \exp \left( -\frac{\omega^2 \cdot \sigma^2_t}{2} \right) \]

5) convolution

Multiplication of a timesignal \( t_0 \) with a function \( g(t) \) corresponds to a convolution in Fourier space.

In NMR the measured timesignals are often multiplied with \( \exp(-kt) \) or \( \exp(-k't^2) \).
(This is equal to a convolution with a lorentzian or a gaussian.)

Example:
however, like those of chromic oxide and the oxide of zinc, in which a shifting of a region of maximum of reflecting-power towards the longer wave-lengths actually occurs when the pigment is heated.

It had been our purpose in the investigation just described to extend our spectro-photometric measurements to the very low temperatures obtainable by the use of solid carbon dioxide, but we have been compelled by lack of time to content ourselves with noting such changes as could be detected with the unaided eye. The change observed was in every case that which would be brought about by increase of reflecting-power. There was no increase in the saturation of the colour, rather, on the other hand, a paling or dilution of the tint, as though there were a tendency towards white. Houston*, who made a similar set of observations at the higher temperatures reached by the evaporation of carbon bisulphide or sulphurous acid, arrived at a similar result. Ackroyd, from theoretical considerations, concluded that as the absolute zero is approached the prevailing tints of pigments will be blues and violets, merging finally into white.

Ackroyd, Hartley, as also Houston and Thomson, and still earlier Schönbein and Brewster, have had something to say concerning the explanation of these phenomena. Their various views need not be touched upon here, unless it be to call attention to the opening paragraph of Ackroyd’s paper, which contains an important statement. Ackroyd says:—

“These changes embrace a class of phenomena, quite as important in their way as phosphorescence and fluorescence, with which in fact they are intimately connected.” It is our opinion that the connexion is indeed a most intimate one, and that every change of colour that pigments undergo is to be regarded simply as a symptom of changes in the radiating-power of the substance.

Physical Laboratory of Cornell University,
June 1891.

II.3. Dynamical Problems in Illustration of the Theory of Gases. By Lord Rayleigh, Sec. R.S.†

Introduction.

While investigations, of which a part is here presented, had

* Loc. cit. p. 128.
† Communicated by the Author.
Illustration of the Theory of Gases.

degree to a want of preparation in the mind of readers, who are confronted suddenly with ideas and processes of no ordinary difficulty. For myself, at any rate, I may confess that I have found great advantage from a more gradual method of attack, in which effort is concentrated upon one obstacle at a time. In order to bring out fundamental statistical questions, unencumbered with other difficulties, the motion is here limited to one dimension, and in addition one set of impinging bodies is supposed to be very small relatively to the other. The simplification thus obtained in some directions allows interesting extensions to be made in others. Thus we shall be able to follow the whole process by which the steady state is attained, when heavy masses originally at rest are subjected to bombardment by projectiles fired upon them indifferently from both sides. The case of pendulums, or masses moored to fixed points by elastic attachments, is also considered, and the stationary state attained under a one-sided or a two-sided bombardment is directly calculated.

Collision Formulae.

If \( u', v' \) be the velocities before collision, \( u, v \) after collision, of two masses \( P, Q \), we have by the equation of energy

\[
P(u'^2 - u^2) + Q(v'^2 - v^2) = 0, \quad \ldots \ldots \ldots \ldots \quad (1)
\]

and by the equation of momentum,

\[
P(u' - u) + Q(v' - v) = 0. \quad \ldots \ldots \ldots \ldots \quad (2)
\]

From (1) and (2)

\[
u' + u = v' + v, \quad \ldots \ldots \ldots \ldots \quad (3)
\]

or, as it may be written,

\[
u' - v' = v - u,
\]

signifying that the relative velocity of the two masses is reversed by the collision. From (2) and (3),

\[
\begin{align*}
(P + Q)u' &= (P - Q)u + 2Qv \\
(P + Q)v' &= 2Pu + (Q - P)v
\end{align*}
\]

As is evident from (1) and (2), we may, in (4), if we please, interchange the dashed and undashed letters. Thus from the first of (4),

\[
(P + Q)u = (P - Q)u' + 2Qv',
\]
or

\[ u' = \frac{P + Q}{P - Q} \cdot u - \frac{2Q}{P - Q} \cdot v' \]

\[ = u + \frac{2Q}{P - Q} (u - v'), \ldots \ldots \ldots \ldots (5) \]

In the application which we are about to make, \( P \) will denote a relatively large mass, and \( Q \) will denote the relatively small mass of what for the sake of distinction we will call a projectile. All the projectiles are equal, and in the first instance will be supposed to move in the two directions with a given great velocity. After collision with a \( P \) the projectile rebounds and disappears from the field of view. Since in the present problem we have nothing to do with the velocity of rebound, it will be convenient to devote the undashed letter \( v \) to mean the given initial velocity of a projectile. Writing also \( q \) to denote the small ratio \( Q : P \), we have

\[ u' = u + \frac{2q}{1 - q} (u - v), \ldots \ldots \ldots (6) \]

If \( u \) and \( v \) be supposed positive, this represents the case of what we may call a favourable collision, in which the velocity of the heavy mass is increased. If the impact of the projectile be in the opposite direction, the velocity \( u'' \), which becomes \( u \) after the collision, is given by

\[ u'' = u + \frac{2q}{1 - q} (u + v), \ldots \ldots \ldots (7) \]

The symbol \( v \) thus denotes the velocity of a projectile without regard to sign, and \( (7) \) represents the result of an unfavourable collision.

**Permanent State of Free Masses under Bombardment.**

The first problem that we shall attack relates to the ultimate effect upon a mass \( P \) of the bombardment of projectiles striking with velocity \( v \), and moving indifferently in the two directions. It is evident of course that the ultimate state of a particular mass is indefinite, and that a definite result can relate only to probability or statistics. The statistical method of expression being the more convenient, we will suppose that a very large number of masses are undergoing bombardment independently, and inquire what we are to expect as the ultimate distribution of velocity among them. If the number of masses for which the velocity lies between \( u \) and \( u + du \) be
denoted by \( f'(u) du \), the problem before us is the determination of the form of \( f'(u) \).

The number of masses, whose velocities lie between \( u \) and \( u + du \), which undergo collision in a given small interval of time, is proportional in the first place to the number of the masses in question, that is to \( f'(u) du \), and in the second place to the relative velocity of the masses and of the projectiles. In all the cases which we shall have to consider \( v \) is greater than \( u \), so that the chance of a favourable collision is always proportional to \( v - u \), and that of an unfavourable collision to \( v + u \). It is assumed that the chances of collision depend upon \( u \) in no other than the above specified ways. The number of masses whose velocities in a given small interval of time are passing, as the result of favourable collisions, from below \( u \) to above \( u \), is thus proportional to

\[
\int_{u'}^{u} f'(w) \cdot (v_1 - w) \, dw, \quad \ldots \ldots \ldots \ldots \quad (8) *
\]

where \( u' \) is defined by (6); and in like manner the number which pass in the same time from above \( u \) to below \( u \), in consequence of unfavourable collisions, is

\[
\int_{u}^{u''} f'(w) \cdot (v_1 - w) \, dw, \quad \ldots \ldots \ldots \ldots \quad (9)
\]

\( u'' \) being defined by (7). In the steady state as many must pass one way as the other, and hence the expressions (8) and (9) are to be equated. The result may be written in the form

\[
v_1 \left\{ \int_{u'}^{u} - \int_{u}^{u''} \right\} f'(w) \, dw = \int_{u'}^{u''} w f'(w) \, dw. \quad \ldots \ldots \ldots \ldots \quad (10)
\]

Now, if \( q \) be small enough, one collision makes very little impression upon \( u \); and the range of integration in (10) is narrow. We may therefore expand the function \( f' \) by Taylor's theorem:

\[
f'(w) = f'(u) + (w - u) f''(u) + \frac{1}{2} (w - u)^2 f'''(u) + \ldots \ldots ;
\]

so that

\[
\int f'(w) \, dw = w f'(u) + \frac{1}{2} (w - u)^2 f''(u) + \frac{1}{6} (w - u)^3 f'''(u) + \ldots \ldots ;
\]

\[
\left\{ \int_{u'}^{u} - \int_{u}^{u''} \right\} f'(w) \, dw = (2u - u' - u'') f'(u) \]

\[
- \frac{1}{2} (u' - u)^2 + (u'' - u)^2 \frac{1}{2} f'''(u) + \ldots \ldots ;
\]

\[
= - \frac{Aq}{1 - q} f'(u) - \frac{Aq^2}{(1 - q)^2} (v^2 + u^2) f''(u) + \text{cubes of } q. \quad (11)
\]

* In the present problem \( v_1 = v \); but it will be convenient at this stage to maintain the distinction.
Also
\[
\int w f'(w) dw = \int \left\{ (w - u) + u \right\} f(w) dw
\]
\[
= \frac{1}{2} (w - u)^2 f'(u) + \frac{1}{4} (w - u)^3 f''(u) + \ldots
\]
\[
+ u f(u) \left\{ w f'(u) + \frac{1}{2} (w - u)^2 f''(u) + \ldots \right\};
\]
so that
\[
\int w f'(w) dw = u f(u) \cdot (u' - u')
\]
\[
+ \left\{ \frac{1}{2} f(u) + \frac{1}{4} u f(u) \right\} \left[ (u'' - u^2) - (u' - u^2)^2 \right] + \ldots
\]
\[
= \frac{4qv}{1-q} u f(u) + \frac{8q^2 v u}{(1-q)^2} \left\{ f(u) + u f'(u) \right\} + \text{cubes of } q. \ (12)
\]
As far as \( q^2 \) inclusive (10) thus becomes
\[
\frac{4qv_1}{1-q} u f(u) + \frac{4q^2 v_1}{(1-q)^2} (v^2 + u^2) f'(u)
\]
\[
+ \frac{4qv}{1-q} u f(u) + \frac{8q^2 u v}{(1-q)^2} \left\{ f(u) + u f'(u) \right\} = 0,
\]
or
\[
u f(u) \{(1-q)v_1 + (1+q)v\} + g f'(u)\{v_1 v^2 + u^2(v_1 + 2v)\} = 0.
\]
If \( v_1 = v \), \( q \) disappears from the first term as it stands, and will do so in any case in the limit when it is made infinitely small. Moreover, in the second term \( u^2 \) is to be neglected in comparison with \( v^2 \). We thus obtain
\[
u f(u) \{1 + v/v_1\} + q v^2 f'(u) = 0 \ldots \ldots \ (13)
\]
as the differential equation applicable to the determination of \( f(u) \) when \( q \) is infinitely small. The integral is
\[
q v^2 \log f(u) + \frac{1}{2} (1 + v/v_1) u^2 = \text{constant},
\]
or
\[
f'(u) = \Lambda e^{-h u^2}, \ldots \ldots \ldots \ldots \ldots \ (14)
\]
where
\[
h = \frac{1 + v/v_1}{2q v^2}; \ldots \ldots \ldots \ldots \ldots \ (15)
\]
or, if \( v_1 = v \),
\[
h = 1/q v^2. \ldots \ldots \ldots \ldots \ldots \ (16)
\]
The ultimate distribution of velocities among the masses is thus a function of the energy of the projectiles and not otherwise of their common mass and velocity. The ultimate state is of course also independent of the number of the projectiles.
Illustration of the Theory of Gases.

The form of \( f \) is that found by Maxwell. To estimate the mean value of \( u^2 \) we must divide

\[
\int_{-\infty}^{+\infty} u^2 f(u) \, du \text{ by } \int_{-\infty}^{+\infty} f(u) \, du.
\]

Now

\[
\int_{-\infty}^{+\infty} u^2 e^{-u^2/(2qv^2)} \, du = \frac{1}{2} qv^2 \left\{ u e^{-u^2/(2qv^2)} - \int e^{-u^2/(2qv^2)} \, dv \right\},
\]

so that

\[
\int_{-\infty}^{+\infty} u^2 e^{-u^2/(2qv^2)} \, du = \frac{1}{2} qv^2 \int_{-\infty}^{+\infty} e^{-u^2/(2qv^2)} \, du.
\]

The ratio in question is thus \( \frac{1}{2} qv^2 \), showing that the mean kinetic energy of a mass is one half that of a projectile, deviating from the law of equal energies first (1815) laid down by Waterston. We must remember, however, that we have thus far supposed the velocities of the projectiles to be all equal.

The value of \( \Lambda \) in (14) may be determined as usual. If \( N \) be the whole (very great) number of masses to which the statistics relate,

\[
N = \int_{-\infty}^{+\infty} f(u) \, du = \Lambda \int_{-\infty}^{+\infty} e^{-u^2/(2qv^2)} \, du = \Lambda v \sqrt{\pi q};
\]

so that

\[
f(u) \, du = \frac{N}{v \sqrt{\pi q}} e^{-u^2/(2qv^2)} \, du, \quad \ldots \quad (15')
\]

If we were to suppose that the chances of a favourable or unfavourable collision were independent of the actual velocity of a mass, there would still be a stationary state defined by writing \( v_t = \infty \) in (15). Under these circumstances the mean energy would be twice as great as that calculated above.

It is easy to extend our result so as to apply to the case of projectiles whose velocities are distributed according to any given law \( F(v) \), of course upon the supposition that the projectiles of different velocities do not interfere with one another. We have merely to multiply by \( F(v) \, dv \) and to integrate between 0 and \( \infty \). Thus from (13) we obtain

\[
2u f(u) \int_{0}^{+\infty} v F(v) \, dv + q f'(u) \int_{0}^{+\infty} v^2 F(v) \, dv = 0. \quad (17)
\]

If \( F(v) = e^{-kv^2} \), we find

\[
\int v^2 e^{-kv^2} \, dv = -\frac{1}{2k} \left \{ v^2 e^{-kv^2} - \int e^{-kv^2} 2v \, dv \right \},
\]

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so that
\[ \int_0^{+\infty} v^3 e^{-kv^2} dv = \frac{1}{k} \int_0^{+\infty} ve^{-kv^2} dv. \]  \hspace{1cm} (18)

Our equation then becomes
\[ 2ku f(u) + uf'(u) = 0, \]
giving
\[ f(u) = Ae^{-ku^2/4}. \]  \hspace{1cm} (19)

The mean energy of the masses is \( \frac{1}{2} q/k, \) and this is now equal to the mean energy of the projectiles. We see that if the mean energy of the projectiles is given, their efficiency is greater when the velocity is distributed according to the Maxwell law than when it is uniform, and that in the former case the Waterston relation is satisfied, as was to be expected from investigations in the theory of gases.

