

# **Numerical Modelling in Geosciences**

**Lecture 3**

**Density**

# Physical properties: density

Density:  $\rho = \text{mass} / \text{Volume}$  ( $\text{Kg} / \text{m}^3$ )

Density may depend on pressure, temperature and composition

Dependence on pressure and temperature are related to volume decrease/increase through two well known thermodynamic quantities:

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} \quad (\text{Isobaric Thermal Expansivity}, K^{-1})$$

$$\beta = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{\rho} \frac{\partial \rho}{\partial P} \quad (\text{Isothermal compressibility}, Pa^{-1})$$

where we used :

$$\frac{\partial V}{V} = \rho \frac{\partial}{\partial \rho} \frac{1}{\rho} = \rho \left( -\frac{1}{\rho^2} \right) \partial \rho = -\frac{1}{\rho} \partial \rho$$

# Physical properties: density

By using the chain rule, we can decompose the density variation as:

$$d\rho(T, P) = \left( \frac{\partial \rho}{\partial T} dT + \frac{\partial \rho}{\partial P} dP \right) = \rho(-\alpha dT + \beta dP) \Rightarrow d \ln \rho = \beta dP - \alpha dT$$

$$\int_{\rho_0}^{\rho} d \ln \rho = \int_{P_0}^P \beta dP - \int_{T_0}^T \alpha dT \Rightarrow \rho = \rho_0 e^{\beta(P-P_0) - \alpha(T-T_0)}$$

*Since both  $\beta(P - P_0)$  and  $\alpha(T - T_0)$  are  $\ll 1 \Rightarrow (e^a = 1 + a); (e^{-a} = 1 - a)$*

$$\rho = \rho_0 [1 + \beta(P - P_0)] \times [1 - \alpha(T - T_0)]$$

This is a relatively simple equation of state (EOS) for density.

EOS = constitutive equation that relates two or more state variables (mass, volume, pressure, temperature, energy, etc.)

# Physical properties: density

However,  $\alpha$  and  $\beta$  depend themselves on P,T, and therefore more realistic EOS are needed, but they are more complicated and often derived empirically- For example, the Birch-Murnaghan EOS (does not taken into account the effect of temperature):

$$P(\rho) = \frac{3B_0}{2} \left[ \left( \frac{\rho}{\rho_0} \right)^{7/3} - \left( \frac{\rho}{\rho_0} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[ \left( \frac{\rho}{\rho_0} \right)^{2/3} - 1 \right] \right\}$$

where B is the bulk modulus, B' its pressure derivative and subscript 0 indicates quantities measured at P = 0.

Alternatively, the molar volume V can be calculated as a function of P,T conditions as:

$$V = V_r \left[ 1 + a(T - T_r) + b(\sqrt{T} - \sqrt{T_r}) \right] \times \left\{ 1 - \frac{B'_r P}{B_r [1 - c(T - T_r)] + B'_r P} \right\}^{1/B'_r}$$

where the subscript r indicates quantities measured at reference conditions and a, b, c are empirical parameters. Together with the molar mass m we can then calculate density = m/V

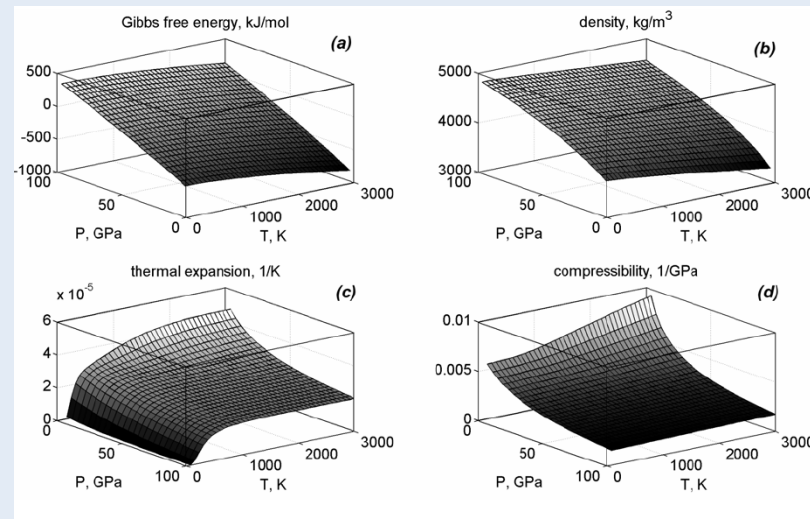
# Physical properties: density

Alternatively, by using thermodynamic databases we can derive thermodynamic potentials (such as the Gibbs free energy  $G_{(P,T)}$ ) and other physical properties of minerals as a function of P,T conditions via standard thermodynamic relations.

$$V = \left( \frac{\partial G_{(P,T)}}{\partial P} \right)_{T=const},$$
$$P = - \left( \frac{\partial F_{(V,T)}}{\partial V} \right)_{T=const},$$
$$V = \frac{m}{\rho},$$

