Chemical potentials in non-hydrostatically stressed anisotropic phases

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SUMMARY

This paper presents expressions for chemical potentials in non-hydrostatically stressed anisotropic phases. Chemical potentials are defined here as the derivative of the Helmholtz energy with respect to the addition of a single chemical component to a material while preserving total volume, temperature and shape of the microscopic domain. An entire class of chemical potentials can be defined which differ according to the boundary conditions at the edges of the domain. Total derivatives of the internal energy and Helmholtz energy are most naturally expressed as a function of a chemical potential defined by isotropically compressing existing material. Conversely, crystal growth and dissolution is most naturally described by interfacial chemical potentials that are defined by uniaxially compressing existing material normal to the crystal surface. The derived chemical potentials are valid for all crystalline and amorphous materials including liquids, and do not depend on rheology. The derivations resolve several points of controversy in the literature.

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1 INTRODUCTION

Non-hydrostatic stresses play a key role in metamorphic processes such as dissolution, precipitation and the generation of microscale fabrics such as cleavage, schistosity and augen gneiss and their associated pressure shadows (Tajčmanová et al., 2014; Hobbs & Ord, 2016; Wheeler, 2018). An essential component of these processes is mass movement of one or more chemical components, and therefore modelling of these processes requires an understanding of the relationship between chemical potentials and non-hydrostatic stresses.

The mathematical treatment of chemical quasi-equilibrium and disequilibrium under non-hydrostatic stress states has a long history. The first treatment by Gibbs (1878) was limited to diffusionless systems with two reacting phases, one of which was an inviscid liquid and the other a one-component solid. The narrow, idealised scope allowed Gibbs (1878) to consider chemical equilibrium from the perspective of (his) classical hydrostatic thermodynamics and classical elastic theory. He did not consider the more general problem of chemical equilibrium in systems with solid solutions, chemical diffusion, or solid-solid contacts.

Since the work of Gibbs, a number of authors have proposed generalisations of his theory to arbitrary numbers of chemical components and phases (Kamb, 1961; Bowen & Wiese, 1969; Robin, 1974; Larché & Cahn, 1973, 1985; McLellan, 1980; Mullins & Sekerka, 1985; Rusanov, 2005; Frolov & Mishin, 2010a,b, 2012a,b; De Groot & Mazur, 2013). These works start from the same premise as Gibbs (1878); that the total internal energy of a system is minimised at constant entropy and temperature, and that chemical equilibrium can be assessed via (relative) chemical potentials; compositional derivatives of a thermodynamic energy.

There are a number of subtle disagreements in the papers discussing chemical potentials (see, for example, discussions in Truesdell, 1984; Cahn, 2013; Hirth, 2014; Tajčmanová et al., 2021). One could probably spend a lifetime reading through and understanding the disagreements in detail. For readable and geologically-relevant discussions from somewhat conflicting perspectives, see Hobbs & Ord (2016); Wheeler (2018); Powell et al. (2018); Hess et al. (2022). The various debates raise the following questions:

- What is the mathematical definition of a chemical potential?
- Does a chemical potential exist under non-hydrostatic stress states (a) at all? (b) only as a relative value? (c) as a scalar or second order tensor quantity? (d) only when interphase diffusion is possible? and/or (e) only when a crystal lattice is present?
- What is the relationship between chemical potential and physical phenomena including diffusion, reaction and viscous or elastic relaxation?

There is not yet a definition of chemical potential under non-hydrostatic stress states that is a direct generalisation of the hydrostatic definition, i.e., a definition that is (i) valid everywhere based only on local state, (ii) the energy conjugate of the number of moles of chemical component, (iii) constant and equal to the hydrostatic definition everywhere at true equilibrium, and (iv) related to a chemical property (e.g., bulk composition) that is continuous under the assumption of local equilibrium. A definition satisfying these requirements could be used to formulate continuum models of diffusion, reaction and textural evolution in materials. In this paper, I show how such a definition may be derived. Symbols used in the paper are given in Table 1.

2 DEFINING CHEMICAL POTENTIALS

2.1 Chemical potentials under hydrostatic and non-hydrostatic states

Under hydrostatic conditions, the internal energy $\mathcal{E}_{\text{hyd}}$ and Helmholtz energy $\mathcal{F}_{\text{hyd}}$ of a homogeneous single phase can be uniquely defined by the domain volume V, entropy N (or temperature T) and a vector of the chemical components in that phase $\boldsymbol{n}$:

$$\mathcal{E}_{\text{hyd}} = \mathcal{E}_{\text{hyd}}(V, N, \boldsymbol{n}),\, \mathcal{F}_{\text{hyd}} = \mathcal{F}_{\text{hyd}}(V, T, \boldsymbol{n}) \tag{1}$$

The chemical potential $\mu_{\text{hyd}i}$ of a component i is defined as the partial derivative of the internal energy (or Helmholtz energy) with respect to the number of moles of that component, fixing the other variables:

$$\mu_{\text{hyd}i} = \left(\frac{\partial \mathcal{E}_{\text{hyd}}}{\partial n_i} \right)_{V,N,\boldsymbol{n}_{j \neq i}} = \left(\frac{\partial \mathcal{F}_{\text{hyd}}}{\partial n_i} \right)_{V,T,\boldsymbol{n}_{j \neq i}} \tag{2}$$

Fixing the domain volume does not fix the molar volume; the addition of material to the domain squeezes existing material. If the initial state is hydrostatic, $\mu_{\text{hyd}i}$ doesn't depend on how existing material is squeezed to accommodate the new material.