It may perhaps be objected that the law \( e^{-ku^2} \) is inconsistent with our assumption that \( v \) is always great in comparison with \( u. \) Certainly there will be a few projectiles for which the assumption is violated; but it is pretty evident that in the limit when \( q \) is small enough, the effect of these will become negligible. Even when the velocity of the projectiles is constant, the law \( e^{-u^2/4q^2} \) must not be applied to values of \( u \) comparable with \( v. \)

The independence of the stationary state of conditions, which at first sight would seem likely to have an influence, may be illustrated by supposing that the motion of the masses is constrained to take place along a straight line, but that the direction of motion of the projectiles, striking always centrically, is inclined to this line at a constant angle \( \theta. \)

If \( u' \) be the velocity of the mass (unity) before impact, and \( u \) after impact, \( B \) the impulsive action between the mass and the projectile,
\[ u - u' = B \cos \theta. \]

Also, if \( v, V \) be the velocities of the projectile (\( q \)) before and after impact,
\[ q(v - V) = B. \]
so that
\[ q(v - V) \cos \theta = u - u'. \]

By the equation of energy
\[ u^2 - u'^2 = q(v^2 - V^2). \]

From these we find, as before,
\[ u' = u - \frac{2q \cos^2 \theta}{1 - q \cos^2 \theta} \left( u - \frac{v}{\cos \theta} \right). \]

This may be regarded as a generalization of (6); and we see that it may be derived from (6) by writing \( v/\cos \theta \) for \( v \), and \( q \cos^2 \theta \) for \( q \). In applying equation (10) to determine the stationary state, we must remember that the velocity of retreat is now no longer \( w \), but \( w \cos \theta \), so that (10) becomes
\[ v \left\{ \int_{u}^{u'} - \int_{w}^{w'} \right\} f(w) dw = \int_{w}^{w'} w \cos \theta f(w) dw. \]

The entire effect of the obliquity \( \theta \) is thus represented by the substitution of \( v/\cos \theta \) for \( v \), and of \( q \cos^2 \theta \) for \( q \), and since these leave \( qv^2 \) unaltered, the stationary state, determined by (15), is the same as if \( \theta = 0 \).

The results that we have obtained depend entirely upon the assumption that the individual projectiles are fired at random, and without distinction between one direction and the other. The significance of this may be illustrated by tracing the effect of a restriction. If we suppose that the projectiles are despatched in pairs of closely following components, we should expect that the effect would be the same as of a doubling of the mass. If, again, the components of a pair were so projected as to strike almost at the same time upon opposite sides, while yet the direction of the first was at random, we should expect the whole effect to become evanescent. These anticipations are confirmed by calculation.

By (5) the velocity \( u'_1 \), which on collision becomes \( u \), is
\[ u'_1 = \frac{1 + q}{1 - q} u + \frac{2q}{1 - q} v; \]

so that the velocity, which after two consecutive collisions upon the same side becomes \( u \), is given by
\[ u''_2 = \frac{1 + q}{1 - q} u'_1 + \frac{2q}{1 - q} v \]
\[ = \frac{1 + 2q + (q^2)}{1 - 2q + (q^2)} u + \frac{4qv}{1 - 2q + (q^2)}. \]
The masses which by single collisions at velocity \( v \) would ultimately produce the same effect as these pairs are therefore very approximately \( 2v \).

If the projectiles be distributed in pairs in such a way that the components of each strike nearly simultaneously and upon opposite sides,

\[
 u'' = \frac{1+q}{1-q} \left\{ \frac{1+q}{1-q} u + \frac{2qv}{1-q} \right\} + \frac{2qv}{1-q}
\]

\[
 = \frac{(1+q)^2}{(1-q)^2} u + \frac{4q^2v}{(1-q)^2}
\]

\[
 = \frac{1+2q+(q^2)}{1-2q+(q^2)} u + \frac{4q \cdot qv}{1-2q+(q^2)};
\]

showing that the effect is the same as if the mass were doubled, and the velocity reduced from \( v \) to \( qv \). Thus, when \( q \) is infinitely small, the effect is negligible in comparison with that obtained when the connexion of the components of a pair is dissolved, and each individual is projected at random.

**Another Method of Investigation.**

The method followed in the formation of equation (10) seems to lead most simply to the required determination of \( f(w) \); but it is an instructive variation to consider directly the balance between the numbers of masses which change their velocities from and to \( u \).

The number of masses whose velocities lie between \( u \) and \( u + du \) being \( f(u)du \), we have as the number whose velocities in a given small interval of time are expelled from the range \( du \),

\[
 f(u)du (v-u) + f(u') du (v+u),
\]

or

\[
 2uvf(u)du.
\]

This, in the steady state, is equal to the number which enter the range \( du \) from the two sides in consequence of favourable and unfavourable collisions; so that

\[
 f(u')(v-u')du' + f(u'')(v+u'')du'' - 2uvf(u)du = 0. \quad (20)
\]

By (6), (7), since \( v \) is constant,

\[
 du' = \frac{1+q}{1-q} du, \quad du'' = \frac{1+q}{1-q} du;
\]

so that

\[
 \frac{1+q}{1-q} f(u') (v-u') + \frac{1+q}{1-q} f(u'') (v+u'') - 2vf(u) = 0.
\]
Now
\[ v - u' = \frac{1 + q}{1 - q} (v - u), \quad v + u'' = \frac{1 + q}{1 - q} (v + u), \]
and thus
\[ \frac{(1 + q)^2}{(1 - q)^3} \{ (v - u) f'(u') + (v + u) f(u'') \} - 2v f(u) = 0. \]
In this
\[ f(u') = f(u) + \frac{2q(u - v)}{1 - q} f'(u) + \frac{2q^2(u - v)^2}{(1 - q)^2} f''(u) + \ldots \]
\[ f(u'') = f(u) + \frac{2q(u + v)}{1 - q} f'(u) + \frac{2q^2(u + v)^2}{(1 - q)^2} f''(u) + \ldots; \]
so that
\[ \frac{(1 + q)^2}{(1 - q)^3} \{ 2v f(u) + \frac{8q v}{1 - q} u f'(u) + \frac{4q^2 v^3}{(1 - q)^2} f''(u) \} - 2v f(u) = 0, \]
or, when \( q \) is small enough,
\[ 8q v \{ f(u) + uf'(u) \} + 4q^2 v^3 f''(u) = 0. \quad (21) \]
Accordingly
\[ f(u) + uf'(u) + \frac{1}{2} q v^2 f''(u) = 0, \quad (22) \]
or on integration
\[ uf(u) + \frac{1}{2} q v^2 f'(u) = C. \]
It is easy to recognize that the constant \( C \) of integration
\[ C = \frac{1}{2} q v^2 f'(0), \]
for \( f(0) \) is not infinite. Now \( f(u) \) is by its nature an even function of \( u \), so that \( f'(0) \) must vanish. We thus obtain the same equation (14) of the first order as by the former process.

**Progress towards the Stationary State.**

Passing from the consideration of the steady state, we will now suppose that the masses are initially at rest, and examine the manner in which they acquire velocity under the impact of the projectiles. In the very early stages of the process the momentum acquired during one collision is practically independent of the existing velocity \( u \) of a mass, and may be taken to be \( \pm 2qv \). Moreover, the change of a collision is at first sensibly independent of \( u \). In the present investigation we are concerned not merely, as in considering the ultimate state, with the mass and velocity of a projectile, but also with the frequency of impact. We will denote by \( v \) the whole number of projectiles launched in both directions.

in the unit of time in the path of each mass. The chance of a collision for a given mass in time $dt$ is thus represented by $v dt$. The number of collisions by which masses are expelled from the range $du$ in time $dt$ is $f(u) du \cdot v dt$. The number which enter the range from the two sides is

$$\{ f(u-2qv) + f(u+2qv) \} du \cdot \frac{1}{2} v dt,$$

so that the excess of the number which enter the range over the number which leave is

$$\{ \frac{1}{2} f(u-2qv) + \frac{1}{2} f(u+2qv) - f(u) \} du \cdot v dt,$$

and this is to be equated to $\frac{df(u,t)}{dt} du - dt$. Thus

$$\frac{df}{v dt} = \frac{1}{2} f(u-2qv) + \frac{1}{2} f(u+2qv) - f(u) = 2q^2 v^2 \frac{df}{du^2},$$  \hspace{1cm} (23)

the well-known equation of the conduction of heat. When $t=0$, $f(u)$ is to be zero for all finite values of $u$. The Fourier solution, applicable under these conditions, is

$$f(u, t') = \frac{A}{\sqrt{t'}} e^{-u^2/4t'},$$

where $t'$ is written for $2q^2 v^2 t$. The total number of masses being $N$, we get to determine $A$

$$N = \int_{-\infty}^{+\infty} f(u, t') du = 2 \sqrt{\pi} \cdot A;$$

so that

$$f(u, t') = \frac{N}{2 \sqrt{\pi t'}} e^{-u^2/4t'}, \quad \ldots \quad (24)$$

If $n$ be the whole number of collisions (for each mass), $n = vt$, and we have

$$At' = 4q^2 v^2 \cdot 2n, \quad \ldots \quad (25)$$

If the unit of velocity be so chosen that the momentum $(2qv)$ communicated at each impact is unity, (24) takes the form

$$f(u, n) = \frac{N}{\sqrt{(2\pi n)}} e^{-u^2/2n}, \quad \ldots \quad (26)$$

which exhibits the distribution of momentum among the masses after $n$ impacts. In this form the problem coincides with one formerly treated* relating to the composition of vibrations of arbitrary phases. It will be seen that there is a

* Phil. Mag. August 1880, p. 73
sharp contrast between the steady state and the early stages of the variable state. The latter depends upon the momentum of the projectiles, and upon the number of impacts; the former involves the energy of the projectiles, and is independent of the rapidity of the impacts.

The mean square of velocity after any number \( n \) of impacts is

\[
N^{-1} \int_{-\infty}^{+\infty} u^2 f(u, n) du = n,
\]

or, if we restore \( 4q^2v^2 \),

\[
\text{mean } u^2 = n \cdot 4q^2v^2.
\]

(27)

It must be distinctly understood that the solution expressed by (24), (25), (26) applies only to the first stages of the bombardment, beginning with the masses at rest. If the same state of things continued, the motion of the masses would increase without limit. But as time goes on, two causes intervene to prevent the accumulation of motion. When the velocity of the masses becomes sensible, the chance of an unfavourable collision increases at the expense of the favourable collisions, and this consideration alone would prevent the unlimited accumulation of motion, and lead to the ultimate establishment of a steady state. But another cause is also at work in the same direction, and, as may be seen from the argument which leads to (13), with equal efficiency. The favourable collisions, even when they occur, produce less effect than the unfavourable ones, as is shown by (6) and (7).

We will now investigate the general equation, applicable not merely to the initial and final, but to all stages of the acquisition of motion. As in (20), (23) we have

\[
\frac{df(u,t)du}{dt} = \frac{vd}{v} \left\{ \frac{1}{2} f(u') \cdot (v-u') du' + \frac{1}{2} f(u'') \cdot (v+u'') du'' - f(u) \cdot v \cdot du \right\};
\]

and thus by the same process as for (22)

\[
\frac{df}{v \, dt} = 4q \frac{d}{du} \{ uf(u) \} + 2q^2v^2 \frac{d^2 f}{du^2}, \quad \ldots \ldots
\]

(28)

If we write, as before,

\[
t = 2q^2v^2 t, \quad \text{and} \quad \gamma = 1/qv^2, \quad \ldots \ldots
\]

(29)

we have

\[
\frac{df}{dt'} = \frac{d^2 f}{du'^2} + 2\gamma \frac{d}{du'} (uf) \quad \ldots \ldots
\]

(30)
Both in the case where the left side was omitted, and also when \( h \) vanished, we found that the solution was of the form
\[
f = \sqrt{\phi} \cdot e^{-\phi u^2}, \quad \ldots \ldots \ldots (31)
\]
where \( \phi \) was constant, or a function of \( t' \) only. We shall find that the same form applies also to the more general solution. The factor \( \sqrt{\phi} \) is evidently necessary in order to make
\[
\int_{-\infty}^{+\infty} f(u) \, du \text{ independent of the time.}
\]
By differentiation of (31),
\[
\frac{df}{dt'} = \frac{1}{2} \phi \cdot e^{-\phi u^2} (1 - 2\phi u^2) \frac{d\phi}{dt'},
\]
\[
\frac{d^2 f}{du^2} = -2\phi^2 e^{-\phi u^2} (1 - 2\phi u^2),
\]
\[
u \frac{df}{du} + f = \phi^2 e^{-\phi u^2} (1 - 2\phi u^2);
\]
so that (30) is satisfied provided \( \phi \) is so chosen as a function of \( t' \) that
\[
\frac{1}{2} \phi^{-1} \frac{d\phi}{dt'} = -2\phi^2 + 2h \phi^4,
\]
or
\[
\frac{1}{4\phi^3} \frac{d\phi}{dt'} = -1 + \frac{h}{\phi}.
\]
Thus
\[
\Delta t' = \int \frac{d\phi^{-1}}{1 - h\phi^{-1}} = -\frac{1}{h} \log (1 - h\phi^{-1}) + \text{const.,}
\]
where, however, the constant must vanish, since \( \phi = \infty \) corresponds to \( t' = 0 \). Accordingly
\[
\phi = \frac{h}{1 - e^{-\alpha t'}}, \quad \ldots \ldots \ldots \ldots \ldots (32)
\]
which with (31) completes the solution.

If \( t' \) is small, (32) gives \( \phi = 1/\Delta t' \), in agreement with (24); while if \( t' \) be great, we have \( \phi = h = 1/\nu^2 \), as in (15').

The above solution is adapted to the case where \( f(u) = 0 \) for all finite values of \( u \), when \( \phi = 0 \). The next step in the process of generalization will be to obtain a solution applicable to the initial concentration of \( f(u) \), no longer merely at zero, but at any arbitrary value of \( u \); that is, to the case where initially all the masses are moving with one constant velocity \( a \).
Illustration of the Theory of Gases.

Assume
\[ f = \sqrt{\phi} e^{-\phi(u-\psi)^2} \quad \ldots \quad (33) \]
where \( \phi, \psi \) are functions of \( t' \) only. Substituting, as before, in (30), we find
\[
\left\{ 1-2\phi(u-\psi)^2 \right\} \left\{ \frac{d\phi}{dt'} + 2\phi^2 - 2h\phi \right\} + 2\phi^2(u-\psi) \left\{ \frac{d\psi}{dt'} + 2h\psi \right\} = 0 ;
\]
so that the equation is satisfied provided
\[ \frac{1}{2} \frac{d\phi}{dt'} + 2\phi^2 - 2h\phi = 0, \quad \ldots \quad (34) \]
and
\[ \frac{d\psi}{dt'} + 2h\psi = 0. \quad \ldots \quad (35) \]
The first is the same equation as we found before, and its solution is given by (32); while (35) gives
\[ \psi = \alpha e^{-2ht'}. \quad \ldots \quad (36) \]
Thus (32), (33), (36) constitute the complete solution of the problem proposed, and show how the initial concentration at \( u = \alpha \) passes gradually into the steady state when \( t' = \infty \). In the early stages of the process,
\[ f(u, t') = \frac{1}{\sqrt{4\pi t'}} e^{-(u-\alpha)^2/4ht'} ; \quad \ldots \quad (37) \]
to which the factor \( N/\sqrt{\pi} \) may be applied, when it is desired to represent that the whole number of masses is \( N \). It appears that during the whole process the law of distribution is in a sense maintained, the only change being in the value of \( u \) round which the grouping takes place, and in the degree of concentration about that value.

