INTRODUCTION TO THE PHYSICS OF THE EARTH'S INTERIOR

SECOND EDITION

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Background of thermodynamics of solids

1.1 Extensive and intensive conjugate quantities

The physical quantities used to define the state of a system can be scalar (e.g. volume, hydrostatic pressure, number of moles of constituent), vectorial (e.g. electric or magnetic field) or tensorial (e.g. stress or strain). In all cases, one may distinguish extensive and intensive quantities. The distinction is most obvious for scalar quantities: extensive quantities are size-dependent (e.g. volume, entropy) and intensive quantities are not (e.g. pressure, temperature).

Conjugate quantities are such that their product (scalar or contracted product for vectorial and tensorial quantities) has the dimension of energy (or energy per unit volume, depending on the definition of the extensive quantities), (Table 1.1). By analogy with the expression of mechanical work as the product of a force by a displacement, the intensive quantities are also called *generalized forces* and the extensive quantities, *generalized displacements.*

If the state of a single-phase system is defined by N extensive quantities e_k and N intensive quantities i_k, the differential increase in energy per unit volume of the system for a variation of e_k is:

$$dU = \sum_k i_k de_k \tag{1.1}$$

The intensive quantities can therefore be defined as partial derivatives of the energy with respect to their conjugate quantities:

$$i_k = \frac{\partial U}{\partial e_k} \tag{1.2}$$

For the extensive quantities, we have to introduce the Gibbs potential

Table 1.1. *Some examples of conjugate quantities*

Intensive quantities	i_k	Extensive quantities	e_k
Temperature	T	Entropy	S
Pressure	P	Volume	V
Chemical potential	μ	Number of moles	n
Electric field	$\mathcal{E}$	Displacement	$\mathbf{D}$
Magnetic field	$\mathbf{H}$	Induction	$\mathbf{B}$
Stress	σ	Strain	ε

(see below):

$$G = U - \sum_k i_k e_k \tag{1.3}$$

$$dG = \sum_k i_k de_k - d\sum_k i_k e_k = -\sum_k e_k di_k \tag{1.4}$$

and we have:

$$e_k = -\frac{\partial G}{\partial i_k} \tag{1.5}$$

Conjugate quantities are linked by *constitutive relations* that express the response of the system in terms of one quantity, when its conjugate is made to vary. The relations are usually taken to be linear and the proportionality coefficient is a *material constant* (e.g. elastic moduli in Hooke's law).

In general, starting from a given state of the system, if all the intensive quantities are arbitrarily varied, the extensive quantities will vary (and vice-versa). As a first approximation, the variations are taken to be linear and systems of linear equations are written (Zwikker, 1954):

$$di_k = K_{k1}de_1 + K_{k2}de_2 + \cdots + K_{kn}de_n \tag{1.6}$$

or

$$de_k = \kappa_{k1}di_1 + \kappa_{k2}di_2 + \cdots + \kappa_{kn}di_n \tag{1.7}$$

The constants:

$$\kappa_{kl} = \left(\frac{\partial e_k}{\partial i_l}\right)_{i1,\ldots,\,in,\ \mathit{except}\ il} \tag{1.8}$$

are called *compliances*, (e.g. compressibility), and the constants:

$$K_{lk} = \left(\frac{\partial i_l}{\partial e_k}\right)_{e1,\ldots,\, en,\ except\ ek} \tag{1.9}$$

are called *stiffnesses* (e.g. bulk modulus).

Note that, in general,

$$K_{lk} \neq \frac{1}{\kappa_{kl}}$$

The linear approximation, however, holds only locally for small values of the variations about the reference state, and we will see that, in many instances, it cannot be used. This is in particular true for the relation between pressure and volume, deep inside the Earth: very high pressures create finite strains and the linear relation (Hooke's law) is not valid over such a wide range of pressure. One, then, has to use more sophisticated equations of state (see below).

1.2 Thermodynamic potentials

The energy of a thermodynamic system is a state function, i.e. its variation depends only on the initial and final states and not on the path from the one to the other. The energy can be expressed as various potentials according to which extensive or intensive quantities are chosen as independent variables. The most currently used are: the *internal energy E*, for the variables volume and entropy, the *enthalpy H*, for pressure and entropy, the *Helmholtz free energy F*, for volume and temperature and the *Gibbs free energy G*, for pressure and temperature:

$$E \tag{1.10}$$

$$H = E + PV \tag{1.11}$$

$$F = E - TS \tag{1.12}$$

$$G = H - TS \tag{1.13}$$

The differentials of these potentials are total exact differentials:

$$dE = TdS - PdV \tag{1.14}$$

$$dH = TdS + VdP \tag{1.15}$$

$$dF = -SdT - PdV \tag{1.16}$$

$$dG = -SdT + VdP \tag{1.17}$$

The extensive and intensive quantities can therefore be expressed as partial differentials according to (1.2) and (1.5):

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \tag{1.18}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P \tag{1.19}$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T \tag{1.20}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \tag{1.21}$$

In accordance with the usual convention, a subscript is used to identify the independent variable that stays fixed.

From the first principle of thermodynamics, the differential of internal energy dE of a closed system is the sum of a heat term $dQ = TdS$ and a mechanical work term $dW = -PdV$. The internal energy is therefore the most physically understandable thermodynamic potential; unfortunately, its differential is expressed in terms of the independent variables entropy and volume that are not the most convenient in many cases. The existence of the other potentials H, F and G has no justification other than being more convenient in specific cases. Their expression is not gratuitous, nor does it have some deep and hidden meaning. It is just the result of a mathematical transformation (Legendre's transformation), whereby a function of one or more variables can be expressed in terms of its partial derivatives, which become independent variables (see Callen, 1985).