Under non-hydrostatic conditions, material can be elastically strained without affecting the domain volume, entropy (temperature) or chemical composition. Five more independent variables are required to uniquely define the internal or Helmholtz energy, and so five more independent variables must also be kept constant to define the chemical potential. These five variables must define how the addition of material to the domain squeezes existing material. Under non-hydrostatic stresses, more energy is required to add material by squeezing along the axis of maximum compressive stress than along the axis of minimum compressive stress, and so we might expect the chemical potential to depend on the choice of these five extra variables.

Let's first consider a set of natural variables for the internal and Helmholtz energies (Equation 1). A sensible choice would be to replace the domain volume V with a second rank tensor that also

Table 1. Symbols and subscripts used in this paper.

Symbol	Units	Description
$\mathcal{E}$, $\mathcal{F}$	J	Internal energy, Helmholtz energy
$\mathcal{F}_{\rho\text{el}}$	$\mathrm{J\,m^{-3}}$	Helmholtz isochoric elastic energy density
V	$\mathrm{m^3}$	Volume
N	$\mathrm{J\,K^{-1}}$	Entropy
T	K	Temperature
$\boldsymbol{F}$, F_{ij}	[unitless]	Hydrostatic deformation gradient tensor
$\boldsymbol{U}$, U_{ij}	[unitless]	Isochoric elastic deformation gradient tensor
$\boldsymbol{M}$, M_{ij}	m	Metric tensor ($\boldsymbol{M} = \boldsymbol{UFM}_0$)
$\boldsymbol{\varepsilon}$, ε_{ij}	[unitless]	Small strain tensor
$\bar{\boldsymbol{\varepsilon}}$, $\bar{\varepsilon}_{ij}$	[unitless]	Non-hydrostatic isochoric small strain tensor ($\bar{\varepsilon}_{ij} = \varepsilon_{ij} - \frac{1}{3}\delta_{ij}\delta_{kl}\varepsilon_{kl}$)
$\hat{\boldsymbol{\varepsilon}}$, $\hat{\varepsilon}_{ij}$	[unitless]	Volumetric strain ($\partial\varepsilon_{ij}/\partial \ln V_{\text{mol}}$)
$\boldsymbol{n}$, n_i	mol	Molar amounts of compositional/structural endmembers
$\boldsymbol{p}$, p_i	[unitless]	Molar proportions of endmembers
n	mol	Total number of moles of compositional/structural endmembers
$\boldsymbol{\sigma}$, σ_{ij}	Pa	Cauchy (“true”) stress
P	Pa	Pressure (-$\delta_{kl}\sigma_{kl}/3$)
$\boldsymbol{\tau}$, τ_{ij}	Pa	Deviatoric stress ($\sigma_{ij} + \delta_{ij}P$)
$\boldsymbol{\mu}$, μ_i	$\mathrm{J\,mol^{-1}}$	Chemical potentials (non-specific)
$\boldsymbol{\mu}_{\hat{\boldsymbol{\varepsilon}}}$, $\mu_{\hat{\boldsymbol{\varepsilon}}i}$	$\mathrm{J\,mol^{-1}}$	Chemical potential (fixed volumetric strain $\hat{\boldsymbol{\varepsilon}}$)
$\boldsymbol{\mu}_{\boldsymbol{M}}$, $\mu_{\boldsymbol{M}i}$	$\mathrm{J\,mol^{-1}}$	Isotropic strain chemical potential (fixed extensive cell tensor $\hat{\boldsymbol{M}}$)
$\boldsymbol{\mu}_{\hat{\boldsymbol{n}}}$, $\mu_{\hat{\boldsymbol{n}}i}$	$\mathrm{J\,mol^{-1}}$	Interfacial chemical potential (fixed uniaxial volumetric strain along $\hat{\boldsymbol{n}}$)
$\boldsymbol{\Xi}$, Ξ_{ijk}	$\mathrm{J\,mol^{-1}}$	Chemical strain energy tensor of component i
$\mathbb{C}_{\text{T}}$, $\mathbb{C}_{\text{T}ijkl}$	Pa	Isothermal stiffness tensor
$\boldsymbol{\beta}_{\text{T}}$, $\beta_{\text{T}ij}$	$\mathrm{Pa^{-1}}$	Isothermal compressibility tensor
β_{TR}	$\mathrm{Pa^{-1}}$	Isothermal Reuss compressibilities
ρ	$\mathrm{kg\,m^{-3}}$	Density
$\boldsymbol{x}$, x_i	m	Spatial position
$\boldsymbol{a}$, a_i	$\mathrm{m\,s^{-2}}$	Acceleration
$\boldsymbol{b}$, b_i	$\mathrm{N\,kg^{-1}}$	Body force
hyd, mol, 0		hydrostatic, molar or standard state property
solid, fluid		solid or fluid property
$\boldsymbol{I}$, δ_{ij}		Identity matrix / Kronecker delta
$\det()$		Determinant function
$\ln_{\text{M}}()$		Matrix logarithm function

defines the domain volume. One such choice is the extensive cell tensor $\boldsymbol{M}$, a tensor describing the local parallelepiped shape of the unit cell of the material and having the volume of the domain:

$$\mathcal{E} = \mathcal{E}(\boldsymbol{M}, N, \boldsymbol{n}), \mathcal{F} = \mathcal{F}(\boldsymbol{M}, T, \boldsymbol{n}) \tag{3}$$

$$\boldsymbol{M} = n^{\frac{1}{3}} \boldsymbol{M}_{\text{mol}} = \left(\frac{n N_A}{Z} \right)^{\frac{1}{3}} \boldsymbol{M}_{\text{unit}} \tag{4}$$

$$V = \det \boldsymbol{M} \tag{5}$$

It follows that one definition of chemical potential could use $\boldsymbol{M}$ as the additional fixed constraint:

$$\mu_{\boldsymbol{M}i} = \left(\frac{\partial \mathcal{E}}{\partial n_i} \right)_{\boldsymbol{M}, N, \boldsymbol{n}_{j \neq i}} = \left(\frac{\partial \mathcal{F}}{\partial n_i} \right)_{\boldsymbol{M}, T, \boldsymbol{n}_{j \neq i}} \tag{6}$$

In this paper, $\mu_{\boldsymbol{M}i}$ is termed the “isotropic strain” chemical potential of component i. The total derivative of the Helmholtz energy can be written:

$$d\mathcal{F} = V \sigma_{ij} d\varepsilon_{ij} - T dN + \mu_{\boldsymbol{M}k} dn_k \tag{7}$$

$$d\varepsilon_{ij} = \frac{1}{2} \left(dM_{ik} M^{-1}_{kj} + dM_{jk} M^{-1}_{ki} \right) \tag{8}$$

The change in infinitesimal strain tensor $d\boldsymbol{\varepsilon}$ is commonly split into two terms, a volumetric term $d \ln V$ and an isochoric term $d\bar{\boldsymbol{\varepsilon}}$. Splitting $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ into traceless and isotropic parts, we have:

$$\sigma_{ij} = \tau_{ij} - \delta_{ij} P \tag{9}$$

$$d\varepsilon_{ij} = d\bar{\varepsilon}_{ij} + \frac{1}{3} \delta_{ij} \delta_{kl} d\varepsilon_{kl} \tag{10}$$

$$= d\bar{\varepsilon}_{ij} + \frac{1}{3} \delta_{ij} d \ln V \tag{11}$$

Substituting these expressions into Equation 7 yields a different expression for the Helmholtz energy:

$$d\mathcal{F} = V(\tau_{ij} - \delta_{ij} P) \left(\frac{1}{3} \delta_{ij} \right) d \ln V + V(\tau_{ij} - \delta_{ij} P) d\bar{\varepsilon}_{ij} - T dN + \mu_{\boldsymbol{M}k} dn_k \tag{12}$$

$$= -P dV + V \tau_{ij} d\bar{\varepsilon}_{ij} - T dN + \mu_{\boldsymbol{M}k} dn_k \tag{13}$$

The small strain tensor $\bar{\boldsymbol{\varepsilon}}$ is the total small strain tensor with an isotropic strain component ($\frac{1}{3} \boldsymbol{I} \otimes \boldsymbol{I} d\boldsymbol{\varepsilon}$) removed (Equation 10). This is not the only possible isochoric strain tensor that could be defined - the trace can be removed from $d\boldsymbol{\varepsilon}$ in many different ways. However, any other choices would not result in the simple form of Equation 13.

Although $\mu_{\boldsymbol{M}i}$ is a natural choice for a chemical potential, it is not the only valid choice. Many other chemical potentials can be defined based on anisotropic strain of existing material inside the domain, just as different heat capacities can be defined depending on what is kept constant: stress (isobaric c_P or isostress $c_{\boldsymbol{\sigma}}$ heat capacity), atomic positions (isometric heat capacity $c_{\boldsymbol{\varepsilon}}$) or volume under hydrostatic conditions (isochoric heat capacity c_V) (Nye et al., 1985)). Nor is $\mu_{\boldsymbol{M}i}$ directly relevant to thermodynamic phenomena in the same way as $\mu_{\text{hyd}i}$ under hydrostatic conditions. In Section 2.2, we will see that μ_{Mi} is not spatially continuous under the assumption of local quasi-equilibrium (chemical equilibrium under non-hydrostatic stresses), which will motivate in Section 2.3 the definition of a general class of chemical potentials.

2.2 Continuity and discontinuity in measures of chemical disequilibrium

In isolated systems, progress towards equilibrium is governed by a monotonic increase in entropy (the second law of thermodynamics). This increase in entropy is related to and concurrent with reduction of spatial gradients in stress, temperature and chemical potential, and also reductions in deviatoric stress and chemical affinity. These reductions could be coupled with each other, as in barodiffusion or thermodiffusion. It is usually assumed that materials are in quasi-equilibrium with nearby materials (De Groot & Mazur, 2013), which implies continuity in stress, temperature and chemical potential, even if the quasi-equilibrium is far from the global equilibrium or even a locally relaxed state. Chemical affinities (relaxed by chemical processes) and deviatoric stresses (relaxed by rheological processes) might be quite large even if they vary continuously across the domain.