There will now be no difficulty in framing the expression applicable to an arbitrary initial distribution of velocity among the masses. For this purpose we need only multiply (33) by \( \chi(\alpha) \, d\alpha \), and integrate over the necessary range. Thus
\[ f(u, t') = \sqrt{\phi} \int_{-\infty}^{+\infty} d\alpha \chi(\alpha) \exp\{-\phi(u-\alpha e^{-2ht'})^2\} ; \quad \ldots \quad (38) \]
\( \phi \) being given, as usual, by (32). The limits for \( \alpha \) are taken \( +\infty \); but we must not forget that the restriction upon the magnitude of \( u \) requires that \( \chi(u) \) shall be sensible only for values of \( u \) small in comparison with \( v \).
When is small, we have from (38),

\[ f(u, \tau) = \frac{1}{\sqrt{(4\pi)}} \int_{-\infty}^{+\infty} d\alpha \chi(\alpha) e^{-\frac{(u-\alpha)^2}{\tau}} = \sqrt{\pi} \cdot \chi(u) \text{ ultimately}; \]

so that

\[ \chi(\alpha) = \frac{1}{\sqrt{\pi}} f(\alpha, 0). \]

Accordingly the required solution expressing the distribution of velocity at \( \tau' \) in terms of that which obtains when \( \tau' = 0 \), is

\[ f(u, \tau') = \sqrt{\frac{\phi}{\pi}} \int_{-\infty}^{+\infty} d\alpha f(\alpha, 0) \exp\{ -\phi(u - a \cdot e^{-\nu \tau'})^2 \}. \quad (39) \]

We may verify this by supposing that \( f(u, 0) = e^{-hu^2} \), representing the steady state. The integration of (39) then shows that

\[ f(u, \tau') = e^{-hu^2}, \]

as of course should be.

An example of more interest is obtained by supposing that initially

\[ f(u, 0) = e^{-hu^2}; \quad \ldots \ldots \ldots \quad (40) \]

that is, that the velocities are in the state which would be a steady state under the action of projectiles moving with an energy different from the actual energy. In this case we find from (32), (39),

\[ f(u, \tau') = \sqrt{(\frac{\phi}{\phi - h + \nu})} e^{-\frac{\phi h u^2}{\phi - h + \nu}}. \quad (41) \]

We will now introduce the consideration of variable velocity of projectiles into the problem of the progressive state. In (28) we must regard \( \nu \) as a function of \( \nu \). If we use \( \nu \, d\nu \) to denote the number of projectiles launched in unit of time with velocities included between \( \nu \) and \( \nu + d\nu \), (28) may be written

\[ \frac{df}{dt} = 4g \int \nu \, d\nu \cdot \frac{d}{du} \{ uf(u) \} + 2g^2 \int \nu \, v^2 \, d\nu \cdot \frac{d^2 f}{d\nu^2}, \quad (42) \]

which is of the same form as before. The only difference is that we now have in place of (29),

\[ \tau' = 2g^2 t \int \nu \, v^2 \, d\nu, \quad \ldots \ldots \ldots \quad (43) \]

\[ h = \int \nu \, d\nu + \frac{g}{2} \int \nu \, v^2 \, d\nu. \quad \ldots \ldots \quad (44) \]

In applying these results to particular problems, there is an important distinction to be observed. By definition \( \nu \, d\nu \) represents the number of projectiles which in the unit time
pass a given place with velocities included within the prescribed range. It will therefore not represent the distribution of velocities in a given space; for the projectiles, passing in unit time, which move with the higher velocities cover correspondingly greater spaces. If therefore we wish to investigate the effect of a Maxwellian distribution of velocities among the projectiles, we are to take, not \( v = Be^{-ku^2} \), but
\[
v = B \nu e^{-ku^2}.
\]
(45)

In this case, by (18),
\[
h = k/\nu; 
\]
(46)
and, as we saw; the mean energy of a mass in the steady state is equal to the mean energy of the projectiles which at any moment of time occupy a given space. From (43),
\[
v' = B\nu^2 e^{-2k u}.
\]
(47)

Pendulums in place of Free Masses.

We will now introduce a new element into the question by supposing that the masses are no longer free to wander indefinitely, but are moored to fixed points by similar elastic attachments. And for the moment we will assume that the stationary state is such that no change would occur in it were the bombardment at any time suspended. To satisfy this condition it is requisite that the phases of vibrations of a given amplitude should have a certain distribution, dependent upon the law of force. For example, in the simplest case of a force proportional to displacement, where the velocity \( u \) is connected with the amplitude (of velocity) \( r \) and with the phase \( \theta \) by the relation \( u = r \cos \theta \), the distribution must be uniform with respect to \( \theta \), so that the number of vibrations in phases between \( \theta \) and \( \theta + d\theta \) must be \( d\theta/2\pi \) of the whole number whose amplitude is \( r \). Thus if \( r \) be given, the proportional number with velocities between \( u \) and \( u + du \) is
\[
\frac{du}{2\pi \sqrt{(r^2 - u^2)}}.
\]
(48)
And, in general, if \( r \) be some quantity by which the amplitude is measured, the proportional number will be of the form
\[
\phi(r, u) du, 
\]
(49)
where \( \phi \) is a determinate function of \( r \) and \( u \), dependent upon the law of vibration. If now \( \chi(r) dr \) denote the number of vibrations for which \( r \) lies between \( r \) and \( r + dr \), we have altogether for the distribution of velocities \( u \),
\[
f(u) = \int \chi(r) \phi(r, u) dr.
\]
(50)
If the vibrators were left to themselves, $\chi(r)$ might be chosen arbitrarily, and yet the distribution of velocity, denoted by $f(u)$, would be permanent. But if the vibrators are subject to bombardment, $f(u)$ cannot be permanent, unless it be of the form already determined. The problem of the permanent state may thus be considered to be the determination of $\chi(r)$ in (50), so as to make $f(u)$ equal to $e^{-\nu u^2}$.

We will now limit ourselves to a law of force proportional to displacement, so that the vibrations are isochronous; and examine what must be the form of $\chi(r)$ in (8) in order that the requirements of the case may be satisfied.

By (15'), if $N$ be the whole number of vibrators,

\[
\frac{N \sqrt{h}}{\sqrt{\pi}} e^{-\frac{h\sigma^2}{u^2}} = \int_{u}^{\infty} \frac{\chi(r)}{2\pi \sqrt{(v^2 - u^2)}} dr. \quad \ldots \quad (51)
\]

The determination of the form of $\chi$ is analogous to a well-known investigation in the theory of gases. We assume

\[
\chi(r) = A e^{-h\sigma^2}, \quad \ldots \quad \ldots \quad (52)
\]

where $A$ is a constant to be determined. To integrate the right-hand member of (51), we write

\[
r^2 = u^2 + \eta^2; \quad \ldots \quad \ldots \quad \ldots \quad (53)
\]

so that

\[
\int_{u}^{\infty} \frac{\chi(r)}{\sqrt{(v^2 - u^2)}} dr = A \int_{0}^{\infty} e^{-h(u^2 + \eta^2)} d\eta = \frac{A \sqrt{\pi}}{2 \sqrt{h}} e^{-hu^2}.
\]

Thus

\[
A = 4hN. \quad \ldots \quad \ldots \quad \ldots \quad (54)
\]

The distribution of the amplitudes (of velocity) is therefore such that the number of amplitudes between $r$ and $r + dr$ is

\[
N \cdot 4hr e^{-hr^2} dr, \quad \ldots \quad \ldots \quad \ldots \quad (55)
\]

while for each amplitude the phases are uniformly distributed round the complete cycle.

The argument in the preceding paragraphs depends upon the assumption that a steady state exists, which would not be disturbed by a suspension, or relaxation, of the bombardment. Now this is a point which demands closer examination; because it is conceivable that there may be a steady state, permanent so long as the bombardment itself is steady, but liable to alteration when the rate of bombardment is increased or diminished. And in this case we could not argue, as before, that the distribution must be uniform with respect to $\theta$.

If $x$ denote the displacement of a vibrator at time $t$,

\[
x = n^{-1} r \sin (n t - \theta), \quad dx/dt = r \cos (nt - \theta).
\]
Illustration of the Theory of Gases.

When \( t=0 \),

\[ x = -n^{-1} r \sin \theta, \quad dx/dt = u = r \cos \theta; \]

and we may regard the amplitude and phase of the vibrator as determined by \( u, \eta \), where

\[ u = r \cos \theta, \quad \eta = r \sin \theta. \]

Any distribution of amplitudes and phases may thus be expressed by

\[ f(u, \eta) \, du \, d\eta. \]

If we consider the effect of the collisions which may occur at \( t=0 \), we see that \( u \) is altered according to the laws already laid down, while \( \eta \) remains unchanged. The condition that the distribution remains undisturbed by the collisions is, as before, that, for every constant \( \eta \), \( f(u, \eta) \) should be of the form \( e^{-hu^2} \), or, as we may write it,

\[ f(u, \eta) = \chi(\eta) \, e^{-hu^2}. \]

But this condition is not sufficient to secure a stationary state, because, even in the absence of collisions, a variation would occur, unless \( f(u, \eta) \) were a function of \( r \), independent of \( \theta \). Both conditions are satisfied, if \( \chi(\eta) = \Lambda \, e^{-hr^2} \), where \( \Lambda \) is a constant; so that

\[ f(u, \eta) \, du \, d\eta = \Lambda \, e^{-h(u^2+r^2)} \, du \, d\eta = 2\pi \Lambda \, e^{-hr^2} \, r \, dr. \]

Under this law of distribution there is no change either from the progress of the vibrations themselves, or as the result of collisions.

The principle that the distribution of velocities in the stationary state is the same as if the masses were free is of great importance, and leads to results that may at first appear strange. Thus the mean kinetic energies of the masses is the same in the two cases, although in the one case there is an accompaniment of potential energy, while in the other there is none. But it is to be observed that nothing is here said as to the rate of progress towards the stationary condition when, for instance, the masses start from rest; and the fact that the ultimate distribution of velocities should be independent of the potential energy is perhaps no more difficult to admit than its independence of the number of projectiles which strike in a given time. One difference may, however, be alluded to in passing. In the case of the vibrators it is necessary to suppose that the collisions are instantaneous; while the result for the free masses is independent of such a limitation.

The simplicity of \( f \) in the stationary state has its origin in the independence of \( \theta \). It is not difficult to prove that this
law of independence fails during the development of the 
vibrations from a state of rest under a vigorous bombardment. 
The investigation of this matter is accordingly more com-
licated than in the case of the free masses, and I do not 
propose here to enter upon it.

In a modification of the original problem of some interest 
even the stationary distribution is not entirely independent 
of phase. I refer to the case where the bombardment is 
from one side only, or (more generally) is less vigorous on 
one side than on the other. It is easy to see that a one-sided 
bombardment would of necessity disturb a uniform distribu-
tion of phase, even if it were already established. The per-
manent state is accordingly one of unequal phase-distribution, 
and is not, as for the symmetrical bombardment, independent 
of the vigour with which the bombardment is conducted.

But in one important particular case the simplicity of the 
symmetrical bombardment is recovered. For if the number 
of projectiles striking in a given time be sufficiently reduced, 
the stationary condition must ultimately become one of uniform 
phase-distribution.

Under this limitation it is easy to see what the stationary 
state must be. Since the ultimate distribution is uniform 
with respect to phase, it must be the same from whichever 
side the bombardment comes. Under these circumstances it 
could not be altered if the bombardment proceeded indiffer-
cently from both sides, which is the case already investigated. 
We conclude that, provided the bombardment be very feeble, 
there is a definite stationary condition, independent both of 
the amount of the bombardment and of its distribution between 
the two directions. It is of course understood that from 
whichever side a projectile be fired, the moment of firing is 
absolutely without relation to the phase of the vibrator which 
it is to strike.

The problem of the one-sided bombardment may also be 
attacked by a direct calculation of the distribution of ampli-
tude in the stationary condition. The first step is to estimate 
the effect upon the amplitude of a given collision. From (6), 
if \( u' \) be the velocity before collision, and \( u \) after,

\[
u = u' + \frac{2q}{1+q} (v-u').\]

The fraction \( 2q/(1+q) \) occurs as a whole, and we might 
retain it throughout. But inasmuch as in the final result
Illustration of the Theory of Gases. 443

only one power of \( q \) need be retained, it will conduce to brevity to omit the denominator at once, and take simply

\[
u = \nu' + 2q(v - \nu'). \quad \ldots \quad (56)\]

Thus if \( \rho, \phi \) and \( r, \theta \) be the amplitude and phase before and after collision respectively,

\[
\begin{align*}
 r \cos \theta &= \rho \cos \phi + 2q(v - \rho \cos \phi), \\
r \sin \theta &= \rho \sin \phi;
\end{align*} \quad (57)
\]

so that

\[
r^2 = \rho^2 + 4\rho q \cos \phi (v - \rho \cos \phi) + 4q^2(v - \rho \cos \phi)^2.
\]

From this we require the approximate value of \( \rho \) in terms of \( r \) and \( \phi \). The term in \( q^2 \) cannot be altogether neglected, but it need only be retained when multiplied by \( v^2 \). The result is

\[
\rho = r - \delta r,
\]

where

\[
\delta r = 2q(v \cos \phi - r \cos^2 \phi) + \frac{2q^2v^2}{r} \sin^2 \phi. \quad (58)
\]

This equation determines for a given \( \phi \) the value of \( \rho \) which the blow converts into \( r \). Values of \( \rho \) nearer to \( r \) will be projected across that value. The chance of a collision at \( \rho, \phi \) is proportional to \( (v - \rho \cos \phi) \). Thus if a number of vibrators in state \( \rho, \phi \) be \( \tilde{F}(\rho) \, d\rho \, d\phi \), the condition for the stationary state is

\[
\int_{0}^{2\pi} d\phi \int_{\rho}^{r} (v - \rho \cos \theta) \tilde{F}(\rho) \, d\rho = 0, \quad (59)
\]

the integral on the left expressing the whole number (estimated algebraically) of amplitudes which in a small interval of time pass outwards through the value \( r \).

By expansion of \( \tilde{F}(\rho) \) in the series

\[
\tilde{F}(\rho) = \tilde{F}(r) + \tilde{F}'(r)(\rho - r) + \ldots,
\]

we find

\[
\int_{\rho}^{r} \tilde{F}(\rho) \, d\rho = \tilde{F}(r) \delta r - \frac{1}{2} \tilde{F}'(r) (\delta r)^2 + \text{cubes of } q,
\]

\[
\int_{\rho}^{r} \rho \tilde{F}(\rho) \, d\rho = v \tilde{F}(r) \delta r - \frac{1}{2} v\delta r (\tilde{F}'(r) + v \tilde{F}'(r) + \text{cubes of } q.
\]

* We here assume that the bombardment is feeble.
Again from (58),

\[ \int_0^{2\pi} \delta r \, d\phi = -q r + q^3 v^2 / r, \]
\[ \int_0^{2\pi} \cos \phi \delta r \, d\phi = q v, \]
\[ \int_0^{2\pi} (\delta r)^2 \, d\phi = 2q^2 v^2, \]
\[ \int_0^{2\pi} \cos \phi (\delta r)^2 \, d\phi = 0. \]

The condition for the stationary state is therefore

\[ v \{ F(r)(-q r + q^3 v^2 / r) - F'(r) q^2 v^2 \} - r F(r) q v = 0, \]

or

\[ F(r) \{ -2 r + q^2 v^2 / r \} - F'(r) q v^2 = 0. \]

Thus, on integration,

\[ r^2 - q v^2 \log r + q v^2 \log F(r) = \text{const.}, \quad \ldots \quad (60) \]

or

\[ F(r) = \Delta r e^{-r^2/q v^2}. \quad \ldots \quad (61) \]

The mean value of \( r^2 \), expressed by

\[ \int_0^\infty r^2 F(r) \, dr = \int_0^\infty r F(r) \, dr, \]

is \( q v^2 \); that is, the mean value of the maximum kinetic energy attained during the vibration is equal to the kinetic energy of a projectile. The mean of all the actual kinetic energies of the vibrators is the half of this; but would rise to equality with the mean energy of the projectiles, if the velocities of the latter, instead of being uniform, as above supposed, were distributed according to the Maxwellian law.