The idea can be easily understood, using as an example a function y of a variable x: $y = f(x)$. The function is represented by a curve in the (x, y) plane (Fig. 1.1), and the slope of the tangent to the curve at point (x, y) is: $p = dy/dx$. The tangent cuts the y-axis at the point of coordinates $(0, \phi)$ and its equation is: $\phi = y - px$. This equation represents the curve defined as the envelope of its tangents, i.e. as a function of the derivative p of $y(x)$.

In our case, we deal with a surface that can be represented as the envelope of its tangent planes. Supposing we want to express $E(S, V)$ in terms of T and P, we write the equation of the tangent plane:

$$\phi = E - \left(\frac{\partial E}{\partial V}\right)_S V - \left(\frac{\partial E}{\partial S}\right)_V S = E + PV - TS = G$$

In geophysics, we are mostly interested in the variables T and P; we will therefore mostly use the Gibbs free energy.

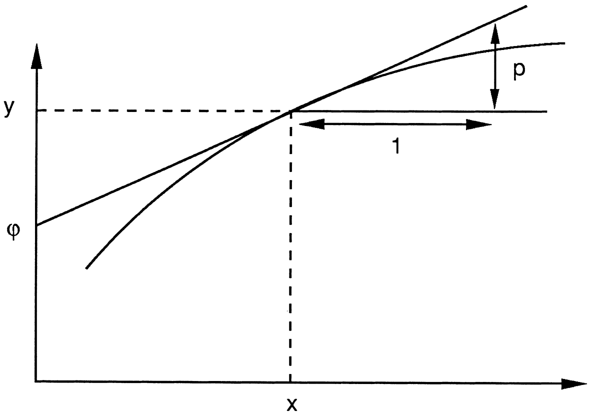

Figure 1.1 Legendre's transformation: the curve $y = f(x)$ is defined as the envelope of its tangents of equation $\phi = y - px$.

1.3 Maxwell's relations. Stiffnesses and compliances

The potentials are functions of state and their differentials are total exact differentials. The second derivatives of the potentials with respect to the independent variables do not depend on the order in which the successive derivatives are taken. Starting from equations (1.18)–(1.21), we therefore obtain *Maxwell's relations*:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{1.22}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1.23}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{1.24}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{1.25}$$

Other relationships between the second partial derivatives can be obtained, using the chain rule for the partial derivatives of a function $f(x, y, z) = 0$:

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{1.26}$$

For instance, assuming a relation $f(P, V, T) = 0$, we have:

Table 1.2. *Derivatives of extensive* (S, V) *and intensive* (T, P) *quantities*

$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$	$\left(\frac{\partial S}{\partial V}\right)_T = \alpha K_T$	$\left(\frac{\partial S}{\partial P}\right)_V = \frac{C_P}{\alpha K_S T}$
$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$	$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{\alpha V T}$	$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$
$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$	$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\alpha K_S T}{C_P}$	$\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\beta P}$
$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$	$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\alpha V}$	$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha V T}{C_P}$
$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T$	$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{K_S}{V}$	$\left(\frac{\partial P}{\partial S}\right)_T = -\frac{1}{\alpha V}$
$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{\alpha V T}$	$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{K_T}{V}$	$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha K_S T}{C_P}$
$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_P}{\alpha K_S T}$	$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{V}{K_S}$	$\left(\frac{\partial V}{\partial S}\right)_T = \frac{1}{\alpha K_T}$
$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$	$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{K_T}$	$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha V T}{C_P}$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V \tag{1.27}$$

With Maxwell's relations, the chain rule yields relations between all derivatives of the intensive and extensive variables with respect to one another (Table 1.2). Second derivatives are given in Stacey (1995).

We must be aware that Maxwell's relations involved only conjugate quantities, but that by using the chain rule, we introduce derivatives of intensive or extensive quantities with respect to non-conjugate quantities. These will have a meaning only if we consider cross-couplings between fields (e.g. thermoelastic coupling, see Section 2.3) and the material constants correspond to second-order effects (e.g. thermal expansion).

In Zwikker's notation, the second derivatives of the potentials are stiffnesses and compliances (Section 1.1):

$$K_{lk} = \frac{\partial i_l}{\partial e_k} = \frac{\partial^2 U}{\partial e_l \partial e_k} \tag{1.28}$$

$$\kappa_{kl} = \frac{\partial e_k}{\partial i_l} = \frac{\partial^2 G}{\partial i_k \partial i_l} \tag{1.29}$$

It follows, since the order of differentiations can be reversed, that:

$$K_{lk} = K_{kl} \tag{1.30}$$

$$\kappa_{kl} = \kappa_{lk} \tag{1.31}$$

Inspection of Table 1.2 shows that, depending on which variables are kept constant when the derivative is taken, we define isothermal, K_T, and adiabatic, K_S, bulk moduli and isobaric, C_P, and isochoric, C_V, specific heats. We must note here that the adiabatic bulk modulus is a stiffness, whereas the isothermal bulk modulus is the reciprocal of a compliance, hence they are not equal (Section 1.1); similarly, the isobaric specific heat is a compliance, whereas the isochoric specific heat is the reciprocal of a stiffness.

Table 1.2 contains extremely useful relations, involving the thermal and mechanical material constants, which we will use throughout this book. Note that, here and throughout the book, V is the specific volume. We will also use the specific mass ρ, with $V\rho = 1$. Often loosely called density, the specific mass is numerically equal to density only in unit systems in which the specific mass of water is equal to unity.