Implicit in the previous paragraph is the idea that chemical potential can be defined under non-hydrostatic state, and that some measure of chemical potential is spatially continuous at local equilibrium. A major problem with this idea was first presented by Gibbs (1878) (Chapter IX, his pages 343-360). Gibbs envisaged an isothermal system containing a crystal and multiple separated fluid reservoirs (Figure 1). The crystal contains only a single chemical component that is able to dissolve into the fluid. The crystal is held in a homogeneous, non-hydrostatically stressed state, with crystal faces aligned with the principal stresses (σ_{xx} and σ_{yy} in Figure 1, $\sigma_{xx} \neq \sigma_{yy}$). The fluid pools are in mechanical equilibrium with the crystal, but are not in contact with each other and do not interact directly with each other. Crystal growth from and dissolution into each of the fluid pools is allowed until an equilibrium is reached.

At mechanical equilibrium, the stress normal to each crystal face must be equal to the pressure of the fluid ($\sigma_{xx} = -p_1$, $\sigma_{yy} = -p_2$). The fluid pressure must therefore be different in the fluid pools adjacent to each face ($p_1 \neq p_2$). As the chemical potential in the fluid is a function of the pressure, the chemical potential must also be different in each fluid pool. It is therefore impossible for a single scalar chemical potential to be continuous across both fluid-crystal interfaces.

If no single scalar chemical potential is continuous across both of the crystal-fluid interfaces, then how can the local equilibrium of the system be demonstrated? Section 2.3 resolves this paradox by considering boundary conditions in the definition of chemical potential.

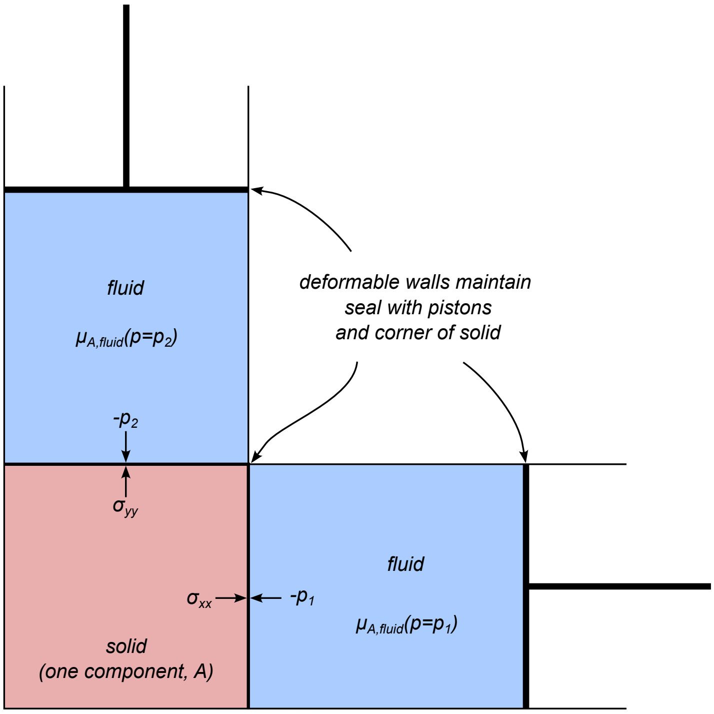

Figure 1. Cartoon of the Gibbs thought experiment. A non-hydrostatically strained solid is maintained in mechanical equilibrium with two inviscid fluid. The pressures, and therefore chemical potentials in the two fluid pools are different. Figure adapted from Hobbs & Ord (2016).

2.3 Local chemical equilibrium and “interfacial” chemical potentials

To understand the role of boundary conditions in defining local equilibrium under non-hydrostatic conditions, let’s focus on a single crystal-fluid interface from Figure 1, in a reference frame fixed to the interface. At equilibrium at a fixed temperature, the Helmholtz energy added to one phase on moving material across the interface should be equal to the amount of energy lost from the other phase. Moving material across the interface strains existing material on both sides. Let us here define the “squeeze” applied to *existing* material as more material is added to the domain as a symmetric (rotation-free) strain tensor:

$$\hat{\varepsilon}_{jk} = \left(\frac{\partial \varepsilon_{jk}}{\partial \ln V_{\mathrm{mol}}} \right) \tag{14}$$

The change in molar volume V_{mol} is itself a function of the strain, leading to the following constraint:

$$\mathrm{Tr}(\hat{\varepsilon}) = 1 \tag{15}$$

As existing material is squeezed, the domain is refilled with new material, such that the domain preserves its original volume and shape (Figure 2). This new material has the same unit cell strain as the preexisting material (we approximate the material inside the domain to be homogeneous in strain, composition and temperature), and so the addition of new material isotropically expands the extensive

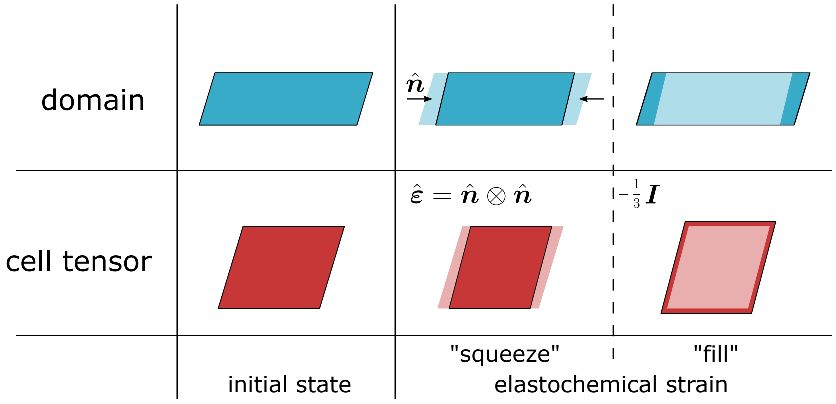

Figure 2. Visual representation of shape changes in the domain (top panels) and extensive cell tensor $\boldsymbol{M}$ (bottom panels) during chemical strain. On the left hand panels are the original shapes of a small parallelepiped element of domain. The addition of new material requires that existing material be squeezed (Equation 14). The squeeze shown in the center panel is for addition of material along a vector $\hat{\boldsymbol{n}}$. As new material is added, the shape of the domain does not change, but the shape of the cell tensor can, and cell elements and the types of strains discussed in the text. Lighter shading represents the shape from before each component of strain was applied, and deeper shading the current shape.