If we are content to assume the law of distribution, \( \rho e^{-h \rho^2} \), leaving only the constant \( h \) to be determined, the investigation may be much simplified. Thus from (57) the gain of energy from the collision is

\[ \frac{1}{2} r^2 - \frac{1}{2} \rho^2 = 2q \rho \cos \phi (v - \rho \cos \phi) + 2q^2 v^2. \]
Discharge of Electricity through Exhausted Tubes.

The chance of the collision in question is proportional to the relative velocity \((v - \rho \cos \phi)\); and in the stationary state the whole gain of energy is zero. Hence

\[
\int \rho e^{-\rho^2} \, d\rho \, d\phi \left\{ 2\rho \cos \phi (v - \rho \cos \phi)^2 + 2\rho^2 v^2 \right\} = 0.
\]

In the integration with respect to \(\phi\) the odd powers of \(\cos \phi\) vanish. Hence

\[
2qv \int_0^\infty \rho \, d\rho \, e^{-\rho^2} (qv^2 - \rho^2) = 0;
\]

so that

\[
h = 1/v^2,
\]

as in (61).

Terling Place, Witham,
August 18, 1801.

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[Continued from p. 336.]

Phosphorescence produced by the Discharge.

The discharge without electrodes produces a very vivid phosphorescence in the glass of the vessel in which the discharge takes place; the phosphorescence is green when the bulb is made of German glass, blue when it is made of lead glass. Not only does the bulb itself phosphoresce, but a piece of ordinary glass tubing held outside the bulb and about a foot from it phosphoresces brightly; while uranium glass will phosphoresce at a distance of several feet from the discharge. Similar effects, but to a smaller extent, are produced by the ordinary spark between the poles of an electrical machine.

The vessel in which the discharge takes place may be regarded as the secondary of an induction-coil, and the discharge in it shows similar properties to those exhibited by currents in a metallic secondary. Thus no discharge is produced unless there is a free way all round the tube; the discharge is stopped if the tube is fused up at any point. In order that the discharge may take place, it is necessary that the molecules of the gas shall be able to form a closed chain without the interposition of any non-conducting substance; indeed the discharge seems to be hindered by the
Appendix B

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Heinrich Hencky: a rheological pioneer

Abstract The literature of continuum mechanics and rheology often mentions the name of Hencky; Hencky strain, Hencky theorems, and many other concepts. Yet there is no coherent appraisal of his contributions to mechanics. Nor is there anywhere any description of his life. This article sets down some of what we have learned so far about this researcher, and appraises his pioneering work on rheology.

Keywords Hencky · Strain · Elasticity · Plasticity · Rheology · Biography

Motivation

The name Hencky is best known to rheologists through the so-called Hencky (or logarithmic) strain, but any student of plasticity theory will also encounter Hencky’s equations and theorems associated with slip-line theory. Hencky’s interpretation of the von Mises yield criterion, and his deformation theory of plastic flow; see, for example, Chakraborty (1987). A search of the internet will also show his contribution to the elastic buckling of loaded rings. A study of citations shows that, 50 years after his death, many of his papers are still frequently cited. In spite of this continuing visibility, very little is available about the life of this man (Tanner and Walters 1998), and our curiosity has led us to write down some of what we have been able to find so far about him. We also discuss his work with a view to evaluating his contributions to solid mechanics and rheology.

Early years

Heinrich Karl Hencky, a Bavarian school administrator whose job meant that he was often moved around so Heinrich Hencky changed schools often. He finished his secondary schooling at Speyer on the Rhine in 1904. He had a brother Karl Georg also born in Ansbach in 1889. Both were mentioned in J.C. Poggendorff’s Biographisch-literarisches Handwörterbuch (Poggendorff 1931).

After the early death of his father, his mother — with two sons and a daughter — settled in Munich. Both brothers were students at the Technische Hochschule in Munich; Heinrich 1904–1908 and Karl 1908–1912.

Heinrich Hencky got his Diploma, Civil Engineering from Munich in 1908. In 1909 he was in military service with the 3rd Pioneer Battalion in Munich. In the programs for the student year 1912/13 and 1913/14 for the Technische Hochschule Darmstadt, Heinrich Hencky is listed as Diplom-Ingenieur Konstruktion. In 1913 he received his doctorate of Engineering from the Technical University of Darmstadt. The title of his thesis was “Über den Spannungszustand in rechteckigen ebene Platten bei gleichmassig verteilter und bei konzentrierter Belastung” (On the stress state in rectangular flat plates under uniformly distributed and concentration loading). The thesis (Hencky 1913) used a numerical method to
study the stresses in flat plates; the thesis has been cited at least 74 times since 1974, and was a substantial contribution to elastic plate theory, which became one of his favourite subjects. He published the findings in the Zeitschrift für Mathematik und Physik (Hencky 1915).

After completing his dissertation he worked on the Alsatian railways from 1 February 1910 until 26 April 1912. In January 1913 he sought a position in the field and got an offer from a company in Kharkov in Ukraine. The war began immediately and he was interned in the Ural region for the period 1915–1918. During this time he met his Russian wife, Alexandru Yuditskaya; they were married in January 1918. She was born in Poltava (now in Ukraine) on 15th June, 1890.

At the end of the war the Henckys were sent back to Germany and went to Munich, where their daughter Lydia was born on 6 December 1918; later, in 1924, they had a son Gerhard Georg, born in Delft on 28 December 1924. Early in the year 1919, after being sent back from Kharkov to Munich, Hencky placed himself at the disposal of the authorities. He was sent to the marine commandos in Warnemünde and was employed as a materials testing engineer on a seaplane project. His departure from there was due to the coming demobilization. In any event, he had found a job. In May 1919, according to papers obtained from the Technical University in Darmstadt, Hencky was a Privatdozent (external lecturer) there, with specialties in statics and building mechanics. In the study-plan for the student years 1919/20 he is listed as Dr. Ing. Heinrich Hencky, Assistant für Ingenieurfach. From Darmstadt he went to the Technical University of Dresden where he felt he would come in contact with more dynamic areas of technical mechanics. There he published (Hencky 1920) his Darmstadt Habilitationsschrift (which gave him a license to teach) on elastic stability, and to this area he contributed substantially during his career.

Following the 1920 paper, he published (Hencky 1921b) a famous paper on the stability of closed elastic circular rings with external loads (Fig. 1). He recognized that although a ring might be loaded by inward-pointing in-plane loads, one had to consider the possibility of out-of-plane buckling in order to get a realistic result for the buckling load. This paper continues to be cited, and the results are also shown on the internet. He also continued to work on thin rectangular plates (Hencky 1921a). Unlike the elegant elastic ring buckling problem, his paper contains a lot of quite detailed numerical computations, related in style to his thesis work of 1913. Some criticism (Weber 1921) of the 1921a paper was made, and Hencky (1921c) replied with a graceful clarification.

A further paper, this time on numerical methods for partial differential equations, was written while he was in Dresden (Hencky 1922b). This survey paper contains not only an example on plate theory, but also an early example of the numerical computation of the streamlines of viscous flow past an obstacle (Fig. 2). Although he was busy doing excellent research in Dresden, there is evidence that he was not a successful teacher there. We found, with the help of Dr A.J.Q. Alkemade, a 1924 letter from Professor Trefftz to Professor J.M. Burgers in Delft (Hencky was there in 1924) stating that a search was underway for a Chair of General Mechanics in Dresden. They did not consider that Hencky was in the first rank, but they sought Burgers's views on him, especially about his teaching. Trefftz said that there was some doubt about his teaching abilities following his time in Dresden and not everyone thought he was a competent teacher. Trefftz went on to say "but who among us is a born teacher?" His Dresden difficulties "could have been a beginner's problem on the problem of overcoming his shyness when talking in front of students". (We are greatly indebted to Dr A.J.Q. (Fons) Alkemade for finding this letter in the Burgers archives at the Technical University in Delft.)

Soon after, Hencky moved to Delft.

The Delft period 1922–1929

On January 26 1922, Hencky was appointed as Lecturer in Applied Mechanics at the Technical University in Delft. He was apparently told that the lectureship should

![Fig. 1] Buckling of a closed ring. Hencky published the correct solution in 1923b. Out-of-plane buckling was considered, in contrast to earlier work.

![Fig. 2] An example of Hencky's early work (Hencky 1922b) on numerical solutions to field problems. Flow of a viscous fluid around a flat plate at a Reynolds number of 10.
become a permanent professorship. Unfortunately this information only related to the University and not to the Technical University and thus his hope for an independent position was not fulfilled. He joined the Department, headed by Professor C.B. Bizezo, situated in the old Mechanical Engineering building which now is an apartment block. J.M. Burgers was also a professor in Delft at the time Hencky was there, and it is from the Burgers Archives that we get some glimpses of Hencky.

Following his move to Delft, Hencky (1922a, 1923a) continued to write on elastic stability theory; the 1922 paper (Hencky 1922a) was a summary of the field. However, in the new environment, possibly under the influence of Burgers and Bizezo, he soon began work on inelastic problems, beginning with plasticity theory and eventually moving on to rheology.

Before continuing with Hencky’s contributions, we shall remind ourselves of the state in 1920 of the yet-to-be-named science of rheology, including metal deformation beyond the elastic range (plasticity).

The sciences of classical small-deformation elasticity, Newtonian fluid mechanics and linear viscoelasticity (Boltzmann 1874) were already essentially complete by 1900, and with the rise of polymer-based industries interest was being shown in going beyond the linear regimes, which were already known to be inadequate in many practical situations. Eugene Bingham’s book “Fluidity and plasticity”, published in 1922 (Bingham 1922), gives us an important reference point. Although the book does not discuss viscosity that varies with shear rate very much, it does contain extensive discussion on slip at solid walls (he concluded that slip did not occur) and on systems with a yield stress. Variable viscosity was already well-known since Schwindel’s (Schwindel 1899) experimental work.

On the theoretical side, Zaremba (1903) had discovered the need to treat the rate of change of stress carefully, and his work was rediscovered by Jaumann (1905, 1911). Jaumann’s work influenced Hencky later on.

In the science of plasticity, which was also to become an important field of activity for Hencky, we note that early work concentrated on predicting how a material would yield under a general stress state. In the familiar tensile test for a metal, the only non-zero stress component is $\sigma \equiv (\text{Load})/\text{Area}$. What happens if a shear stress, or more normal stresses, are also imposed on the sample? For many metals it was found that hydrostatic pressure had no effect on yielding (Hill 1950). H. Trese (Trese 1864) had suggested that the maximum shear stress caused yielding, R. von Mises (von Mises 1913) had suggested another criterion, involving the six stress components. The Trese and so-called von Mises criteria give quite similar results for many metals (Chakrabarty 1987). M. Levy (Levy 1871) and R. von Mises (von Mises 1913) had used total strain (that is, elastic plus plastic strain) in constructing constitutive relations connecting stress and strain but an acceptable set of such relations for plastically deforming metals was not at hand in 1920, and was clearly an active area of research, especially in Germany.

Hencky (1923b) is perhaps his most famous paper. In it he studied statically determined cases of a rigid-plastic body, in the plane case, using the Trese (maximum shear stress) yield criterion. Several theorems on slip lines, now named after Hencky, were produced. In these problems Hencky showed how to satisfy the equations of equilibrium and the yield criterion; there is no mention of deformation in such problems, and so no discussion of a constitutive equation was made. Richard von Mises (von Mises 1925) referred to this “beautiful discovery” of Hencky. This paper is discussed in every book on plasticity theory (e.g. Chakrabarty 1987) and is still cited; we found 80 citations in the Science Citation Index between 1974 and 2000. Several examples of applications of the theory given in this paper.

In 1924 the First International Congress for Applied Mechanics was held in Delft and Hencky (1924a) read a paper on his deformation theory of plasticity. It provoked considerable discussion, some of a sceptical nature, from Ludwig Prandtl, T. von Karman and others. The full text of this work (Hencky 1924b) was published in the Zeitschrift für angewandte Mathematik und Mechanik (ZaMM) and is still frequently cited (77 citations since 1974) and is found in all texts. In this paper he proposed his energy criterion for yielding, and the result is sometimes called the Hencky-von Mises criterion. For some time Hencky’s deformation theory of plasticity found favour for practical applications (Nedai 1950) but one has to recognize that it does not reflect the physics of plasticity accurately, and may only be used in restricted circumstances. At the time it was published it was the only work which tried to incorporate both elastic and plastic general responses, but Prandtl (1924) (two-dimensional case) and finally Reuss (1930) produced the now accepted Prandtl-Reuss constitutive relations soon after. The limitations of Hencky’s total deformation theory are spelt out by Chakrabarty (1987). Basically, provided loads and stresses increase monotonically, so that the deviatoric stresses are always in the same ratio to one another, then the Hencky and Prandtl-Reuss theories give the same result. When unloading-reloading cycles are considered, with reloading to a different stress state, the results of the Hencky theory will often be erroneous.

Hencky (1925b) continued to write in ZaMM, (then the leading journal on mechanics) and this 1925 paper set up a general tensorial formulation of his deformation theory of plasticity. However, for rheology it is more significant for a paragraph near the end of the paper...
(paragraph 4, page 146), in which the idea of a coordinate system embedded in the material and deforming with the material is introduced. Later, Oldroyd (1950) and Lodge (1964, 1974) were much influenced by this suggestion in their formulation of fundamental rheological constitutive relations, and so this paper is a milestone. By contrast, the third 1925 paper (Hencky 1925c) recapitulates his current ideas on plasticity theory, and appears to contain nothing new. Hencky (1925a) looked at rolling, pressing and drawing problems using his deformation theory, and here he also began to think about the relation of viscous fluid theory to plasticity.

The Second International Congress for Applied Mechanics was held in Zürich in September 1926 (Hencky 1927). Hencky’s contribution was a strange one – he considered using general tensor calculus, no doubt influenced by Schouten’s book (Schouten 1924), to study the elastic, which was a several-hundred-year-old problem. This paper has not been recently cited, as far as we can tell.

In 1928 Hencky began work in a new research area – finite elastic deformations. His paper (Hencky 1928) looks for the form of the finite deformation equations for elastic bodies. Curiously, he did not assume incompressibility, and he also stuck with the classical definition of strain. We recall that it was not until 1948 that Rivlin (Tanner and Walters 1998) managed to solve a significant number of finite strain elasticity problems. Nevertheless, Hencky’s paper has been cited 37 times since 1974.

Hencky’s first paper in English was published with Professor Biezeno in the Dutch Academy of Sciences (Biezeno and Hencky 1928, 1929). It is a long paper in two parts entitled “On the general theory of elastic stability”, of no great significance now perhaps. However, 1929 was a year of great interest in Hencky’s life.

Hencky (1929a) introduced into finite deformation elasticity the logarithmic, or so-called Hencky strain: $e = \ln \left( \frac{L}{L_0} \right)$ (final length/original length)

(1)
and continued his attempts to define plastic flow models of the deformation type, and models for rubberlike elasticity. The motivation for defining the Hencky strain was the following (Ludwik 1909). Instead of computing a strain increment de by using the increment of length dx divided by the original length (x), where integration provides the linear result $e = (x-x_0)/x_0$, one can refer the increase dx to the current length (x), so that we get $de = dx/x$, and hence by integration $e = \ln(x/x_0)$.

