Pressure—Volume—Temperature Equation of State

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Equations relating state variables (pressure, temperature, volume, or energy).

\[ f(P, V, T) = 0 \]
• Backgrounds
• Equations
• Limitations
• Applications
Ideal Gas Law

\[ PV = nRT \]
Ideal Gas Law

• Volume increases with temperature
• Volume decreases with pressure
• Pressure increases with temperature

\[ P V = n R T \]
Stress ($\sigma$) and Strain ($\varepsilon$)

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl},$$
Bridgmanite in the Mantle

Graph showing the relationship between pressure (GPa) and $V/V_0$ at 300 K.
Strain in the Mantle

20-30%
$P-V-T$ EOS

Bridgmanite
Energy

\[ dU = TdS - PdV, \]
\[ dH = TdS + VdP, \]
\[ dF = -SdT - PdV, \]
\[ dG = -SdT + VdP. \]
A Few Terms to Remember

- Isothermal
- Isobaric
- Isochoric
- Isentropic
- Adiabatic
Energy

\[ dU = T \, dS - P \, dV, \]
\[ dH = T \, dS + V \, dP, \]
\[ dF = -S \, dT - P \, dV, \]
\[ dG = -S \, dT + V \, dP. \]

\[ T = \left( \frac{\partial U}{\partial S} \right)_V = \left( \frac{\partial H}{\partial S} \right)_P, \]
\[ S = -\left( \frac{\partial F}{\partial T} \right)_V = -\left( \frac{\partial G}{\partial T} \right)_P, \]
\[ P = -\left( \frac{\partial U}{\partial V} \right)_S = -\left( \frac{\partial F}{\partial V} \right)_T, \]
\[ V = \left( \frac{\partial H}{\partial P} \right)_S = \left( \frac{\partial G}{\partial P} \right)_T. \]
Thermodynamic Parameters

Isothermal bulk modulus

\[ K_T = -V \left( \frac{\partial P}{\partial V} \right)_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T. \]
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Thermal expansion parameter

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p. \]
Thermodynamic Parameters

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\[ K_T = -V \left( \frac{\partial P}{\partial V} \right)_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T = \frac{\partial^2 F}{\partial V^2} \bigg|_T. \]

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Grüneisen parameter

\[ \gamma = V \left( \frac{\partial P}{\partial U} \right)_V = \frac{1}{\rho C_V} \left( \frac{\partial P}{\partial T} \right)_V. \]
\[ P-V-T \] of EOS

- \( K_T \)
- \( \alpha \)
- \( \gamma \)
$P-V-T$ EOS

![Diagram showing $P-V$ relationship at different temperatures (300 K, 1000 K, 2000 K, 3000 K, 4000 K).](image_url)
Shape of EOS
Shape of EOS

$\frac{V}{V_0}$ vs Pressure (GPa) for different temperatures:

- 300 K
- 1000 K
- 2000 K
- 3000 K
- 4000 K

Arrows indicate change in $P_{total}$. 
Shape of EOS

$P_{st}$

$P_{th}$

$V/V_0$ vs. Pressure (GPa)

- 300 K
- 1000 K
- 2000 K
- 3000 K
- 4000 K
Thermal Pressure

\[ F_{\text{total}} = F_{st} + F_{\text{vib}} + F_{\text{elec}} \]

\[ P(V, T) = P_{st}(V, T_0) + \Delta P_{th}(V, T) \]
Isothermal EOS

\[ K = - \frac{dP}{d \ln V} = \frac{dP}{d \ln \rho} \]

\[ V = V_0 \exp \left[ \frac{-P}{K_0} \right] \]

Assumes that \( K \) does not change with \( P, T \)
Murnaghan EOS

\[ K = K_0 + K'_0 P \]

\[ \rho = \rho_0 \left( 1 + \frac{K'_0}{K_0} P \right) \]

However, \( K \) increases nonlinearly with pressure
Birch-Murnaghan EOS

\[ F = \alpha + bf + cf^2 + df^3 + \ldots \]

\[ \frac{V_0}{V} = (1 + 2f)^{3/2} \]

\[ F : \text{Energy (} U \text{ or } F) \]
\[ f : \text{Eulerian finite strain} \]

Birch (1978)
Second Order BM EOS

\[ F = a + bf + cf^2 \]

\[ P = 3K_0f(1 + 2f)^{5/2} = \frac{3K_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \]

\[ K = -V \frac{dP}{dV} = \frac{K_0}{2} \left[ 7 \left( \frac{V_0}{V} \right)^{7/3} - 5 \left( \frac{V_0}{V} \right)^{5/3} \right] = K_0(1 + 7f)(1 + 2f)^{5/2} \]