cell tensor $\boldsymbol{M}$. A general class of chemical potentials $\mu_{\hat{\varepsilon}}$ can be defined for all possible normalised strains $\hat{\varepsilon}$:

$$\mu_{\hat{\varepsilon} i} = \left(\frac{\partial \mathcal{E}}{\partial n_i}\right)_{V,\hat{\varepsilon},N,\boldsymbol{n}_{j\neq i}} = \left(\frac{\partial \mathcal{F}}{\partial n_i}\right)_{V,\hat{\varepsilon},T,\boldsymbol{n}_{j\neq i}} \tag{16}$$

The chemical potential $\mu_{\boldsymbol{M}i}$ is a special case of this class that corresponds to an isotropic squeeze:

$$\hat{\varepsilon}_{jk} = \frac{1}{3}\delta_{jk} \tag{17}$$

Even under initially hydrostatic conditions, in anisotropic materials with elastic symmetries lower than cubic this isotropic squeeze could generate non-hydrostatic stresses. Maintaining hydrostatic stresses would require instead a strain related to the isothermal compressibility tensor:

$$\hat{\varepsilon}_{jk} = \frac{\beta_{\text{Thyd}jk}}{\beta_{\text{TRhyd}}} \tag{18}$$

In uniaxial compression along a unit normal vector $\hat{\boldsymbol{n}}$, the strain is equal to $\hat{\boldsymbol{n}} \otimes \hat{\boldsymbol{n}}$:

$$\hat{\varepsilon}_{jk} = \hat{n}_j \hat{n}_k \tag{19}$$

Uniaxial strain is relevant to material exchange across an interface with normal $\hat{\boldsymbol{n}}$. Chemical equilibrium across the interface is achieved when the "interfacial" chemical potential $\mu_{\hat{\boldsymbol{n}}i}$ is equal on both sides of the interface

$$\mu_{\hat{\boldsymbol{n}}i} = \left(\frac{\partial \mathcal{E}}{\partial n_i}\right)_{V,(\hat{\boldsymbol{n}}\otimes\hat{\boldsymbol{n}}),N,\boldsymbol{n}_{j\neq i}} = \left(\frac{\partial \mathcal{F}}{\partial n_i}\right)_{V,(\hat{\boldsymbol{n}}\otimes\hat{\boldsymbol{n}}),T,\boldsymbol{n}_{j\neq i}} \tag{20}$$

3 MATERIAL PROPERTIES USING EQUATION OF STATE VARIABLES

The theoretical development in Section 2 is only of practical use when combined with a hyperelastic, anisotropic equation of state. One practical equation of state is outlined in Section 3.1. An introduction to useful sets of variables and some useful derivations of partial derivatives can be found in Section 3.2. Sections 3.3 and 3.4 introduce expressions for the stress and chemical potentials.

3.1 A hyperelastic equation of state

Let us consider an equation of state where the extensive Helmholtz energy is defined as a function of molar volume V_{mol}, temperature T, molar proportions of species $\boldsymbol{p}$, the total number of moles of species n, and a finite rotation-free deformation gradient $\boldsymbol{U}$ that describes the deviation from a hydrostatic state of strain at constant volume:

$$\det \boldsymbol{U} = 1 \tag{21}$$

$$\boldsymbol{U} = \boldsymbol{U}^{\text{T}} \tag{22}$$

For hyperelastic materials, it is convenient to formulate an expression for elastic energy in terms of $\ln_{\text{M}} \boldsymbol{U}$, rather than $\boldsymbol{U}$, because $\ln_{\text{M}} \boldsymbol{U}$ will be traceless at constant volume (this arises from the mathematical identity $\det \boldsymbol{U} = \exp(\text{Tr}(\ln_{\text{M}} \boldsymbol{U}))$ as given by Petersen & Pedersen, 2012, their Eq. 502), i.e,

$$(\ln_{\text{M}} \boldsymbol{U})_{ii} = 0 \tag{23}$$

The Helmholtz energy can be split into hydrostatic and isochoric components:

$$\mathcal{F}(V_{\text{mol}}, T, \boldsymbol{p}, n, \boldsymbol{U}) = n\mathcal{F}_{\text{hydmol}}(V_{\text{mol}}, T, \boldsymbol{p}) + nV_{\text{mol}}\mathcal{F}_{\rho\text{el}}(V_{\text{mol}}, T, \boldsymbol{p}, \boldsymbol{U}) \tag{24}$$

$$\mathcal{F}_{\rho\text{el}}(V_{\text{mol}}, T, \boldsymbol{p}, \boldsymbol{U}) = \frac{1}{2}(\ln_{\text{M}} \boldsymbol{U})_{ij}\mathbb{C}_{\text{T,hyd}ijkl}(V_{\text{mol}}, T, \boldsymbol{p})(\ln_{\text{M}} \boldsymbol{U})_{kl} \tag{25}$$