His final paper (Hencky 1929b) from Delft is of great interest to rheologists. A translation of the title is “The superposition law of a finitely deforming elastic continuum capable of relaxation and its importance for an exact derivation of the equations for a viscous fluid in the Euler form”. In a long preamble he discusses the need for clarity in forming equations for continua. It seems to have been inspired by reading some work by Reiger (1919) and in fact the paper contains a not-too-easy to follow set of arguments beginning with finite strains (logarithmic strain is mentioned, of course) and proceeding to the formulation of a Maxwell-type model, but including finite elastic strains.

If we take Hencky’s Maxwell-type superposition, we have, in his notation, a co-rotational type of stress derivative (p. 627 of his paper):

$$\frac{\partial \sigma_{nm}}{\partial t} = \frac{\partial \sigma_{mm}}{\partial t} + v_i \frac{\partial \sigma_{mn}}{\partial x_i} + \sigma_{ni} \dot{\gamma}_{ln} + \sigma_{nl} \dot{\gamma}_{in}$$

(2)

where $\sigma_{mn}$ are the stress components, $v_i$ are the velocity components and the vorticity tensor $\omega_{lm}$ is defined here as (p. 624)

$$\omega_{lm} = \frac{1}{2} \left( \frac{\partial v_l}{\partial x_m} - \frac{\partial v_m}{\partial x_l} \right)$$

(3)

The Maxwell-type model is then (p. 628)

$$\frac{\partial \sigma_{nm}}{\partial t} = \frac{\phi_{nm} - \sigma_{nm}}{T}$$

(4)

where T is the relaxation time and $\phi_{nm}$ is a function of various quantities:

$$\phi_{nm} = \phi_{nm} \left( \frac{\partial r_i}{\partial x_j}, \sigma_{mn}, \frac{\partial \sigma_{mn}}{\partial x_i} \right)$$

(5)

If we let

$$\phi_{nm} = G \left( \frac{\partial v_l}{\partial x_m} + \frac{\partial v_m}{\partial x_l} \right)$$

(6)

be a viscous term, where GT is the viscosity ($\eta$) then Eq. (4) becomes

$$T \frac{\partial \sigma_{nm}}{\partial t} + \sigma_{nm} = GT \left( \frac{\partial v_l}{\partial x_m} + \frac{\partial v_m}{\partial x_l} \right)$$

(7)

which is a co-rotational Maxwell model. Clearly, as $T \to 0$ but $GT \to \eta$, we return to viscous fluid flow. No questions of objectivity of $\phi_{nm}$ were explicitly discussed.

Let us compute the response in a steady simple shearing flow. Hencky did not do this, perhaps because he was concerned with the compressibility of the material, in which he set the pressure equal to $-1/3 \sigma_{xx}$. We set $v_1 = \gamma$, $v_2 = v_3 = 0$, a simple shearing flow.

The components of the vorticity tensor $\omega_{mn}$ are all zero except $\omega_{12} = -\dot{\gamma}/2$ and $\omega_{13} = \omega_{23} = \gamma/2$. Solving, we find

$$\sigma_{11} = \sigma_{22} = \sigma_{33} = 0$$
$$\sigma_{12} = \sigma_{21} = \sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = 0$$
$$\sigma_{11} = -\sigma_{12} \gamma T, \sigma_{22} = -\sigma_{11}$$
Except for the minus signs, this is the response expected for the co-rotational Maxwell model. We believe Hencky's equations are in error, since this is intended to be a co-rotational model (see for example Chakravarty 1987, p. 33, Eq. (39) and p. 42, Eq. (81)). A change in the definition of \( w_{\eta} \) (i.e. \(-w_{\eta}\)) would leave the results unchanged except that now we would get the familiar result:

\[
\sigma_{11} = \frac{\sigma_{11}G(T)}{(1 + T)^2} \quad (8)
\]

\[
\sigma_{22} = -\sigma_{11}
\]

and

\[
N_1 = \sigma_{11} - \sigma_{22} = \frac{2G(T)}{1 + T^2}\frac{d^2}{(1 + T)^2} \quad (9)
\]

Without this correction the Hencky model does not fall into the general Oldroyd model category (see Tanner 2000, p. 157) and is not objective. Subsequent work by Fromm (1933, 1947), which built on Hencky's results, gave the correct corotational results (Eqs. 8 and 9); see Tanner and Walters (1998).

Hencky in this important paper was influenced by his 1928 work on deformation and by his work on buckling (Biezne and Hencky 1928, 1929), leading to the corotational ideas, but he was also preoccupied, as was Fromm (1933, 1947), with the volumetric response. Hencky, followed by Fromm, set the pressure \( p = -\frac{1}{3}\sigma_{ii} \). Researchers do not seem to have realized, in these early days, that the pressure is determined, in an incompressible medium, by the momentum balance, not by the constitutive equation.

In spite of the lack of examples and the errors detected above, this paper is a milestone in rheology, leading ultimately to Oldroyd's work (Oldroyd 1950) on convected derivatives. It is not very widely known (12 citations since 1974). Hencky sent this paper to the Annalen der Physik on 7 July 1929, and then departed for the United States. Clearly his research career was going well at Delft, but he was 44 years old and not yet a professor, and one needs to understand his situation to see the motives for leaving Delft. By 1929 it was apparent that relations between Hencky and Biezne were not good and that Hencky was not happy with his position in the Department at Delft. Biezne was told that Hencky wanted leave for a year but later he found out that Hencky intended to stay in the U.S.A. In a letter to Burgers he states that he "has heard lately that Hencky can stay in the U.S.A. Let us hope so!"

On the 26th July 1929 Hencky left Delft for the USA where his family joined him. In June 1930 he took up the position of Associate Professor at the Massachusetts Institute of Technology (MIT) in Cambridge, Mass.

According to the administrative archives Hencky resigned from his position at Delft on the 1st of July 1931.

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**Life in America**

From June 1st 1920 to June 1933 Hencky was Associate Professor of Mechanics in the Department of Mechanical Engineering at MIT. A photograph of him (courtesy of MIT Museum) at that time is shown in Fig. 3. The MIT President's report 1929–1930 states: "Professor Hencky, who came to the Institute a year ago has spent the greater part of his time on an investigation of the plastic flow of material under stress and on lectures in Rheology to a class of graduate students". The 1930–1931 MIT Directory of Officers and Students states: The following additions have been made to the faculty—Dr. Heinrich Hencky: Associate Professor of Mechanics. While at MIT Hencky taught what was, we believe, the first ever course in Rheology (at that time a year-long graduate elective course in Course II (Mechanical Engineering) numbered 2.341).

The course description, taken from the MIT course catalogue of 1931, is as follows:

**2.341, 2.342. Rheology (A).**

A study of the science of the flow of matter, especially being given to the relations between experimental results and theory. The theory is developed as far as possible to meet the needs of the research engineer. Examples taken from the theories of hydrodynamics, elasticity and plasticity are given to illustrate the general principles underlying the laws of the flow of matter. A special study is made of the behavior of semi-elastic and semi-plastic fluids of metals at high temperatures used in forging and in welding and in the rolling mill, as well as the behavior of materials under forced vibrations, the fatigue of metals and frictional resistances in such bodies.

The course taught by Hencky was listed in the 1930, 1931 and 1932 catalogues at MIT.

Hencky's MIT office was Room 1–321, now used as the Mechanical Engineering student office for graduate students.

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**Fig. 3** Professor Dr. Heinrich Hencky about 1930, at MIT. (Courtesy MIT Museum)
students in Mechanics and Materials. Information about the theses he supervised and co-supervised was found in the catalogue and on microfiche in the MIT library. Hyman Friedman’s (1931) B.S. thesis entitled “The law of elasticity of rubber” was supervised by H. Hencky and H.W. Hayward. H.W. Hayward the co-supervisor was Professor of Materials and Engineering and Assistant Director, Division of Industrial Cooperation and Research. Theodore Pan’s 1931 thesis “Yield conditioning of plates and shells by Mises-Hencky Criterion” and Robert Conrad’s 1932 “Stress field of a plate reinforced by a longitudinal guide and subject to tension” were also supervised by Hencky.

Hencky had a difficult position as a basic scientist at MIT in a department mainly interested in very practical problems. President Stratton, who had supported his candidate, died and in 1932 Hencky was made redundant during a reorganization. He started a business as a consultant engineer, living in Lisbon, New Hampshire. As a consultant, Hencky travelled a lot. On a temporary basis and only for a short time he found employment at Lafayette College in Easton, Penn., courtesy of E.C. Bingham.

We now consider his American-based work.

By 1929 the word “rheology” had been invented by Bingham and his colleagues at Lafayette College, and Hencky began to study finite deformations in rubber elasticity and publish in the Journal of Rheology, beginning in April 1931. His paper (Hencky 1931) deals with finite deformation, and, naturally, explains the logarithmic strain. He continued to assume a constant shear modulus for high deformations, but the compression (bulk) modulus was allowed to be more complex. He was in contact with Percy Bridgman at Harvard who was doing experiments under high pressures and Hencky fitted Bridgman’s experimental data with a bulk behaviour rule. In the Summary of his 1931 paper, Hencky says that he has developed a law of elasticity which “is theoretically incontestible”. A lively discussion ensued, Dr Karer asked about logarithmic strain, and Hencky replied that “the logarithmic measure of deformation was already used by the technologist, Ludwik (sic). I think everybody comes to the same idea automatically”. The Ludwik reference is to Ludwik (1909). Mr. Peak asked about treating shear, but Hencky never discussed what happens to the shear strain in the logarithmic case, and he perhaps wisely avoided the question (or it avoided him).

Corresponding to the logarithmic principal strains $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$, one can rotate to non-principal axes and observe what the shear components then become — clearly the result is not simple, and this represents one of the weaknesses of using the logarithmic formulation for general mechanics problems. This paper has had 10 citations since 1974.

Another paper in the Journal of Rheology (Hencky 1932b) on hardening in polycrystalline metals followed; the log strain is again in evidence. Hencky (1932a) was published in the prestigious Philosophical Magazine and, inspired by Bridgman’s work, it discusses wave propagation in materials under variable pressure, with particular concern for the increase of pressure as one descends into the Earth’s interior. The log strain again crops up.

Returning to rubber mechanics, a paper (Hencky 1933c) was published in the Journal of Applied Mechanics (an American Society of Mechanical Engineers Journal, begun in 1933). Again we see the log strain, but it is really unnecessary since it mainly appears as $e^t$, which simply gives the stretches. Some experiments were given, data were fitted using a Mooney-like equation, and some discussion is reported. One of his MIT colleagues (Professor William Hoygaard) was sceptical about using rubber for steam locomotive tyres, and asked whether this had actually been done (it had not, but eventually the Paris Metro began to use some rubber-type stock, but not for steam locomotives). He also said that Hencky had “a (mathematical) development which is somewhat difficult to follow …”. We believe Hencky waffled somewhat in reply. He was somewhat sharp to other discussers, saying that “... in reading their discussion I could not only not detect a proof of this statement, but also no relation to my own work”. This was in reply to a long discussion by Karpov and Templin (from the Aluminum Company of America). In another ASME paper (Hencky 1933a) he returned to plasticity and creep of metals, and a Maxwell-type model is introduced, plus the unavoidable log strain. No discussion was reported. Hencky (1933b) discusses the behaviour of vulcanized rubber. A semi-popular article on stresses in rubber tyers (Hencky 1935) in the ASME magazine Mechanical Engineering, which naturally contains the log-strain again, and which is, in our view, inconclusive, completes the scientific publications of Hencky in the U.S.A. Note that, by 1935, he was living on a farm at Lisbon, New Hampshire, and was no longer with MIT.

Hencky, formerly of MIT, was listed as a member of the advisory board of the Philosophy of Science quarterly published by the Philosophy of Science Association. The first issue appeared in January 1934.

The Russian years

We have some information about the years 1936–1937. Before leaving the United States, Hencky was in a difficult position as he had no fixed job. He was unable to find work in Germany and then an invitation came in 1935 from Galarkin of the Russian Scientific Academy in Moscow. They had become acquainted at the International Conference on Mechanics held in Delft in 1924 and Galarkin had shown an interest in Hencky’s work.
As he had no other possibilities, considering the political climate, he stated in his 1938 CV that he was forced to take up the proposal. The proposition was made for a professorship in Technical Mechanics at the Kharkov (Charkow) Chemical Technical Institute and also a leadership role in various research institutions. He led the scientific teaching and activities of the researchers in the Institute for Civil Engineering and was in two other institutions as well. He was advisor to the active material testing team under the Scientific Institute for Rubber Testing in the Mechanics Institute of Moscow University, with A.A. Il'yushin.

Hencky's scientific work made a successful takeoff in Russia but his ordinary life was too difficult to bear and he stated that he soon felt a prisoner in his location. In 1938 he and his family were told, with 24 h notice, to leave Russia.

The Mainz years

After the Henckys left Russia they were met in Germany by his brother Karl, who had a high position in Leverkusen at IG Farben. The Henckys stayed two months with brother Karl who helped obtain a position for him at the MAN (Maschinenfabrik-Augsburg-Nürnberg) Company in the Gustavsburg district near Mainz, under the direction of Dr. Richard Reinhardt (Superintendent of MAN Gustavsburg). In the Foreword of his 1951 book (Hencky 1951a) Hencky thanked Reinhardt and the leaders of the MAN company for the welcome support of his research.

After his American and Russian residencies he was clearly regarded as politically unsound by the Nazi party in Germany and a document in the MAN archives was annotated by the local SS unit to say that he was not to be given access to secret data. He was critical of the Nazi regime and joined no political party. He seems to have survived because his supervisor at MAN (Dr. Richard Reinhardt) was able to argue that Hencky was a very valuable technical person.

Hencky began work with MAN on 1st January 1938. His children left that year for the U.S. where they settled. Hencky was given a position with employment in various MAN departments working on specialist problems in the area of statics, dynamics and materials engineering. He was also asked to lecture in the continuing education and training program of the company and to work on specialist articles for publication in journals. In 1941 he was promoted to the position of Chief Engineer. In 1943 he received an Honorarium for a publication published in Der Stahlbau (Hencky 1943).

Hencky worked at MAN for 13 years retiring on 31st December 1950 but he continued consulting for the company in the following year.

On July 6th 1951 Hencky died in a mountain sports accident; he had been an enthusiastic mountaineer. This information was found in Z. Angew Math Mech 31(10):332 (Oct 1951) in the news section. He was 65 years old.

Hencky's scientific output naturally diminished when he was with MAN in Gustavsburg/Mainz, but in June 1941 he submitted a paper on plates and shells to an ASME Applied Mechanics Division meeting in Philadelphia (Hencky 1942). At this time the Second World War was in full swing although the USA was not yet directly involved until 1942. He gives his position only as "Mechanical Engineer, Mainz". The paper is a useful contribution to the energy method for studying critical loads in plates and shells under initial stress. It has been cited several times, and does not refer to logarithmic strain.

His next paper (Hencky 1943) is a short summary of plasticity and contains no new work. At the end of the war (1944) he wrote on shear stresses in flat plates using a virtual work method and he gives an estimate of shear stresses in plates; the work was published about three years after it was received by the editor. (Hencky 1947) and has been highly cited, we found 69 citations since 1974.

