Dr. Ashlie Martini
Purdue University

Compressibility of Liquids: Current Methods and Future Directions

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The presentation will begin at:
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8:30 a.m. Pacific
9:30 a.m. Mountain
11:30 a.m. Eastern
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Presenter Introduction

• Dr. Ashlie Martini
  – PhD in Mechanical Engineering
  – Assistant Professor at Purdue University
  – STLE Board of Directors
  – TLT Magazine Contributor
  – STLE Nanotribology Technical Committee
Compressibility of Liquids: Current Methods and Future Directions

Dr. Ashlie Martini
Outline

• What is compressibility
• Why and when is it important
• How is it measured
• Empirical models
• Predictive modeling
• Model validation
• Bulk vs thin film compressibility
• Future directions
What is Compressibility

- Change of density with pressure
  - $\frac{\rho}{\rho_0} = \frac{\text{Density at Pressure}}{\text{Ambient Density}}$
  - $\frac{V_0}{V} = \frac{\text{Ambient Volume}}{\text{Volume at Pressure}}$

$$\frac{\rho}{\rho_0} = \frac{(m/V)}{(m/V_0)} = \frac{V_0}{V}$$

What is Compressibility

• Bulk modulus
  • Pressure to cause a given decrease in volume
  • Elasticity of the liquid
  • Units of pressure
  • Reciprocal of compressibility
  • Larger bulk modulus $\rightarrow$ less compressible
What is Compressibility

- Secant bulk modulus: $K = V_0 \cdot \Delta P / \Delta V$
  - If $P_0 = 1$ atm, then $K = V_0 \cdot P / \Delta V$

- Tangent bulk modulus: $\beta = V (\partial P / \partial V)$
  - Near $V/V_0 \approx 1$, $\beta$ can be linearly approximated as $K$
What is Compressibility

• Pressure-dependence of the isothermal bulk modulus for liquids

Linear approximation:
\[ K = K_0 + mP \]

<table>
<thead>
<tr>
<th></th>
<th>Mineral Oil</th>
<th>Water</th>
<th>Water Glycol</th>
<th>Water in Oil Emulsion</th>
<th>Phosphate Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_0, 30 \text{ C} )</td>
<td>18.1 kbar</td>
<td>22.4 kbar</td>
<td>31.1 kbar</td>
<td>19.0 kbar</td>
<td>25.0 kbar</td>
</tr>
<tr>
<td>( m )</td>
<td>5.6</td>
<td>3.4</td>
<td>4.5</td>
<td>5.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>
What is Compressibility

- Temperature-dependence

\[ K = K_0 + mP \]

\[ K_0 = f(T) \]
What is Compressibility

• Note the difference between thermal expansion and the effect of temperature on compressibility
  • Effect of temperature on density is characterized by the coefficient of thermal expansion, $\alpha = -(1/\rho) \cdot \partial \rho / \partial T$

<table>
<thead>
<tr>
<th>$10^{-4}/ \text{C}$</th>
<th>Mineral Oil</th>
<th>Water</th>
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</thead>
<tbody>
<tr>
<td>$\alpha, 40 \text{ C}$</td>
<td>7.00</td>
<td>3.60</td>
</tr>
<tr>
<td>$\alpha, 80 \text{ C}$</td>
<td>7.00</td>
<td>6.24</td>
</tr>
<tr>
<td>$\alpha, 120 \text{ C}$</td>
<td>7.00</td>
<td>8.40</td>
</tr>
</tbody>
</table>

Hydraulic Control Systems, N. Manring

• Temperature also affects the rate of change of density with pressure (bulk modulus)
What is Compressibility

- **Nomenclature**
  - Ambient volume, $V_0$, is the volume at atmospheric pressure ($P=1\text{ atm, } P_g=0$) and some temperature
  - Relative volume, $V_R$, is the volume at some pressure and $T=T_R$ (reference temperature)

\[
\frac{V}{V_0} = \frac{V_R}{V} > 1
\]

\[
V = V(P_g=0.2 \text{ GPa, } T=120\degree C)
\]

\[
V_R = V(P_g=0.2 \text{ GPa, } T_R=20\degree C)
\]

High Pressure Rheology for Quantitative Elastohydrodynamics, S. Bair
Why is it Important