Isothermal partial derivatives of the elastic energy density $\mathcal{F}_{\rho\text{el}}$, which will become important in the following sections, are

$$\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \ln V_{\text{mol}}} = \frac{1}{2}(\ln_{\text{M}} \boldsymbol{U})_{pq}\frac{\partial \mathbb{C}_{\text{T,hyd}pqrs}}{\partial \ln V_{\text{mol}}}(\ln_{\text{M}} \boldsymbol{U})_{rs} \tag{26}$$

$$\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial p_j} = \frac{1}{2}(\ln_{\text{M}} \boldsymbol{U})_{pq}\frac{\partial \mathbb{C}_{\text{T,hyd}pqrs}}{\partial p_j}(\ln_{\text{M}} \boldsymbol{U})_{rs} \tag{27}$$

$$\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial (\ln_{\text{M}} \boldsymbol{U})_{rs}} = (\ln_{\text{M}} \boldsymbol{U})_{rs}\mathbb{C}_{\text{T,hyd}pqrs} \tag{28}$$

In Myhill (2022, 2024), I introduced a self-consistent equation of state for near-hydrostatic conditions which defined the cell tensor via a hydrostatic deformation gradient tensor $\boldsymbol{F}_{\text{hyd}}$ and rotation tensor $\boldsymbol{R}_\text{hyd}$:

$$M_{\text{hyd}ij}(V_\text{mol}, T, \boldsymbol{p}, n) = R_{\text{hyd}ik} F_{\text{hyd}kl}(V_\text{mol}, T, \boldsymbol{p}) M_{0lj}(\boldsymbol{p}, n) \tag{29}$$

In the equation of state, $\boldsymbol{F}_\text{hyd}$ is symmetric, and $\boldsymbol{R}_\text{hyd}$ rotates the deformed cell tensor so that it is returned to the unit cell reference frame. For orthotropic materials, $\boldsymbol{R}_\text{hyd} = \boldsymbol{I}$, and in general, $\boldsymbol{R}_\text{hyd}$ is only a function of the reference frame convention (i.e., the orientations of the crystal axes relative to the coordinate axes) and $\boldsymbol{F}_\text{hyd}$. For a nonhydrostatic equation of state, the isochoric strain $\boldsymbol{U}$ is applied after hydrostatic deformation:

$$M_{\text{nonhyd}ij}(V_\text{mol}, T, \boldsymbol{p}, n, \boldsymbol{U}) = R'_{ik} U_{kl} M_{\text{hyd}lj} \tag{30}$$

where $\boldsymbol{R}'$ is a rotation matrix that rotates the deformed cell tensor to any desired final orientation. V_mol and $\ln_\text{M} \boldsymbol{U}$ (and therefore the Helmholtz energy) can be determined if the temperature, composition and state of strain $\boldsymbol{M}_\text{nonhyd}$ are known:

$$V_\text{mol} = \frac{\det \boldsymbol{M}_\text{nonhyd}}{n} \tag{31}$$

$$\boldsymbol{U} = \left(\sqrt{\boldsymbol{M}_\text{nonhyd}^T \boldsymbol{M}_\text{nonhyd}}\right) \left(\boldsymbol{M}_\text{hyd}(V_\text{mol}, T, \boldsymbol{n})\right)^{-1} \tag{32}$$

3.2 Variable sets and partial derivatives

The Helmholtz energy and cell tensor in Section 3.1 are defined as a function of the variable set $\{V_\text{mol}, T, \boldsymbol{p}, n, \ln_\text{M} \boldsymbol{U}\}$. In contrast, thermodynamic properties are naturally defined as a function of a different variable set: $\{\boldsymbol{\varepsilon}^*, T^*, \boldsymbol{n}^*\}$ and the class of chemical potentials in Section 2.3 as a function of a third variable set: $\{V^\circ, \hat{\boldsymbol{\varepsilon}}^\circ, T^\circ, \boldsymbol{n}^\circ\}$. The superscripts $*$ and $\circ$ here and in the following sections are used to differentiate between variable sets. Partial derivatives of one set as a function of derivatives of another can be found by change of variables.

3.2.1 The partial derivative of material properties with respect to infinitesimal material strain at fixed temperature and composition

The following derivation is required to derive an expression for the deviatoric stress as a function of the equation of state variables (Section 3.3). Starting with any function X described in terms of the equation of state variables:

$$X = X(V_\text{mol}(\boldsymbol{\varepsilon}^*, \boldsymbol{n}^*), T(T^*), \boldsymbol{p}(\boldsymbol{n}^*), n(\boldsymbol{n}^*), \ln_\text{M} \boldsymbol{U}(\boldsymbol{\varepsilon}^*, T^*, \boldsymbol{n}^*))$$

partial derivatives with respect to infinitesimal material strain can be written using the chain rule:

$$\frac{\partial}{\partial \varepsilon^*_{ij}} = \frac{\partial \ln V_{\mathrm{mol}}}{\partial \varepsilon^*_{ij}} \frac{\partial}{\partial \ln V_{\mathrm{mol}}} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}}{\partial \varepsilon^*_{ij}} \frac{\partial}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}} \tag{33}$$

$$= \delta_{ij} \frac{\partial}{\partial \ln V_{\mathrm{mol}}} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}}{\partial \varepsilon^*_{ij}} \frac{\partial}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}} \tag{34}$$