The next paper (Hencky 1949) is in English and its title is "Mathematical Principles of Rheology". It is, regrettably, poor in terms of organization, explanation and content, and we simply quote Clifford Truesdell's review (Truesdell 1950): "Author obtains "universal equations of rheology". His claim that paper "demands from reader some concentrated penetrating thinking" is substantiated by scarcity of logical definitions and reasoning, and by superfluity of confusing misprints. The notation changes in middle of paper; reviewer uses author's second system here. After an incorrect statement of history of finite strain theory, author introduces "projective strain and rotation" $\varepsilon_i$ and $\omega_i$, which are respectively the symmetric and skew parts of $\varepsilon_0 + \omega_0$, where $\varepsilon_0$ is velocity vector and $\omega_0$ is an unknown vector. If parameter $\tau$ used in definition of $\varepsilon_t$ time, $\varepsilon_t$ and $\omega_0$ have the dimension of rates. Author's general dynamical equations are of incremental or rate type, although in treating case of simple extension he unexpectedly interprets $\varepsilon_t$ as his earlier logarithmic finite strain measure. The vague considerations motivating these proposals are not understood by reviewer."

Hencky says, in summary "Elasticity and hydrodynamics are now connected by the same set of equations and form a whole, as was anticipated by Maxwell and corroborated by the founders of the Society of Rheology."

He also states his indebtedness to R. Reinhardt, the Superintendent of MAN-Gustavsburg, for sponsoring his research. A German summary of the ideas in this paper was published posthumously (Hencky 1951b).
He sent a book manuscript (title Neure Verfahren in der Festigkeitslehre – New Pathways in Solid Mechanics) to the publisher in 1943. Unfortunately, most of the manuscript was burnt in a fire in that year, and only the remaining fragment was published in 1951 (Hencky 1951a). Again he thanks the direction of MAN-Gustavshurg for their support. The book was produced under great difficulties (especially a paper shortage) and it mainly deals with elastic problems. Daniel Drucker (Drucker 1951) reviewed it for Applied Mechanics Reviews as follows: "Many typographical errors occur, and at times rather sweeping claims are made and difficult points passed over. These difficulties are undoubtedly due to the circumstances under which the book was published".

The legacy of Heinrich Hencky

As a researcher in mechanics, Hencky's career was disrupted by two world wars, the Russian revolution and the 1930 economic depression. His academic career (Delft, MIT) spanned only about 14 years, mostly at Delft, which was undoubtedly his most creative period. He worked (alone) in many branches of mechanics, but the ones we are most concerned with may be summarized as follows:

1. Elasticity. This section includes his initial work on plates, and subsequent work on buckling of rings and shells. As mentioned, he was an expert in this area and citations of his work continue to be made. The circular ring buckling load problem and the estimation of shear in plates are prime examples of his work.

2. Plasticity. His 1923 paper on slip line theorems continues to be heavily cited. It is not clear why he did no further work on this new area, which ultimately led to practical solutions to many rigid-plastic flow problems (see, for example, Hill 1950). His deformation theory of plasticity also continues to be cited, even though it is not a model that can be used in complex loading paths. It was, when invented and soon after, used in practice to solve some problems.

3. Finite deformations in materials. He discovered the virtues of the logarithmic strain measure in 1929 and championed it thereafter. He says, in the discussion of his 1931 Journal of Rheology paper, that P. Ludwik invented this measure in about 1909. While Hencky never discussed how to deal with shear in the logarithmic strain (wisely) he may claim to have been the foremost user and exploiter of the concept, and so perhaps the present emended nomenclature "Hencky strain" is not inappropriate.

4. Rheology. Aside from his work on elasticity and plasticity, three of his papers (and one posthumous abstract) are explicitly concerned with relaxing materials. His 1925 paper on convected coordinates and his 1929 paper, although not widely cited now, have influenced rheologists via the work of Oldroyd (1950) and Lodge (1974) following Zaremba (1903) and Fromm (1933, 1947).

One must admit that his life was not easy – the early Russian internment and later problems with the Soviets, his teaching problems in Dresden, his difficulties with Biezeno in Delft, and ultimately his loss of the MIT position, need to be borne in mind. Despite these troubles, his scientific achievement was outstanding. His sponsorship by Dr Reinhardt at MAN kept him going for more than ten years, but again luck was not with him and most of his book manuscript was destroyed by fire in 1943. His death in a mountain-sports accident in July 1951 was an unexpected end to a notable career in mechanics and rheology.

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Appendix C


§ 1. Über die Beeinflussung der Bewegung einer Flüssigkeit durch eine sehr kleine in derselben suspendierte Kugel.

Es liege eine inkompressible homogene Flüssigkeit mit dem Reibungskoeffizienten \( k \) der Betrachtung zugrunde, deren Geschwindigkeitskomponenten \( u, v, w \) als Funktionen der Koordinaten \( x, y, z \) und der Zeit gegeben seien. Von einem beliebigem Punkt \( x_0, y_0, z_0 \) aus denken wir uns die Funktionen \( u, v, w \) als Funktionen von \( x-x_0, y-y_0, z-z_0 \) nach
dem Taylorschen Satze entwickelt und um diesen Punkt ein so kleines Gebiet $G$ abgegrenzt, daß innerhalb desselben nur die linearen Glieder dieser Entwicklung berücksichtigt werden müssen. Die Bewegung der in $G$ enthaltenen Flüssigkeit kann dann bekanntlich als die Superposition dreier Bewegungen aufgefaßt werden, nämlich:

1. einer Parallelverschiebung aller Flüssigkeitsteilchen ohne Änderung von deren relativer Lage,

2. einer Drehung der Flüssigkeit ohne Änderung der relativen Lage der Flüssigkeitsteilchen,

3. einer Dilatationsbewegung in drei aufeinander senkrechten Richtungen (den Hauptdilatationsrichtungen).

Wir denken uns nun im Gebiete $G$ einen kugelförmigen starren Körper, dessen Mittelpunkt im Punkte $x_0, y_0, z_0$ liege und dessen Dimensionen gegen diejenigen des Gebietes $G$ sehr klein seien. Wir nehmen ferner an, daß die betrachtete Bewegung eine so langsame sei, daß die kinetische Energie der Kugel sowie diejenige der Flüssigkeit vernachlässigt werden können. Es werde ferner angenommen, daß die Geschwindigkeitskomponenten eines Oberflächenelementes der Kugel mit den entsprechenden Geschwindigkeitskomponenten der unmittelbar benachbarten Flüssigkeitsteilchen übereinstimme, d. h., daß auch die (kontinuierlich gedachte) Trennungsfläche überall einen nicht unendlich kleinen Koeffizienten der inneren Reibung aufweise.

Es ist ohne weiteres klar, daß die Kugel die Teilbewegungen 1. und 2. einfach mitmacht, ohne die Bewegung der benachbarten Flüssigkeit zu modifizieren, daß sich bei diesen Teilbewegungen die Flüssigkeit wie ein starrer Körper bewegt, und daß wir die Wirkungen der Trägheit vernachlässigt haben.


$$x - x_0 = \xi,$$
$$y - y_0 = \eta,$$
$$z - z_0 = \zeta,$$
Neue Bestimmung der Moleküldimensionen.

so läßt sich jene Bewegung, falls die Kugel nicht vorhanden ist, durch die Gleichungen darstellen:

\[
\begin{align*}
    u_0 &= A \xi, \\
    v_0 &= B \eta, \\
    w_0 &= C \zeta;
\end{align*}
\]

(1)

\(A, B, C\) sind Konstanten, welche wegen der Inkompressibilität der Flüssigkeit die Bedingung erfüllen:

\[A + B + C = 0.\]

(2)

Befindet sich nun im Punkte \(x_0, y_0, z_0\) die starre Kugel mit dem Radius \(R\), so ändert sich in der Umgebung derselben die Flüssigkeitsbewegung. Im folgenden wollen wir der Bequemlichkeit wegen \(P\) als „endlich“ bezeichnen, dagegen die Werte von \(\xi, \eta, \zeta\), für welche die Flüssigkeitsbewegung durch die Kugel nicht mehr merklich modifiziert wird, als „unendlich groß“.

Zunächst ist wegen der Symmetrie der betrachteten Flüssigkeitsbewegung klar, daß die Kugel bei der betrachteten Bewegung weder eine Translation noch eine Drehung ausführen kann, und wir erhalten die Grenzbedingungen:

\[u = v = w = 0\quad \text{für}\quad \varphi = P,\]

wobei

\[\varphi = \sqrt{\xi^2 + \eta^2 + \zeta^2} > 0\]

gesetzt ist. Hierbei bedeuten \(u, v, w\) die Geschwindigkeitskomponenten der nun betrachteten (durch die Kugel modifizierten) Bewegung. Setzt man

\[
\begin{align*}
    u &= A \xi + u_1, \\
    v &= B \eta + v_1, \\
    w &= C \zeta + w_1,
\end{align*}
\]

(3)

so müßte, da die in Gleichungen (3) dargestellte Bewegung im Unendlichen in die in Gleichungen (1) dargestellte übergehen soll, die Geschwindigkeiten \(u_1, v_1, w_1\) im Unendlichen verschwinden.

Die Funktionen \(u, v, w\) haben den Gleichungen der Hydrodynamik zu genügen unter Berücksichtigung der inneren Reibung.
und unter Vernachlässigung der Trägheit. Es gelten also die Gleichungen

\[ \begin{align*}
\frac{\partial p}{\partial \xi} &= k \Delta u, \quad \frac{\partial p}{\partial \eta} = k \Delta v, \quad \frac{\partial p}{\partial \zeta} = k \Delta w, \\
\frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} &= 0,
\end{align*} \]

wobei \( \Delta \) den Operator

\[ \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2} \]

und \( p \) den hydrostatischen Druck bedeutet.

Da die Gleichungen (1) Lösungen der Gleichungen (4) und letztere linear sind, müssen nach (3) auch die Größen \( u_1, v_1, w_1 \) den Gleichungen (4) genügen. Ich bestimmte \( u_1, v_1, w_1 \) und \( p \) nach einer im § 4 der erwähnten Kirchhoffschen Vorlesung angegebenen Methode\(^2\) und fand:

---

2) „Aus den Gleichungen (4) folgt \( \Delta p = 0 \). Ist \( p \) dieser Bedingung gemäß angenommen und eine Funktion \( V \) bestimmt, die der Gleichung

\[ \Delta V = \frac{1}{k} p, \]

genügt, so erfüllt man die Gleichungen (4), wenn man

\[ u = \frac{\partial V}{\partial \xi} + u', \quad v = \frac{\partial V}{\partial \eta} + v', \quad w = \frac{\partial V}{\partial \zeta} + w', \]

setzt und \( u', v', w' \) so wählt, daß \( \Delta u' = 0, \Delta v' = 0 \) und \( \Delta w' = 0 \) und

\[ \frac{\partial u'}{\partial \xi} + \frac{\partial v'}{\partial \eta} + \frac{\partial w'}{\partial \zeta} = -\frac{1}{k} p \]

ist.\(^a\)

Setzt man nun

\[ \frac{p}{k} = 2c \frac{\partial^2}{\partial \xi^2} \]

und im Einklang hiermit

\[ V = c \frac{\partial^2 q}{\partial \xi^2} + b \frac{\partial^2 q}{\partial \xi^2} + \frac{\partial}{\partial \xi} \left( \xi^2 - \frac{\eta^2}{2} - \frac{\zeta^2}{2} \right) \]

und

\[ \frac{\partial}{\partial \xi} \frac{1}{2} \]

\[ u' = -2c \frac{\partial q}{\partial \xi}, \quad v' = 0, \quad w' = 0, \]

so lassen sich die Konstanten \( a, b, c \) so bestimmen, daß für \( q = P \)

\( u = v = w = 0 \) ist. Durch Superposition dreier derartiger Lösungen erhält man die in den Gleichungen (5) und (5 a) angegebene Lösung.
Neue Bestimmung der Moleküldimensionen. 293

\[ p = -\frac{\xi}{\frac{3}{2} k} P^3 \left\{ A \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \xi^2} + B \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \eta^2} + C \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \zeta^2} \right\} + \text{konst.} \]

\[ w = A \frac{\xi}{\frac{3}{2} P^3 A} \frac{\xi}{\frac{3}{2} P^3 A} - B \frac{D}{\eta^2}, \]

\[ v = B \eta - \frac{\xi}{\frac{3}{2} P^3 B} \frac{\eta}{\frac{3}{2} P^3 B} - B \frac{D}{\eta^2}, \]

\[ w = C \zeta - \frac{\xi}{\frac{3}{2} P^3 C} \frac{\zeta}{\frac{3}{2} P^3 C} - B \frac{D}{\eta^2}, \]

wobei

\[ D = A \left\{ \frac{\xi}{\frac{3}{2} P^3} \frac{\partial^2 \xi}{\partial \xi^2} + \frac{P^3}{\frac{3}{2} P^3} \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \zeta^2} \right\} \]

\[ + B \left\{ \frac{\xi}{\frac{3}{2} P^3} \frac{\partial^2 \xi}{\partial \eta^2} + \frac{P^3}{\frac{3}{2} P^3} \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \eta^2} \right\} \]

\[ + C \left\{ \frac{\xi}{\frac{3}{2} P^3} \frac{\partial^2 \xi}{\partial \zeta^2} + \frac{P^3}{\frac{3}{2} P^3} \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \zeta^2} \right\}. \]

Es ist leicht zu beweisen, daß die Gleichungen (5) Lösungen der Gleichungen (4) sind. Denn da

\[ \Delta \xi = 0, \quad \Delta \frac{1}{q} = 0, \quad \Delta q = \frac{2}{q} \]

und

\[ \Delta \left( \frac{\xi}{q^2} \right) = - \frac{\partial}{\partial \xi} \left\{ \Delta \left( \frac{1}{q} \right) \right\} = 0, \]

erhält man

\[ k \Delta u = - k \frac{\partial}{\partial \xi} \left\{ \Delta D \right\} = - k \frac{\partial}{\partial \xi} \left\{ \frac{\xi}{\frac{3}{2} P^3 A} \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \xi^2} + \frac{P^3}{\frac{3}{2} P^3 B} \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \eta^2} + \ldots \right\}. \]

Der zuletzt erhaltene Ausdruck ist aber nach der ersten der Gleichungen (5) mit \( \partial n / \partial \xi \) identisch. Auf gleiche Weise zeigt man, daß die zweite und dritte der Gleichungen (4) erfüllt ist. Ferner erhält man

\[ \frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} = \left( \Delta + B + C \right) \]

\[ + \frac{\xi}{\frac{3}{2} P^3} \left\{ A \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \xi^2} + B \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \eta^2} + C \frac{\partial^2 \left( \frac{1}{q} \right)}{\partial \zeta^2} \right\} - \Delta D. \]
Da aber nach Gleichung (5a)

\[ A \frac{\partial^2}{\partial \xi^2} + B \frac{\partial^1}{\partial \eta^1} + C \frac{\partial^2}{\partial \zeta^2} = 0 \]

so folgt, daß auch die letzte der Gleichungen (4) erfüllt ist. Was die Grenzbedingungen betrifft, so gehen zunächst für unendlich große \( \varphi \) unsere Gleichungen für \( u, v, w \) in die Gleichungen (1) über. Durch Einsetzen des Wertes von \( D \) aus Gleichung (5a) in die zweite der Gleichungen (5) erhält man:

\[
\begin{cases}
  u &= A \xi^2 - B \xi^2 + C \xi^2 \\
  &+ D \xi^2 + E \xi^2 + F \xi^2 - G \xi^2
\end{cases}
\]

Man erkennt, daß \( u \) für \( \varphi = P \) verschwindet. Gleiches gilt aus Symmetriegründen für \( v \) und \( w \). Es ist nun bewiesen, daß durch die Gleichungen (5) sowohl den Gleichungen (4) als auch den Grenzbedingungen der Aufgabe Genüge geleistet ist.