(who cares about compressibility?)
Why and when is it Important

A typical oil will decrease about 0.5% in volume for every 1000 psi (~7 MPa) increase in pressure

Volume change is important for high pressure applications
Why and when is it Important

• Elastohydrodynamic lubrication (EHL)
  – Typical pressures on the order of 1GPa

• Hydraulics
  – Low pressure ~ 7 MPa (gerotor pump)
  – Medium pressure ~ 21 MPa (gear and vane pumps)
  – High pressure ~ 42 MPa (Radial and axial piston pumps)
Why and when is it Important

- EHL is characterized by high pressures and thin films (GPa) (µm)

Fundamentals of Fluid Film Lubrication, Hamrock, Schmid, Jacobson

Absence of boundary lubricants

Elastohydrodynamic (non-conformal contacts only)

Coefficient of friction, µ

Wear rate

Relative load

Boundary

Hydrodynamic

Elastohydrodynamic

Severe wear

Hydrodynamic

Unlubricated

Seizure
Why and when is it Important

• The EHL film thickness is **directly** affected by compressibility


\[ h = h_{\text{incomp}} \left( \frac{V}{V_0} \right) \]

\[ \frac{V}{V_0} < 1 \]

\[ h < h_{\text{incomp}} \]
Why and when is it Important

- EHL case study:
  - \( P=1 \text{ Gpa}=10 \text{ kbar}, T=30^\circ \text{C}, \text{Mineral Oil} \)

\[
K \sim K_0 + mP
\]

\[
K \sim (18.1 \text{ kbar}) + (5.6)(10 \text{ kbar})
\]

\[
K \sim 74.1 \text{ kbar}
\]

\[
K = V_0 \cdot P/\Delta V
\]

\[
V/V_0 = 1 - P/K
\]

\[
V/V_0 = 1 - 10/74.1
\]

\[
V/V_0 = 0.86
\]

\[
h/h_{\text{incomp}} \sim V/V_0 = 0.86 \rightarrow \sim 15\% \text{ thinner film}
\]
Why and when is it Important

Film parameter:

$$\Lambda = \frac{h_{\text{min}}}{\left( R_{q,a}^2 + R_{q,b}^2 \right)^{1/2}}$$

Friction coefficient:

$$\mu_{\text{EHL}} \propto \frac{1}{h}$$

Fundamentals of Fluid Film Lubrication, Hamrock, Schmid, Jacobson
Why and when is it Important

• Hydraulics
  – Loaded actuator doesn’t move until fluid upstream is compressed
  – Energy stored in fluid causes actuator to keep moving after the valve is closed

Must be accounted for in accurate predictions of performance
Why and when is it Important

10,000 lb

A=19.6 in²
K=2.2x10⁵ psi
L = 4 in

• If there is no power loss due to compression, input and output displacement will be the same

\[ \Delta X_{\text{comp}} = \frac{\Delta V_{\text{comp}}}{A} = \Delta X_{\text{in}} - \Delta X_{\text{out}} \]

\[ \Delta V_{\text{comp}} = \frac{PV_0}{K} \]

\[ \Delta V_{\text{comp}} = \frac{(F/A)(AL)}{K} = \frac{(10,000 \text{ lb})(4 \text{ in})}{(2.2 \times 10^5 \text{ psi})} \]

\[ \Delta V_{\text{comp}} = 0.18 \text{ in}^3 \]

Fluid Power System Dynamics
W. Durfee and Z. Sun

Leads to power loss
Why and when is it Important

- Power loss in hydraulic actuators

\[ W_L = P \cdot \Delta V_{\text{comp}} \]

\[ \Delta V_{\text{comp}} = V_0 \cdot P / K \]

\[ W_L = P^2 \cdot V_0 / K \quad \Rightarrow \quad hp_L = P^2 \cdot V_0 / (K \cdot t) \]

Power loss due to compressibility decreases with increasing bulk modulus

\[ W_L = P \cdot \Delta V_{\text{comp}} = (F/A) \cdot \Delta V_{\text{comp}} \]

\[ W_L = (10,000 \text{ lb} / 19.6 \text{ in}^2) \cdot (0.18 \text{ in}^3) = 92 \text{ in-lb} \]
Why and when is it Important