Birch (1978)
Third Order BM EOS

\[ F = a + bf + cf^2 + df^3 \]

\[ P = \frac{3K_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \xi \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \]

\[ \xi = \frac{3}{4} \left( 4 - K'_0 \right) \]

Birch (1978)
Truncation Problem

\[ F = a + bf + cf^2 + df^3 + \ldots \]

\[ \frac{V_0}{\bar{V}} = (1 + 2f)^{3/2} \]

- Higher order terms can be large at high P
- 2nd order BM assumes \( K_0' = 4 \)
- 3rd order BM assumes complex relation among \( K_0, K_0', \) and \( K_0'' \)
Helmholtz Free Energy

\[ dF = -SdT - PdV \]

\[ P = -\left( \frac{dF}{dV} \right)_T \]

Therefore, knowing the functional form of free energy with respect to volume change is important for EOS.
Figure 1. Universal binding energy relation—scaled binding energy ($E^*$) versus scaled separation ($a^*$)—for diatomics (•, $H_2$ (molecule)), adhesion (○, Al–Zn (interface)), chemisorption (□, oxygen (chemisorbed)), and cohesion (△, Mo (bulk)).
Vinet EOS

\[ P = \frac{3K_0(1-x)}{x^2} \exp[\eta(1-x)] \]

\[ x = (V/V_0)^{1/3} \quad \eta = \frac{3}{2}(K'_0 - 1) \]
Example: Isotherm Fitting

SiC, Nisr et al., in prep.

(a) Unit-Cell Volume / Z (Å³) vs. Pressure (GPa)

(b) ΔP (GPa) vs. Pressure (GPa)
Parameters to Fit

$V_0, \ K_0, \ K'_0$
Example: Isotherm Fitting

SiC, Nisr et al., in prep.
Example: Isotherm Fitting

Strong correlation between $K_0$ and $K_0'$. 

SiC, Nisr et al., in prep.
Table 1. Model parameters for the equations of state of NaCl-B2, Solid Ne, Au, and Pt

<table>
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<tr>
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<th>Ne*</th>
<th>Au†</th>
<th>Pt‡</th>
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<tr>
<td>$V_0$, Å³</td>
<td>41.35</td>
<td>88.967</td>
<td>67.850(4)</td>
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<td>$K_{0T}$, GPa (Vinet)</td>
<td>26.86(2.90)</td>
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<td>5.25(26)</td>
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<td>$\theta_0$, K</td>
<td>290</td>
<td>75.1</td>
<td>170</td>
<td>230</td>
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<tr>
<td>$\gamma_0$</td>
<td>1.70</td>
<td>2.05</td>
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<td>$q_0$</td>
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Fei et al. (2007)
Caution

Do not mix equations and fitting results

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\[ \alpha K_T(V, T) = \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial \Delta P_{th}}{\partial T} \right)_V \]
Thermodynamic Approach

\[ \Delta P_{th} = P_{th}(V, T) - P_{th}(V, T_0) = \int_{T_0}^{T} [\alpha K_T]_V dT \]
Lattice Dynamic Approach

\[ \Delta P_{th} = \frac{1}{V} \sum_i \gamma_i E_i \approx \frac{\gamma(V)}{V} \Delta E_{th}[\theta(V), T] \]

\[ \gamma = \gamma_0 \left( \frac{V}{V_0} \right)^q \]

\[ \theta = \theta_0 \exp \left( \frac{\gamma_0 - \gamma}{q} \right), \text{ Debye temperature} \]

\[ E_{th} = \frac{9nR}{x^3} \int_0^x \frac{\xi^3}{\exp \xi - 1} d\xi, \text{ Debye model} \]
Parameters to Fit

\[ V_0, K_0, K'_0, \gamma_0, q, \theta_0 \]
Example: \( P-V-T \) Fitting

SiC, Nisr et al., in prep.
Derivation of Thermodynamic Parameters

• Many useful parameters can be derived from Birch-Murnaghan-Debye and Vinet-Debye EOS.