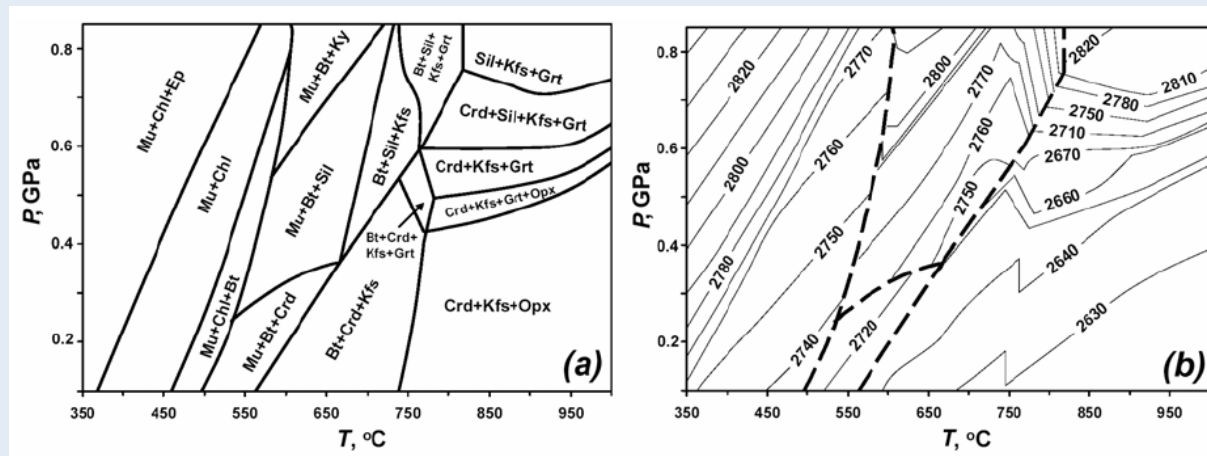
$$G_{m(P,T)} = \Delta H_r - T \cdot S_r + \int_{\bar{r}}^T [C_{p_r(T)}] dT - T \cdot \int_{\bar{r}}^T [C_{p_r(T)}/T] dT + \int_{P_r}^P [V_{(P,T)}] dP,$$

Example below is for MgO – periclase



# Physical properties: density

Density of rocks depends strongly on the mineral assemblage that is given by the composition and P-T conditions



The mineral assemblage is derived from thermodynamic equilibrium by minimizing the Gibbs free energy of the assemblage. Then, rock density for  $n$  mineral phases, each of density  $\rho$  and volume fraction  $X$ , is calculated as:

$$\rho_{rock} = \sum_{i=1}^n \rho_i X_i$$

# Exercise with density

**Exercise 2.1.** Molar Gibbs potential of periclase (MgO, molar mass  $m=0.0403044$  kg/mol) is given by the following equation (Gerya et al., 2004b)

$$G_{m(P,T)} = H_r + V_r \Psi + \sum_{i=1}^3 c_i [RT \ln(1-e_i) - \Delta H_i e_{oi} / (1-e_{oi})],$$

$$e_i = \exp[-(\Delta H_i + \Delta V_i \Psi) / RT],$$

$$e_{oi} = \exp(-\Delta H_i / RT_r),$$

$$\Psi = 5/4(P_r + \phi)^{1/5} [(P + \phi)^{4/5} - (P_r + \phi)^{4/5}],$$

where  $R=8.314$  J/mol is the gas constant,  $P_r=100000$  Pa and  $T_r=298.15$  K are the reference pressure and temperature respectively, and  $H_r=-601500.00$  J,  $V_r=1.12228 \times 10^{-5}$  J/Pa,  $\phi=30179500000$  Pa,  $c_1=1.96612$ ,  $c_2=4.12756$ ,  $c_3=0.53690$ ,  $\Delta H_1=2966.88$  J,  $\Delta H_2=5621.69$  J,  $\Delta H_3=27787.19$  J,

$\Delta V_1=\Delta V_2=3.52971 \times 10^{-8}$  J/Pa,  $\Delta V_3=1.9849568 \times 10^{-6}$  J/Pa are empirical parameters.