Es läßt sich auch beweisen, daß die Gleichungen (5) die einzige mit den Grenzbedingungen der Aufgabe verträgliche Lösung der Gleichungen (4) sind. Der Beweis soll hier nur angedeutet werden. Es mögen in einem endlichen Raume die Geschwindigkeitskomponenten \( u, v, w \) einer Flüssigkeit den Gleichungen (4) genügen. Existierte noch eine andere Lösung \( U, V, W \) der Gleichungen (4), bei welcher an den Grenzen des betrachteten Raumes \( U = u, V = v, W = w \) ist, so ist \( (U - u, V - v, W - w) \) eine Lösung der Gleichungen (4), bei welcher die Geschwindigkeitskomponenten an der Grenze des Raumes verschwinden. Der in dem betrachteten Raume befindlichen Flüssigkeit wird also keine mechanische Arbeit zugeführt. Da wir die lebendige Kraft der Flüssigkeit vernachlässigt haben, so folgt daraus, daß auch die im betrachteten Raume in Wärme verwandelte Arbeit gleich Null ist. Hieraus folgert man, daß im ganzen Raume \( u = u_1, v = v_1, w = w_1 \) sein muß, falls der Raum wenigstens zum Teil durch ruhende Wände begrenzt ist. Durch Grenzübergang kann dies Resultat auch auf den Fall ausgedehnt werden, daß, wie in dem oben betrachteten Falle, der betrachtete Raum unendlich ist. Man kann so dartun, daß die oben gefundene Lösung die einzige Lösung der Aufgabe ist.
Wir legen nun um den Punkt \( x_0, y_0, z_0 \) eine Kugel vom Radius \( R \), wobei \( R \) gegen \( P \) unendlich groß sei, und berechnen die Energie, welche in der innerhalb der Kugel befindlichen Flüssigkeit (in der Zeiteinheit) in Wärme verwandelt wird. Diese Energie \( W \) ist gleich der der Flüssigkeit mechanisch zugeführten Arbeit. Bezeichnet man die Komponenten des auf die Oberfläche der Kugel vom Radius \( R \) ausgeübten Druckes mit \( X_n, Y_n, Z_n \), so ist:

\[
W = \int (X_n u + Y_n v + Z_n w) \, ds,
\]

wobei das Integral über die Oberfläche der Kugel vom Radius \( R \) zu erstrecken ist. Hierbei ist:

\[
\begin{align*}
X_n &= -\left( X_\xi \frac{\xi}{q} + X_\eta \frac{\eta}{q} + X_\zeta \frac{\zeta}{q} \right), \\
Y_n &= -\left( Y_\xi \frac{\xi}{q} + Y_\eta \frac{\eta}{q} + Y_\zeta \frac{\zeta}{q} \right), \\
Z_n &= -\left( Z_\xi \frac{\xi}{q} + Z_\eta \frac{\eta}{q} + Z_\zeta \frac{\zeta}{q} \right),
\end{align*}
\]

wobei

\[
\begin{align*}
X_\xi &= p - 2k \frac{\partial u}{\partial \xi}, \\
Y_\eta &= p - 2k \frac{\partial v}{\partial \eta}, \\
Z_\zeta &= p - 2k \frac{\partial w}{\partial \zeta},
\end{align*}
\]

Die Ausdrücke für \( u, v, w \) vereinfachen sich, wenn wir beachten, daß für \( q = \infty \) die Glieder mit dem Faktor \( P^5/\zeta^5 \) gegenüber denen mit dem Faktor \( P^3/\zeta^3 \) verschwinden. Wir haben zu setzen:

\[
\begin{align*}
\begin{cases}
  u &= A \frac{\xi}{q^5} - \frac{1}{2} P^3 \frac{\xi}{q^5} (A \xi^2 + B \eta^2 + C \zeta^2), \\
  v &= B \eta - \frac{1}{2} P^3 \frac{\eta}{q^5} (A \xi^2 + B \eta^2 + C \zeta^2), \\
  w &= C \zeta - \frac{1}{2} P^3 \frac{\zeta}{q^5} (A \xi^2 + B \eta^2 + C \zeta^2).
\end{cases}
\end{align*}
\]

Für \( p \) erhalten wir aus der ersten der Gleichungen (5) durch die entsprechenden Vernachlässigungen

\[
p = -5k P^3 \frac{A \xi^2 + B \eta^2 + C \zeta^2}{q^5} + \text{konst}.
\]
Wir erhalten zunächst:

\[ X_\xi = -2k^2 + 10kP^3 \frac{A \xi^2}{q^3} - 25kP^3 \frac{\xi^2(A \xi^2 + B \eta^2 + C \zeta^2)}{q^3} \]

\[ X_\eta = +15kP^3 \frac{A \xi \eta}{q^3} - 25kP^3 \frac{\xi \eta(A \xi^2 + B \eta^2 + C \zeta^2)}{q^3} \]

\[ X_\zeta = +15kP^3 \frac{A \xi \zeta}{q^3} - 25kP^3 \frac{\xi \zeta(A \xi^2 + B \eta^2 + C \zeta^2)}{q^3} \]

und hieraus

\[ X_n = 2A k \frac{\xi}{q} - 10A k P^3 \frac{\xi}{q^3} + 25kP^3 \frac{\xi(A \xi^2 + B \eta^2 + C \zeta^2)}{q^3} \]

Mit Hilfe der durch zyklische Vertauschung abzuleitenden Ausdrücke für \( X_n \) und \( Z_n \) erhält man unter Vernachlässigung aller Glieder, die das Verhältnis \( P/q \) in einer höheren als der dritten Potenz enthalten:

\[ X_n u + Y_n v + Z_n w + \frac{2k}{q} (A^2 \xi^2 + B^2 \eta^2 + C^2 \zeta^2) \]

\[ -10kP^3 \frac{(A^2 \xi^2 + B^2 \eta^2 + C^2 \zeta^2)}{q^3} + 20kP^3 \frac{(A \xi^2 + B \eta^2 + C \zeta^2)}{q^3} \]

Integriert man über die Kugel und berücksichtigt, daß

\[ \int ds = 4 \pi R^2 \]

\[ \int \xi^2 ds = \int \eta^2 ds = \int \zeta^2 ds = \frac{1}{4} \pi R^2 \]

\[ \int \xi^4 ds = \int \eta^4 ds = \int \zeta^4 ds = \frac{1}{8} \pi R^6 \]

\[ \int \eta^2 \zeta^2 ds = \int \zeta^2 \eta^2 ds = \int \xi^2 \eta^2 ds = \frac{1}{16} \pi R^6 \]

\[ \int (A \xi^2 + B \eta^2 + C \zeta^2)^2 ds = \frac{1}{30} \pi R^6 (A^2 + B^2 + C^2) \]

so erhält man:

\[ W = \frac{5}{3} \pi R^2 k \delta^2 - \frac{5}{3} \pi P^3 k \delta^2 = 2 \delta^2 k (V + \frac{1}{2} \Phi) \]

wobei

\[ \delta = A^2 + B^2 + C^2 \]

\[ \frac{5}{3} \pi R^3 = V \]

und

\[ \frac{5}{3} \pi P^3 = \Phi \]

gesetzt ist. Wäre die suspendierte Kugel nicht vorhanden \((\Phi = 0)\), so erhielte man für die im Volumen \( V \) verzehrte Energie

\[ W_0 = 2 \delta^2 k V \]
Durch das Vorhandensein der Kugel wird also die verzehrte Energie um $2 \delta^2 k \Phi$ verkleinert. Es ist bemerkenswert, daß der Einfluß der suspendierten Kugel auf die Größe der verzehrten Energie gerade so groß ist, wie er wäre, wenn durch die Anwesenheit der Kugel die Bewegung der sie umgebenden Flüssigkeit gar nicht modifiziert würde.

§ 2. Berechnung der Reibungskoeffizienten einer Flüssigkeit, in welcher sehr viele kleine Kugeln in regelloser Verteilung suspendiert sind.

Wir haben im vorstehenden den Fall betrachtet, daß in einem Gebiete $G$ von der oben definierten Größenordnung eine relativ zu diesem Gebiete sehr kleine Kugel suspendiert ist und untersucht, wie dieselbe die Flüssigkeitsbewegung beeinflußt. Wir wollen nun annehmen, daß in dem Gebiete $G$ unendlich viele Kugeln von gleicher, und zwar so kleinem Radius regellost verteilt sind, daß das Volumen aller Kugeln zusammen sehr klein sei gegen das Gebiet $G$. Die Zahl der auf die Volumeneinheit entfallenden Kugeln sei $n$, wobei $n$ allenthalben in der Flüssigkeit bis auf Vernachlässigbares konstant sei.

Wir gehen nun wieder aus von einer Bewegung einer homogenen Flüssigkeit ohne suspendierte Kugeln und betrachten wieder die allgemeinste Dilatationsbewegung. Sind keine Kugeln vorhanden, so können wir bei passender Wahl des Koordinatensystems die Geschwindigkeitskomponenten $u_0, v_0, w_0$ in dem beliebigen Punkte $x, y, z$ des Gebietes $G$ darstellen durch die Gleichungen:

\[ u_0 = A x, \]
\[ v_0 = B y, \]
\[ w_0 = C z, \]

wobei

\[ A + B + C = 0. \]

Eine im Punkte $x, y, z_1$ suspendierte Kugel beeinflußt nun diese Bewegung in der aus Gleichung (6) ersichtlichen Weise. Da wir den mittleren Abstand benachbarter Kugeln als sehr groß gegen deren Radius wählen, und folglich die von allen
suspendierten Kugeln zusammen herrührenden zusätzlichen Geschwindigkeitskomponenten gegen $u_0, v_0, w_0$ sehr klein sind, so erhalten wir für die Geschwindigkeitskomponenten $u, v, w$ in der Flüssigkeit unter Berücksichtigung der suspendierten Kugeln und unter Vernachlässigung von Gliedern höherer Ordnungen:

\[
\begin{align*}
    u &= A x - \sum \left\{ \frac{1}{2} \frac{p^5}{q^5} \xi_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right. \\
    &\quad - \left. \frac{1}{2} \frac{p^5}{q^5} \xi_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right\}, \\
    v &= B y - \sum \left\{ \frac{1}{2} \frac{p^5}{q^5} \eta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right. \\
    &\quad - \left. \frac{1}{2} \frac{p^5}{q^5} \eta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right\}, \\
    w &= C z - \sum \left\{ \frac{1}{2} \frac{p^5}{q^5} \zeta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right. \\
    &\quad - \left. \frac{1}{2} \frac{p^5}{q^5} \zeta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2) \right\},
\end{align*}
\]

(8)

wobei die Summation über alle Kugeln des Gebietes $G$ zu erstrecken ist und

\[
\begin{align*}
    \xi_\nu &= x - x_\nu, \\
    \eta_\nu &= y - y_\nu, \\
    \zeta_\nu &= z - z_\nu
\end{align*}
\]

gesetzt ist. $x_\nu, y_\nu, z_\nu$ sind die Koordinaten der Kugelmittelpunkte. Aus den Gleichungen (7) und (7a) schließen wir ferner, daß die Anwesenheit jeder der Kugeln bis auf unendlich kleines höherer Ordnung eine Verringerung der Wärmeproduktion pro Zeiteinheit um $2 \delta^2 k \Phi$ zum Gefolge hat und daß im Gebiete $G$ die pro Volumeneinheit in Wärme verwandelte Energie den Wert hat:

\[
W = 2 \delta^2 k - 2 n \delta^2 k \Phi,
\]

oder

\[
W = 2 \delta^2 k (1 - \varphi),
\]
wobei \( q \) den von den Kugeln eingenommenen Bruchteil des Volumens bedeutet.

Gleichung (7b) erweckt den Anschein, als ob der Reibungskoeffizient der von uns betrachteten inhomogenen Mischung von Flüssigkeit und suspendierten Kugeln (im folgenden kurz "Mischung" genannt) kleiner sei als der Reibungskoeffizient \( k \) der Flüssigkeit. Dies ist jedoch nicht der Fall, da \( A, B, C \) nicht die Werte der Hauptdilatationen der in Gleichungen (8) dargestellten Flüssigkeitsbewegung sind; wir wollen die Hauptdilatationen der Mischung \( A^2, B^2, C^2 \) nennen. Aus Symmetriegründen folgt, daß die Hauptdilatationsrichtungen der Mischung den Richtungen der Hauptdilatationen \( A, B, C \), also den Koordinatenrichtungen parallel sind. Schreiben wir die Gleichungen (8) in der Form:

\[
\begin{align*}
    u &= A x + \sum u_r, \\
    v &= B y + \sum v_r, \\
    w &= C z + \sum w_r,
\end{align*}
\]

so erhalten wir:

\[
A^2 = \left( \frac{\partial u}{\partial x} \right)_{x=0} = A + \sum \left( \frac{\partial u_r}{\partial x} \right)_{x=0} = A - \sum \left( \frac{\partial u_r}{\partial x} \right)_{x=0}.
\]

Schließen wir die unmittelbaren Umgebungen der einzelnen Kugeln von der Betrachtung aus, so können wir die zweiten und dritten Glieder der Ausdrücke von \( u, v, w \) weglassen und erhalten für \( x = y = z = 0 \):

\[
\begin{align*}
    u_r &= -\frac{5}{2} \frac{P^3}{r^3} \frac{A x_r^2 + B y_r^2 + C z_r^2}{r^3}, \\
    v_r &= -\frac{5}{2} \frac{P^3}{r^3} \frac{A x_r^2 + B y_r^2 + C z_r^2}{r^3}, \\
    w_r &= -\frac{5}{2} \frac{P^3}{r^3} \frac{A x_r^2 + B y_r^2 + C z_r^2}{r^3},
\end{align*}
\]

wobei

\[
r_r = \sqrt{x_r^2 + y_r^2 + z_r^2} > 0
\]

gesetzt ist. Die Summierung erstrecken wir über das Volumen einer Kugel \( K \) von sehr großem Radius \( R \), deren Mittelpunkt im Koordinatenursprung liegt. Betrachten wir ferner die
regellos verteilten Kugeln als gleichmäßig verteilt und setzen an Stelle der Summe ein Integral, so erhalten wir:

\[ A^* = A - n \int_\mathcal{K} \frac{\partial u_v}{\partial x_v} \, dx_v \, dy_v \, d\nu, \]
\[ = A - n \int \frac{u_v}{r_v} \, ds, \]

wobei das letzte Integral über die Oberfläche der Kugel \( \mathcal{K} \) zu erstrecken ist. Wir finden unter Berücksichtigung von (9):

\[ A^* = A - \frac{5}{8} \frac{P^3}{R^3} n \int x_0^3 (A x_0^3 + B y_0^2 + C z_0^2) \, ds, \]
\[ = A - n \left( \frac{5}{8} P^3 \pi \right) A = A(1 - \varphi). \]

Analog ist

\[ B^* = B(1 - \varphi), \]
\[ C^* = C(1 - \varphi). \]

Setzen wir

\[ \delta^* = A^{*2} + B^{*2} + C^{*2}, \]

so ist bis auf unendlich Kleines höherer Ordnung:

\[ \delta^{*2} = \delta^2 (1 - 2 \varphi). \]

Wir haben für die Wärmeeentwicklung pro Zeit- und Volumeneinheit gefunden:

\[ W^* = 2 \delta^2 k (1 - \varphi). \]

Bezeichnen wir mit \( k^* \) den Reibungskoeffizienten des Gemisches, so ist:

\[ W^* = 2 \delta^{*2} k^*. \]

Aus den drei letzten Gleichungen erhält man unter Vernachlässigung von unendlich Kleinem höherer Ordnung:

\[ k^* = k(1 + \varphi). \]

Wir erhalten also das Resultat:

Wenden in einer Flüssigkeit sehr kleine starre Kugeln suspendiert, so wächst dadurch der Koeffizient der inneren Reibung um einen Bruchteil, der gleich ist dem Gesamt-
volumen der in der Volumeneinheit suspendierten Kugeln; vorausgesetzt, daß dieses Gesamtvolumen sehr klein ist.