- Hydraulics case study:
  - 3000 psig system
  - K=200,000 psi
  - Stroke 10 in
  - Response 100 Hz
  - Power Loss=6.75 hp/in²

Hydraulics and Pneumatics, HF George and A Barber
How is it Measured

(ok so it’s important...how do I get it?)
How is it Measured

- 1661: Florentine Academicians → Water is NOT compressible

- 1761: John Canton → Yes it is...
How is it Measured

• Conceptual measurement:

\[ K = \frac{V_0 \cdot P}{\Delta V} \]

\[ V_0 = l_0 A \]

\[ V = A(l_0 - x) \]

\[ K = l_0 \cdot \frac{P}{(l_0 - x)} \]
How is it Measured

• Dilatometer
  – Piston/cylinder arrangement where the cylinder provides the pressure containment
  – Displacement of piston is measured to find compression
  – Errors in both the volume compression and the pressure arise from deformations of the cylinder

High Pressure Rheology for Quantitative Elastohydrodynamics, S. Bair
How is it Measured

- Differential dilatometer
  - Experiment made more accurate by performing a direct measurement of the difference in compression of the sample and a material of known and low compressibility
  - Water has become a standard reference material
How is it Measured

• Bellows piezometer
  – Sample liquid is contained in the bellows and a bulb provides additional volume to improve the sensitivity
  – Change in length of the bellows is detected by a potentiometer that is immersed in the pressurizing medium along with the bellows
  – Now the standard instrument although it was one of the first

High Pressure Rheology for Quantitative Elastohydrodynamics, S. Bair
A metal bellows piezometer used to measure relative volume as a function of temperature and pressure to 400 MPa. The length of the bellows, measured with a potentiometer, is linearly related to the volume contained.
Empirical Models

(who has time for all those measurements)
Empirical Models

• What do we do with these measurements?
  • Fit data to empirical models
  • Empirical models then used as input to other predictive models and design tools

\[
\frac{\partial}{\partial x} \left( \frac{\rho}{12 \eta^*} h^3 \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\rho}{12 \eta^*} h^3 \frac{\partial p}{\partial y} \right) = U \frac{\partial (\rho h)}{\partial x} + \frac{\partial (\rho h)}{\partial t}
\]
Empirical Models

• Many such models exist
• They can be written in standard form using two parameters

\[
\frac{V}{V_0} = \frac{\rho_0}{\rho} = f(K_0, K'_0)
\]

\[
K'_0 = \left[ \frac{dK}{dp} \right]_{p=0}
\]

\[
K_0 = \left[ K \right]_{p=0}
\]
Empirical Models

- Dowson-Higginson
  - Very commonly used for EHL modeling
  - Originally obtained by curve fitting (1966) experimental data on mineral oil up to \( \sim 350 \) MPa
  - Contains two ‘universal’ constants
    - \( K_0 = 1.67 \) GPa and \( K_0' = 6.67 \)

\[
\frac{V}{V_0} = \frac{\rho_0}{\rho} = 1 + \frac{K_0' - 1}{2K_0} p \\
1 + \frac{K_0' + 1}{2K_0} p
\]

Empirical Models

• Tait
  – Considered to be more accurate at high pressures
  – Fluid-specific data available for many common liquids

\[
\frac{V}{V_0} = \frac{\rho_0}{\rho} = 1 - \frac{1}{1 + K'} \ln \left[ 1 + \frac{p}{K_0} (1 + K') \right]
\]
Empirical Models

- Murnaghan
  - Accurate; more useful than Tait under some conditions, especially for mineral oil

\[
\frac{V}{V_0} = \frac{\rho_0}{\rho} = \left(1 + \frac{K'_0}{K_0} p\right)^{-\frac{1}{K'_0}}
\]

High Pressure Rheology for Quantitative Elastohydrodynamics, S. Bair
Empirical Models