Substituting the total *material* strain $\boldsymbol{\varepsilon}$ into the above expression and rearranging:

$$\frac{\partial \varepsilon_{kl}}{\partial \varepsilon^*_{ij}} = \delta_{ij} \frac{\partial \varepsilon_{kl}}{\partial \ln V_{\mathrm{mol}}} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}}{\partial \varepsilon^*_{ij}} \frac{\partial \varepsilon_{kl}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}} \tag{35}$$

$$\delta_{ik}\delta_{jl} = \delta_{ij} \hat{\varepsilon}_{\boldsymbol{U}kl} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{mn}}{\partial \varepsilon^*_{ij}} \delta_{km}\delta_{ln} \tag{36}$$

$$\frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{kl}}{\partial \varepsilon^*_{ij}} = \delta_{ik}\delta_{jl} - \delta_{ij} \hat{\varepsilon}_{\boldsymbol{U}kl} \tag{37}$$

By using $\hat{\boldsymbol{\varepsilon}}_{\boldsymbol{U}}$ in this expression we not stating explicitly how the *material* is deformed. Under hydrostatic conditions, $\hat{\boldsymbol{\varepsilon}}_{\boldsymbol{U}}$ is given by Equation 18, but this is not generally true under nonhydrostatic conditions because of the nonlinear relationship between $\boldsymbol{M}$ and $\boldsymbol{U}$ (Equation 32). The partial derivative of material properties with respect to material strain as a function of the equation of state variables can be found by substituting Equation 37 into Equation 34:

$$\frac{\partial}{\partial \varepsilon^*_{ij}} = \delta_{ij} \frac{\partial}{\partial \ln V_{\mathrm{mol}}} + \left(\delta_{ik}\delta_{jl} - \delta_{ij} \hat{\varepsilon}_{\boldsymbol{U}kl}\right) \frac{\partial}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{kl}} \tag{38}$$

3.2.2 The partial derivative of material properties with respect to composition at fixed domain volume, shape and temperature

The following derivation is required to derive expressions for chemical potentials as a function of the equation of state variables (Section 3.4). Starting with any function X described in terms of the equation of state variables:

$$X = X(V_{\mathrm{mol}}(V^\circ, \boldsymbol{n}^\circ), T(T^\circ), \boldsymbol{p}(\boldsymbol{n}^\circ), n(\boldsymbol{n}^\circ), \ln_{\mathrm{M}} \boldsymbol{U}(V^\circ, \hat{\boldsymbol{\varepsilon}}^\circ, T^\circ, \boldsymbol{n}^\circ)) \tag{39}$$

partial derivatives with respect to composition can be written:

$$\frac{\partial}{\partial n^\circ_i} = \frac{\partial \ln V_{\mathrm{mol}}}{\partial n^\circ_i} \frac{\partial}{\partial \ln V_{\mathrm{mol}}} + \frac{\partial p_j}{\partial n^\circ_i} \frac{\partial}{\partial p_j} + \frac{\partial n}{\partial n^\circ_i} \frac{\partial}{\partial n} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{pq}}{\partial n^\circ_i} \frac{\partial}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{pq}} \tag{40}$$

$$= -\frac{1_i}{n} \frac{\partial}{\partial \ln V_{\mathrm{mol}}} + \left(\frac{\delta_{ij} - 1_i p_j}{n}\right) \frac{\partial}{\partial p_j} + 1_i \frac{\partial}{\partial n} + \frac{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{pq}}{\partial n^\circ_i} \frac{\partial}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U}\right)_{pq}} \tag{41}$$

If the domain $\mathcal{D}$ does not change volume or shape on changing composition, and so the total *domain* strain $\boldsymbol{\varepsilon}_{\mathcal{D}} = \mathbf{0}$. Substituting $\boldsymbol{\varepsilon}_{\mathcal{D}}$ into Equation 41:

$$\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial n_i^\circ} = 0_{kli} = -\frac{1_i}{n}\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial \ln V_{\text{mol}}} + \left(\frac{\delta_{ij} - 1_i p_j}{n}\right)\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial p_j} + 1_i \frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial n} + \frac{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}}{\partial n_i^\circ}\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}} \tag{42}$$

$$= -\frac{1_i}{n}\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial \ln V_{\text{mol}}} + \left(\frac{\delta_{ij} - 1_i p_j}{n}\right)\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial p_j} + 1_i \frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial n} + \frac{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}}{\partial n_i^\circ}\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}} \tag{43}$$

$$= -\frac{1_i}{n}\hat{\varepsilon}_{kl} + \left(\frac{\delta_{ij} - 1_i p_j}{n}\right)\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial p_j} + 1_i \frac{\delta_{kl}}{3n} + \frac{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}}{\partial n_i^\circ}\delta_{kp}\delta_{lq} \tag{44}$$

then rearranging

$$\frac{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{kl}}{\partial n_i^\circ} = \frac{1_i}{n}\hat{\varepsilon}_{kl} - \left(\frac{\delta_{ij} - 1_i p_j}{n}\right)\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial p_j} - 1_i \frac{\delta_{kl}}{3n} \tag{45}$$

$$= \frac{1}{n}\left(1_i\left(\hat{\varepsilon}_{kl} - \frac{\delta_{kl}}{3}\right) - \left(\delta_{ij} - 1_i p_j\right)\frac{\partial \varepsilon_{\mathcal{D}kl}}{\partial p_j}\right) \tag{46}$$