§ 3. Über das Volumen einer gelösten Substanz von im Vergleich zum Lösungsmittel großem Molekularvolumen.

Es liege eine verdünnte Lösung vor eines Stoffes, welcher in der Lösung nicht dissoziiert. Ein Molekül des gelösten Stoffes sei groß gegenüber einem Molekül des Lösungsmittels und werde als starre Kugel vom Radius $P$ aufgefaßt. Wir können dann das in § 2 gewonnene Resultat anwenden. Bedeutet $k^*$ den Reibungskoeffizienten der Lösung, $k$ denjenigen des reinen Lösungsmittels, so ist:

$$\frac{k^*}{k} = 1 + \varphi,$$

wobei $\varphi$ das Gesamtvolumen der in Lösung befindlichen Moleküle pro Volumeneinheit ist.

Wir wollen $\varphi$ für eine 1 proz. wässerige Zuckerlösung berechnen. Nach Beobachtungen von Burkhard (Tabellen von Landolt und Börnstein) ist bei einer 1proz. wässerigen Zuckerlösung $k^*/k = 1,0245$ (bei $20^\circ$ C), also $\varphi = 0,0245$ für (beinahe genau) 0,01 g Zucker. Ein Gramm in Wasser gelöster Zucker hat also auf den Reibungskoeffizienten denselben Einfluß wie kleine suspendierte starre Kugeln vom Gesamtvolumen 2,45 cm$^3$.

Es ist nun daran zu erinnern, daß 1 g festen Zuckers das Volumen 0,61 cm$^3$ besitzt. Dasselbe Volumen findet man auch für das spezifische Volumen $s$ des in Lösung befindlichen Zuckers, wenn man die Zuckerlösung als eine Mischung von Wasser und Zucker in gelöster Form auffaßt. Die Dichte einer 1proz. wässerigen Zuckerlösung (bezogen auf Wasser von denselben Temperatur) bei 17,5$^\circ$ ist nämlich 1,00388. Man hat also (unter Vernachlässigung des Dichteunterschiedes von Wasser von 4$^\circ$ und Wasser von 17,5$^\circ$):

$$\frac{1}{1,00388} = 0,99 + 0,01 s;$$

also

$$s = 0,61.$$

Während also die Zuckerlösung, was ihre Dichte anbelangt, sich wie eine Mischung von Wasser und festem Zucker ver-
hält, ist der Einfluß auf die innere Reibung vielmal größer, als er aus der Suspensionsdauer der gleichen Zuckermenge resultieren würde. Es scheint mir dies Resultat im Sinne der Molekulartheorie kaum anders gedeutet werden zu können, als indem man annimmt, daß das in Lösung befindliche Zuckermolekül die Beweglichkeit des unmittelbar angrenzenden Wassers hemme, so daß ein Quantum Wasser, dessen Volumen ungefähr das Dreifache des Volums des Zuckermoleküls ist, an das Zuckermolekül gekettet ist.

Wir können also sagen, daß ein gelöstes Zuckermolekül (bez. das Molekül samt dem durch dasselbe festgehaltene Wasser) in hydrodynamischer Beziehung sich verhält wie eine Kugel vom Volumen $2,45 \cdot 342 \cdot N \text{cm}^3$, wobei 342 das Molekulargewicht des Zuckers und $N$ die Anzahl der wirklichen Moleküle in einem Grammolekül ist.

§ 4. Über die Diffusion eines nicht dissozierten Stoffes in flüssiger Lösung.

Es liege eine Lösung vor, wie sie in § 3 betrachtet wurde. Wirkt auf das Molekül, welches wir als eine Kugel vom Radius $P$ betrachten, eine Kraft $K$, so bewegt sich das Molekül mit einer Geschwindigkeit $\omega$, welche durch $P$ und den Reibungskoeffizienten $k$ des Lösungsmittels bestimmt ist. Es besteht nämlich die Gleichung 1):

$$ \omega = \frac{K}{6\pi k P} .$$  

Diese Beziehung benutzen wir zur Berechnung des Diffusionskoeffizienten einer nicht dissozierten Lösung. Bedeutet $p$ den osmotischen Druck der gelösten Substanz, welcher bei der betrachteten verdünnten Lösung als die einzige bewegende Kraft anzusehen sei, so ist die auf die gelöste Substanz pro Volumeneinheit der Lösung in Richtung der $x$-Achse ausgeübte Kraft $-\partial p/\partial x$. Befinden sich $\rho$ Gramm in der Volumeneinheit und ist $m$ das Molekulargewicht des gelösten Stoffes, $N$ die Anzahl wirklicher Moleküle in einem Grammolekül, so ist $(\rho/m)N$ die Anzahl der (wirklichen) Moleküle in der Vo-

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lumeneinheit und die auf ein Molekül infolge des Konzentrations-
egefälles wirkende Kraft:

\[
K = - \frac{m}{qN} \frac{\partial p}{\partial x}.
\]

(2)

Ist die Lösung genügend verdünnt, so ist der osmotische
Druck durch die Gleichung gegeben:

\[
p = \frac{R}{m} \varrho T,
\]

(3)

wobei \(T\) die absolute Temperatur und \(R = 8,31 \cdot 10^7\) ist. Aus
den Gleichungen (1), (2) und (3) erhalten wir für die Ge-
schwindigkeit der Wanderung der gelösten Substanz:

\[
\omega = - \frac{R T}{6 \pi k} \frac{1}{NP} \frac{1}{\varrho} \frac{\partial \varrho}{\partial x},
\]

Die pro Zeiteinheit durch die Einheit des Querschnittes
in Richtung der \(X\)-Achse hindurchtrete Stoffmenge ist
endlich:

\[
\omega \varrho = - \frac{R T}{6 \pi k} \frac{1}{NP} \frac{1}{\varrho} \frac{\partial \varrho}{\partial x}.
\]

(4)

Wir erhalten also für den Diffusionskoeffizienten \(D\):

\[
D = \frac{R T}{6 \pi k} \frac{1}{NP}.
\]

Man kann also aus dem Diffusionskoeffizienten und dem
Koeffizienten der inneren Reibung des Lösungsmittels das Pro-
dukt aus der Anzahl \(N\) der wirklichen Moleküle in einem
Grammolekül und dem hydrodynamisch wirksamen Molekular-
radius \(P\) berechnen.

In dieser Ableitung ist der osmotische Druck wie eine
auf die einzelnen Moleküle wirkende Kraft behandelt worden,
was offenbar der Auffassung der kinetischen Molekulartheorie
nicht entspricht, da gemäß letzterer in dem vorliegenden Falle
der osmotische Druck nur als eine scheinbare Kraft aufzu-
fassen ist. Diese Schwierigkeit verschwindet jedoch, wenn man
denkt, daß den (scheinbaren) osmotischen Kräften, welche
den Konzentrationsverschiedenheiten der Lösung entsprechen,
durch ihnen numerisch gleiche, entgegengesetzt gerichtete, auf
die einzelnen Moleküle wirkende Kräfte das (dynamische) Gleich-
gewicht geleistet werden kann, wie auf thermodynamischem Wege leicht eingesehen werden kann.

Der auf die Masseneinheit wirkenden osmotischen Kraft
\(- \frac{1}{q} \frac{\partial P}{\partial x}\) kann durch die (an den einzelnen gelösten Molekülen angreifende) Kraft \(- P_x\) das Gleichgewicht geleistet werden, wenn
\[- \frac{1}{Q} \frac{\partial P}{\partial x} - P_x = 0.\]

Denkt man sich also an der gelösten Substanz (pro Masseneinheit) die zwei sich gegenseitig aufhebenden Kräfte systeme \(P_x\) und \(- P_x\) angreifend, so leistet \(- P_x\) dem osmotischen Drucke das Gleichgewicht und es bleibt nur die dem osmotischen Drucke numerisch gleiche Kraft \(P_x\) als Bewegungssursache übrig. Damit ist die erwähnte Schwierigkeit beseitigt.\(^1\)

§ 5. Bestimmung der Moleküldimensionen mit Hilfe der erlangten Relationen.

Wir haben in § 3 gefunden:
\[\frac{k^*}{k} = 1 + \varphi = 1 + n \cdot \frac{3}{2} \pi P^3,\]
wobei \(n\) die Anzahl der gelösten Moleküle pro Volumeneinheit und \(P\) den hydrodynamisch wirksamen Molekülradius bedeutet. Berücksichtigt man, daß
\[\frac{n}{N} = \frac{q}{m},\]
wobei \(q\) die in der Volumeneinheit befindliche Masse des gelösten Stoffes und \(m\) dessen Molekulargewicht bedeutet, so erhält man:
\[N P^3 = \frac{3}{4 \pi} \frac{m}{q} \left( \frac{k^*}{k} - 1 \right).\]
Andererseits wurde in § 4 gefunden:
\[N P = \frac{R T}{6 \pi k} \frac{1}{D}.\]
Diese beiden Gleichungen setzen uns in den Stand, die Größen \(P\) und \(N\) einzeln zu berechnen, von welchen sich \(N\) als un-

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Wir wollen die Rechnung für wässerige Zuckerlösung durchführen. Nach den oben mitgeteilten Angaben über die innere Reibung der Zuckerlösung folgt zunächst für 20° C.:

\[ N P^3 = 200. \]

Nach Versuchen von Graham (berechnet von Stefan) ist der Diffusionskoeffizient von Zucker in Wasser bei 9,5° C. 0,384, wenn der Tag als Zeiteinheit gewählt wird. Die Zähigkeit des Wassers bei 9,5° ist 0,0135. Wir wollen diese Daten in unsere Formel für den Diffusionskoeffizienten einsetzen, trotzdem sie an 10 proz. Lösungen gewonnen sind und eine genaue Gültigkeit unserer Formel bei so hohen Konzentrationen nicht zu erwarten ist. Wir erhalten

\[ N P = 2,08 \cdot 10^{15}. \]

Aus den für \( NP^3 \) und \( NP \) gefundenen Werten folgt, wenn wir die Verschiedenheit von \( P \) bei 9,5° und 20° vernachlässigigen,

\[ P = 9,9 \cdot 10^{-8} \text{ cm}, \]
\[ N = 2,1 \cdot 10^{23}. \]

Der für \( N \) gefundene Wert stimmt der Größenordnung nach mit den durch andere Methoden gefundenen Werten für diese Größe befriedigend überein.

Bern, den 30. April 1905.

(Eingegangen 19. August 1905.)

Nachtrag:

In der neuen Auflage der physikalisch-chemischen Tabellen von Landolt und Börnstein finden sich weit brauchbarere Angaben zur Berechnung der Größe des Zuckermoleküls und der Anzahl \( N \) der wirklichen Moleküle in einem Grammmolekül.

Thovert fand (Tab. p. 372) für den Diffusionskoeffizienten von Zucker in Wasser bei 18,5° C. und der Konzentration
0,005 Mol./Liter den Wert 0,33 cm²/Tage. Aus einer Tabelle mit Beobachtungsresultaten von Hosking (Tab. p. 81) findet man ferner durch Interpolation, daß bei verdünnter Zuckerlösung einer Zunahme des Zuckergehaltes um 1 Proz. bei 18,5° C. eine Zunahme des Viskositätskoeffizienten um 0,00025 entspricht.

Unter Zugrundelegung dieser Angaben findet man

\[ P = 0,78 \cdot 10^{-6} \text{ mm} \]

und

\[ N = 4,5 \cdot 10^{23} \]

Bern, Januar 1906.
11. Berichtigung zu meiner Arbeit:
„Eine neue Bestimmung der Molekül-
dimensionen“ 1);
von A. Einstein.


Auf p. 296 der genannten Abhandlung stehen Ausdrücke für die Spannungskomponenten $X_y$ und $X_z$, die durch einen Fehler im Differenzieren der Geschwindigkeitskomponenten $v$, $v$, $w$ gefälscht sind. Es muß heißen:

$$X_x = -2kA + 10kP^3 \frac{A \xi^2}{\eta^5} - 25kP^3 \frac{M \xi^2}{\eta^5},$$

$$X_y = 5kP^3 \frac{(A + B) \xi \eta}{\eta^5} - 25kP^3 \frac{M \xi \eta}{\eta^5},$$

$$X_z = 5kP^3 \frac{(A + C) \xi \zeta}{\eta^5} - 25kP^3 \frac{M \xi \zeta}{\eta^5},$$

wobei gesetzt ist

$$M = A \xi^2 + B \eta^2 + C \zeta^2.$$  

Berechnet man dann die pro Zeiteinheit auf die in der Kugel vom Radius $R$ enthaltene Flüssigkeit durch die Druckkräfte übertragene Energie, so erhält man statt Gleichung (7) auf p. 296:

(7) $$\dot{W} = 2 \delta^2 k (\bar{V} + \frac{1}{2} \Phi).$$

Unter Benutzung dieser berichtigten Gleichung erhält man dann statt der in § 2 entwickelten Gleichung \( k^* = \kappa (1 + \varphi) \) die Gleichung
\[
\kappa^* = \kappa (1 + 2.5 \varphi).
\]

Der Viskositätskoeffizient \( k^* \) der Suspension wird also durch das Gesamtvolumen \( \varphi \) der in der Volumeinheit suspendierten Kugeln 2,5 mal stärker beeinflußt als nach der dort gefundenen Formel.

Legt man die berichtigte Formel zugrunde, so erhält man für das Volumen von 1 g in Wasser gelöstem Zucker statt des in § 3 angegebenen Wertes 2,45 cm³ den Wert 0,98, also einen vom Volumen 0,61 von 1 g festem Zucker erheblich weniger abweichenden Wert. Endlich erhält man aus der inneren Reibung und Diffusion von verdünnten Zuckerlösungen statt des im Anhange jener Arbeit angegebenen Wertes \( N = 4.15 \cdot 10^{23} \) für die Anzahl der Moleküle im Grammolekül den Wert 6,56 \( \cdot 10^{23} \).

Zürich, Januar 1911.

(Eingegangen 21. Januar 1911.)
Abbildung der roten Od-Linie durch verschiedene Interferenzspektroskope.
Die vertikalen Striche deuten die Breite des Dispersionsspektrums an.

P. P. Koch.