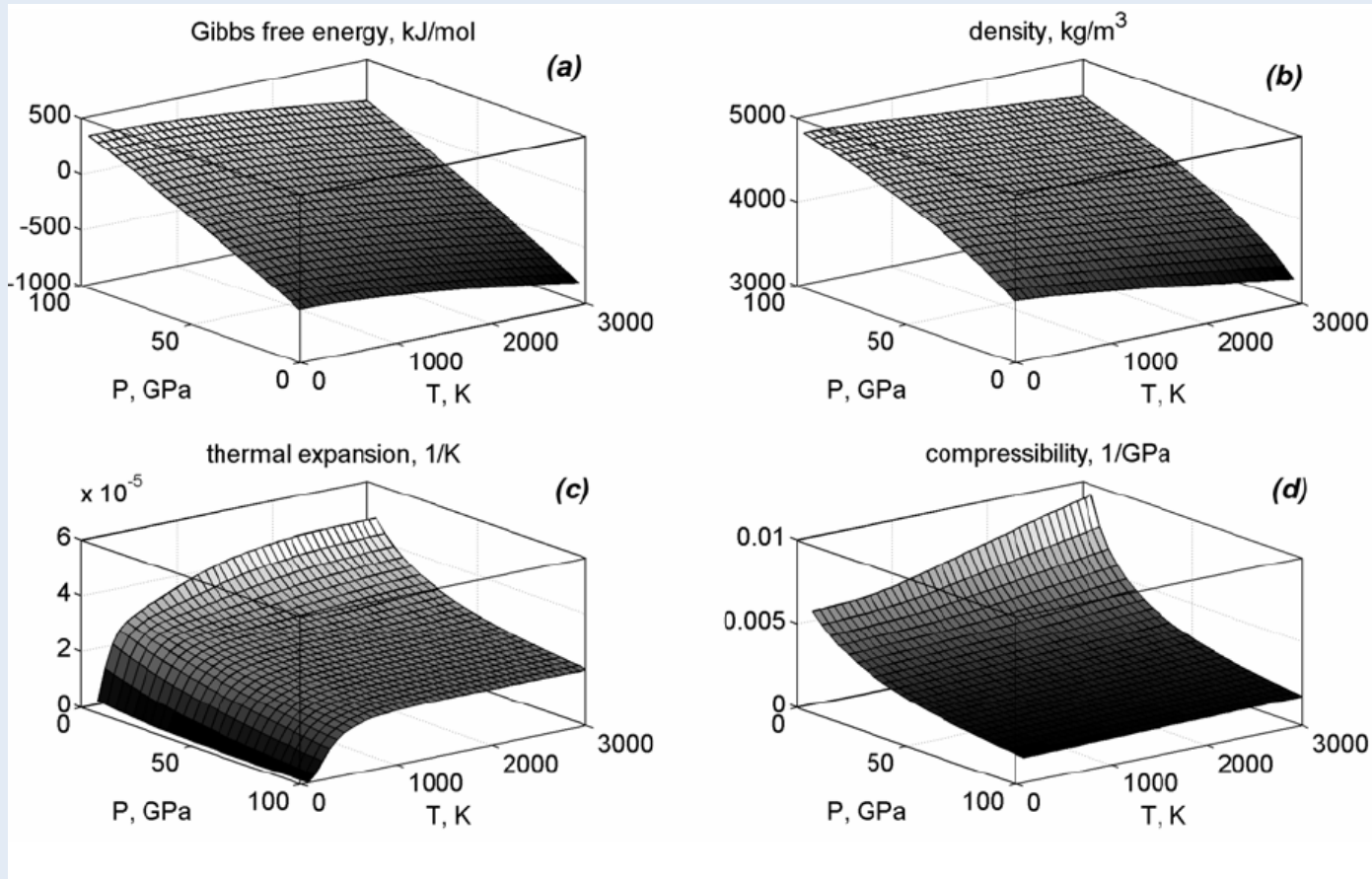
Calculate and plot 1) Gibbs free energy, 2) density, 3) thermal expansivity and 4) compressibility in the (P;T) range: (1-100 GPa; 100-4000K) by using the following relations:

$$\rho_{(P,T)} = \frac{m}{V_{(P,T)}}, \text{ where } V_{(P,T)} = \left( \frac{\partial G_{m(P,T)}}{\partial P} \right)_{T=const} \approx \frac{\Delta G_{m(P,T)}}{\Delta P} = \frac{G_{m(P+\Delta P,T)} - G_{m(P,T)}}{\Delta P}$$

$$\alpha_{(P,T)} = -\frac{1}{\rho_{(P,T)}} \times \frac{\partial \rho_{(P,T)}}{\partial T} \approx -\frac{1}{\rho_{(P,T)}} \times \frac{\Delta \rho_{(P,T)}}{\Delta T} = -\frac{1}{\rho_{(P,T)}} \times \frac{\rho_{(P,T+\Delta T)} - \rho_{(P,T)}}{\Delta T},$$

$$\beta_{(P,T)} = \frac{1}{\rho_{(P,T)}} \times \frac{\partial \rho_{(P,T)}}{\partial P} \approx \frac{1}{\rho_{(P,T)}} \times \frac{\Delta \rho_{(P,T)}}{\Delta P} = \frac{1}{\rho_{(P,T)}} \times \frac{\rho_{(P+\Delta P,T)} - \rho_{(P,T)}}{\Delta P},$$

# Exercise result

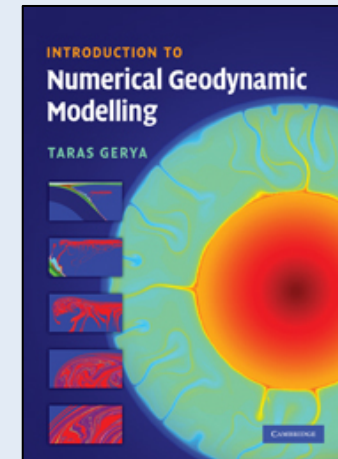




# Homework

**Read pp. 25-30 of textbook:**

Gerya, T. *Introduction to numerical geodynamic modelling*.  
Cambridge University Press, 345 pp. (2010)



**Calculate state variables according to the exercise discussed during the class**