• See Jackson and Rigden (1996, PEPI) for detail

• For example, $K$, $\alpha$, $(\partial K/\partial T)_V$, $(\partial K/\partial T)_S$ at any given pressure and temperature
### Lower Mantle Minerals


<table>
<thead>
<tr>
<th>Mineral</th>
<th>$K_0$ (GPa)</th>
<th>$γ_0$</th>
<th>$q$</th>
<th>$θ_0$ (K)</th>
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<tr>
<td>Bridgmanite</td>
<td>250-260</td>
<td>1.3-1.7</td>
<td>1.2-1.7</td>
<td>1000</td>
</tr>
<tr>
<td>Ferropericlaske</td>
<td>160-165</td>
<td>1.4</td>
<td>1.3</td>
<td>673</td>
</tr>
<tr>
<td>CaSiO$_3$ Pv</td>
<td>220-250</td>
<td>2</td>
<td>0.6</td>
<td>1000</td>
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- Density and elasticity of pyrolite agree reasonably well with those of PREM.
- Density of MORB is 2-3% higher than pyrolite throughout the lower mantle.
Pressure Scale

Shim et al. 2001
Pressure Scale: Post-Spinel

Ye et al. 2014
Pressure Scale: Post-Perovskite

Shim 2008
So What is Problem?

- Stress conditions
- Temperature conditions
- Extreme thermal contribution — electronic contribution in metal pressure standards
$P(Au) - P(Pt) - P(MgO)$

Ye et al. (2016) in prep.
Bridgmanite

$\text{Mg}^{2+}\text{Si}^{4+}\text{O}_3$

$\text{Fe}^{2+} \quad \text{Fe}^{3+} \quad \text{Al}^{3+}$
Bridgmanite

Fe$^{2+}$

Lundin et al. 2008
Bridgmanite

Fe$^{3+}$

Al$^{3+}$

Catalli et al. 2011
Ferropericlase

Fei et al. 2007
Ferropericlase

Wentzcovitch (2009)
Stishovite: Effect of Water

- $\delta -$AIOOH
- Phase H (Nishi et al. 2014)
- $\delta -$H (Ohtani et al. 2014)
- $\text{SiO}_2$ (Spektor et al. 2011)

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$
Stishovite: Effect of Water

Nisr et al., in prep.
Nexus for Exoplanet System Science

Hot Jupiter
- Example: 51 Pegasi b
- Mass: about 0.5 Jupiter masses
- Orbit radius: Less than 4.9 million miles (7.9 million kilometers)
- A Hot Jupiter is a massive gas giant planet orbiting close to its star

Hot Neptune
- Example: Gliese 436 b
- Mass: about 22 Earth masses
- Orbit radius: 2.7 million miles (4.4 million km)
- A Hot Neptune is a gas giant planet orbiting close to its star

Cthonian Planet
- Example: COROT-7b
- Mass: less than 9 Earth masses
- Orbit radius: 1.6 million miles (2.58 million km)
- A Cthonian planet is believed to be a Hot Jupiter that has lost all of its thick atmosphere, leaving the rocky core

Super-Earth
- Example: HAT-P-11b
- Mass: 25 Earth masses
- Orbit radius: 4.9 million miles (7.9 million km)
- A super-Neptune is somewhat larger and more massive than Neptune

Super Neptune
- Example: Kepler-22b
- Mass: not available (radius is 2.4 times that of Earth)
- Orbit radius: 79 million miles (127 million km)
- A Super Earth is larger than Earth but smaller than a gas giant such as Neptune

Water World
- Example: GJ 1214b
- Mass: 6.55 Earth masses
- Orbit radius: 1.33 million miles (2.14 million km)
- A water world is a Super-Earth that may have vast oceans of liquid water

Terrestrial Planet
- Example: Earth
- Mass: 0.003 Jupiter mass
- Orbit radius: 93 million miles (150 million km)
- A goal of the exoplanet search is to find an alien analog of Earth, or an "exo-Earth"

Gas Giant
- Example: Jupiter
- Mass: 318 Earth masses
- Orbit radius: 484 million miles (778 million km)
- A gas giant is a huge planet with a thick atmosphere of mostly hydrogen and helium surrounding a tiny, rocky core

HABITABLE ZONE
where an Earth-size planet can have liquid water on its surface

http://www.nexss.io
Mass-Radius Relations

Seager (2007)
Earth-Like Exoplanets

Pepe et al. (2013) Nature
Elemental Abundances

Bond et al. (2010)
Carbide Planets

Nisr et al., in prep.
Further Readings

• Jackson and Rigden (1996) PEPI
• Anderson (2000) GJI
• Shim and Duffy (2000) AmMin
Future

• Better description of thermal part
• Better description of electronic contribution
• New experimental techniques
• Demand from exoplanet field
• Database with community agreement (?)