- Temperature-dependence
  - $K_0'$ usually taken to be independent of $T$

a) $K_0 = C_0 + C_1(T - T_R) + C_2(T - T_R)^2$

  Cutler et al, J Chem Phys 29 (1958) 727

  \[
  \begin{align*}
  C_0 & \sim 1 \text{ GPa} \\
  C_1 & \sim -0.006 \text{ GPa/°C} \\
  C_2 & \sim 10^{-5} \text{ GPa/°C}^2
  \end{align*}
  \]

b) $K_0 = K_\infty + \frac{\dot{K}_0}{T}$

  Bair et al, ASME J Tribol. 123 (2001) 50

  \[
  \begin{align*}
  K_\infty & \sim -0.8 \text{ Gpa} \\
  \dot{K}_0 & \sim 600 \text{ GPa} \cdot \text{K} \\
  K_0 & \sim 0 \text{ ~500 °C}
  \end{align*}
  \]

c) $K_0 = K_{00} \exp(-b_K T)$


  \[
  \begin{align*}
  K_{00} & \sim 9 \text{ Gpa} \\
  b_K & \sim 0.006 \text{ K}^{-1}
  \end{align*}
  \]
Empirical Models

\[ V = \frac{\rho_0}{\rho} = 1 - \frac{1}{1 + K' \left(1 + K'_0\right)} \ln \left[ 1 + \frac{p}{K_0} \right] \]

\[ K_0 = K_{00} \exp\left(-b_K T\right) \]

| Squalane   | 10.85 | 8.824 | 0.006321 |
| BCH       | 11.018 | 12.26 | 0.006479 |
| Z25       | 11.150 | 5.127 | 0.006119 |
| DBEB      | 11.786 | 14.49 | 0.006444 |
| DOP       | 10.647 | 11.005 | 0.006327 |

Predictive Modeling

(isn’t there a better way?)
Predictive Modeling

- Minimize time consuming and expensive experiments
- Design new lubricants with targeted compressibility
- Correlate liquid molecular structure to lubricant performance
Predictive Modeling

\[ E = k(r - r_0)^2 \]

\[ E = k(\theta - \theta_0)^2 \]
Predictive Modeling

\[ E = (\frac{r_o}{r})^{12} - (\frac{r_o}{r})^6 \]

Repulsive + Attractive
Predictive Modeling

Interaction Model

\[ U = f(r) \]

Initial Positions \( r(t=0) \)

Calculate Total Force on all Atoms

\[ F = \frac{dU}{dr} \]

Calculate Acceleration of Each Atom

\[ F = ma \]

Calculate Velocity of Each Atom

\[ v = \int adt \]

Move All Atoms to New Positions

\[ \Delta r = v \Delta t \]
Predictive Modeling

- Well-characterized model liquids

Predictive Modeling

[Diagram showing a molecular model with labels such as 'Initial Film Thickness', 'Pressure', and '6.4 nm'.]
Predictive Modeling

Film Thickness (nm)

Time Step (ps)

Pressure

$l_0$ (l0 - x)

477 MPa

955 MPa

1432 MPa

2149 MPa

AEM

Webinar Series
Association Equipment Manufacturers
Predictive Modeling

![Graphs showing film thickness over time and density versus pressure](image-url)
Model Validation

(yeah, but does it work?)
Validation
Validation

3.2 nm = \lambda_0

6.4 nm = \lambda_0

9.6 nm = \lambda_0

Heptane (h_0=3.2 nm)

Heptane (h_0=6.4 nm)

Heptane (h_0=9.6 nm)
Validation

a. Heptane ($h_0 = 3.2$ nm)
b. Heptane ($h_0 = 6.4$ nm)
c. Heptane ($h_0 = 9.6$ nm)
d. Squalane ($h_0 = 3.2$ nm)
e. Squalane ($h_0 = 6.4$ nm)
f. Squalane ($h_0 = 9.6$ nm)
g. PEB8 ($h_0 = 3.2$ nm)
h. PEB8 ($h_0 = 6.4$ nm)
i. PEB8 ($h_0 = 9.6$ nm)
Validation

<table>
<thead>
<tr>
<th>Initial Film Thickness (nm)</th>
<th>Heptane</th>
<th>Squalane</th>
<th>PEB8</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
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<tr>
<td>4</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
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<td>0.97</td>
<td>0.97</td>
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<tr>
<td>6</td>
<td>0.96</td>
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<td>7</td>
<td>0.95</td>
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<td>0.94</td>
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<td>10</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
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<table>
<thead>
<tr>
<th></th>
<th>Maximum difference (%)</th>
<th>Mean difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>3.01</td>
<td>0.89</td>
</tr>
<tr>
<td>Squalane</td>
<td>1.06</td>
<td>0.75</td>
</tr>
<tr>
<td>PEB8</td>
<td>1.01</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Heptane Experimental Measurements


1.41% Difference
Bulk vs Thin Films

(why do those little tiny gaps get so much attention?)
Bulk vs Thin Film

Elasto-hydrodynamic Lubrication

Ti, TiO\textsubscript{2}, Cr, Al

Film thickness (nm)
Rolling speed (mm s\textsuperscript{-1})

Surface and Interface Analysis 2001; 32: 286–288
Bulk vs Thin Film

Graph 1: Film thickness vs Rolling speed (nm vs mm s⁻¹)

Graph 2: Normalized Density vs Initial Film Thickness (nm)

- Ti, TiO₂, Cr, Al
- EHL
- Tait
- Heptane, Squalane, PEB8
Bulk vs Thin Film

[Graph showing atomic density and orientation parameter compared between bulk and thin film materials.]

Glass Disk
Steel Ball
Spectrometer
Bulk vs Thin Film

- Bulk Density
- Cross Channel Location (nm)
- Atomic Density

Graph:
- X-axis: Initial Film Thickness (nm)
- Y-axis: Normalized Density
- Data points showing decrease in density with increasing thickness

- % Bulk Liquid

Reference:
Webinar Series
Association Equipment Manufacturers
Bulk vs Thin Film

- The predictive model is applicable when the ratio of characteristic molecular length scale to film thickness is greater than ~30

\[ \bar{h}_{\text{limit}} = \frac{h_{\text{minimum}}}{h_{\text{molecule}}} = \frac{10}{0.3} = 33 \]
Summary

(so now what?)
Summary

• What is compressibility
  – Change of density with pressure
  – Quantified by the bulk modulus
    • Increases with pressure
    • Decreases with temperature

\[ \frac{\rho}{\rho_0} \]
Summary

• Why and when is it important
  – Compressibility directly effects lubricant film thickness
    \[ h = h_{\text{incomp}}(V/V_0) \]
  – Compressibility can result in power loss in hydraulic applications
    \[ h_{\text{pL}} = P^2 \cdot V_0/(K \cdot t) \]
  – Its effect must be accounted for to make accurate predictions in many cases
Summary

- How is it measured
  - Dilatometer
  - Differential dilatometer
  - Bellow piezometer
Summary

• Empirical models
  – Experimental data fit to empirical equations that can be used for research and design
  – Tait model accurate to high pressures and parameters are available for many lubricants
Summary

- Predictive modeling
  - Relate molecular structure to compressibility
  - Computational experiment

\[
\begin{align*}
\text{CH}_2 &- \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\
\text{C} &- \text{C} \\
\text{H} &- \text{H}
\end{align*}
\]
Summary

- Model validation
  - Direct comparison to experimentally-fit Tait equation
  - Difference within experimental error

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Maximum difference (%)</th>
<th>Mean difference (%)</th>
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Summary

• Bulk vs Thin Films
  – Thin films behavior may be different than bulk because of molecular layering effects
  – The model can predict bulk compressibility with the dimensionless film thickness is greater than about 30
Future Directions

• Where are we now
  – Highly accurate measurement devices
  – Empirical formulations that capture liquid behavior
  – Partially validated predictive models

\[
\frac{V}{V_0} = \frac{\rho_0}{\rho} = 1 - \frac{1}{1 + K'} \ln \left[ 1 + \frac{p}{K_0} \left( 1 + K' \right) \right]
\]
Future Directions

- Compressibility is only going to become more important
  - Smaller components
  - Tighter tolerances
  - Higher pressure systems

| Thinner lubricating gaps | Higher fluid pressure |
Future Directions

• Where can we go from here

  – Perform extensive model validation with known and well-characterized lubricants
  – Predict compressibility using models and then measure it
  – Design lubricants to have desired compressibility behavior; application-specific lubricant design
Thank you!
Questions?
Contact Information

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Chad Chichester  
Dow Corning  
Lubrication Beyond Oil & Grease  
August 17, 2011

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Conclusion

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THANK YOU!