Substituting Equation 46 into Equation 41:

$$\begin{aligned} n\frac{\partial}{\partial n_i^\circ} &= -1_i \frac{\partial}{\partial \ln V_{\text{mol}}} + \left(\delta_{ij} - 1_i p_j\right)\frac{\partial}{\partial p_j} + 1_i \frac{\partial}{\partial \ln n} \\ &+ \left(1_i\left(\hat{\varepsilon}_{pq} - \frac{\delta_{pq}}{3}\right) - \left(\delta_{ij} - 1_i p_j\right)\frac{\partial \varepsilon_{\mathcal{D}pq}}{\partial p_j}\right)\frac{\partial}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}} \end{aligned} \tag{47}$$

3.3 Stress and pressure

The true stress (Cauchy stress) is defined as

$$\sigma_{ij} = \frac{1}{V}\frac{\partial \mathcal{F}}{\partial \varepsilon^*_{ij}} \tag{48}$$

Splitting the Helmholtz energy $\mathcal{F}$ into hydrostatic and non-hydrostatic parts as in Equation 24:

$$V\sigma_{ij} = \frac{\partial}{\partial \varepsilon^*_{ij}}\left(n\mathcal{F}_{\text{hydmol}}(V_{\text{mol}}, T, \boldsymbol{p}) + (nV_{\text{mol}})\mathcal{F}_{\rho\text{el}}(V_{\text{mol}}, T, \boldsymbol{p}, \boldsymbol{U})\right) \tag{49}$$

$$= -\delta_{ij} V P_{\text{hyd}} + \mathcal{F}_{\rho\text{el}}\frac{\partial V}{\partial \varepsilon^*_{ij}} + V\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \varepsilon^*_{ij}} \tag{50}$$

$$= -\delta_{ij} V P_{\text{hyd}} + \mathcal{F}_{\rho\text{el}} V \delta_{ij} + V\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \varepsilon^*_{ij}} \tag{51}$$

$$\sigma_{ij} = \delta_{ij}\left(\mathcal{F}_{\rho\text{el}} - P_{\text{hyd}}\right) + \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \varepsilon^*_{ij}} \tag{52}$$

The total pressure ("mean" stress) is given by:

$$P = -\frac{\delta_{kl}}{3}\sigma_{kl} = P_{\text{hyd}} - \mathcal{F}_{\rho\text{el}} - \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \varepsilon^*_{kl}}\frac{\delta_{kl}}{3} \tag{53}$$

Combining Equations 52 and 53 yields the deviatoric stress tensor:

$$\begin{aligned} \tau_{ij} &= \sigma_{ij} + \delta_{ij} P && (54) \\ &= \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \varepsilon^*_{ij}} - \delta_{ij} \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \varepsilon^*_{kl}} \frac{\delta_{kl}}{3} && (55) \\ &= \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \varepsilon^*_{kl}} \left(\delta_{ik}\delta_{jl} - \delta_{ij} \frac{\delta_{kl}}{3} \right) && (56) \end{aligned}$$

The first term on the RHS of Equation 56 can be expanded using Equation 38:

$$\begin{aligned} \tau_{ij} &= \left(\delta_{kl} \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \ln V_{\mathrm{mol}}} + \left(\delta_{km}\delta_{ln} - \delta_{kl} \hat{\varepsilon}_{\boldsymbol{U}mn} \right) \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U} \right)_{mn}} \right) \left(\delta_{ik}\delta_{jl} - \delta_{ij} \frac{\delta_{kl}}{3} \right) && (57) \\ &= \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U} \right)_{mn}} \left(\delta_{km}\delta_{ln} \right) \left(\delta_{ik}\delta_{jl} - \delta_{ij} \frac{\delta_{kl}}{3} \right) && (58) \\ &= \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U} \right)_{kl}} \left(\delta_{ik}\delta_{jl} - \delta_{ij} \frac{\delta_{kl}}{3} \right) && (59) \end{aligned}$$

And by pre- and post-multiplying with the unit vector $\hat{\boldsymbol{n}}$ the difference between the pressure (mean stress) and stress parallel to $\hat{\boldsymbol{n}}$ is:

$$\hat{n}_i \tau_{ij} \hat{n}_j = \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U} \right)_{kl}} \left(\hat{n}_k \hat{n}_l - \frac{\delta_{kl}}{3} \right) \tag{60}$$

3.4 Chemical potentials

3.4.1 The class of chemical potentials

The class of chemical potentials $\mu_{\hat{\boldsymbol{\varepsilon}}i}$ described in Section 2.3 can be expressed as a function of the equation of state variables by partial differentiation of the Helmholtz energy $\mathcal{F}$ (Equation 24) with respect to n°_i at fixed $\hat{\boldsymbol{\varepsilon}}^\circ$, V° and T°:

$$\begin{aligned} \mu_{\hat{\boldsymbol{\varepsilon}}i} &= \frac{\partial \mathcal{F}}{\partial n^\circ_i} = \frac{\partial}{\partial n^\circ_i} \left(\mathcal{F}_{\mathrm{hyd}}(V_{\mathrm{mol}}, T, \boldsymbol{p}) + V \mathcal{F}_{\rho\mathrm{el}}(V_{\mathrm{mol}}, T, \boldsymbol{p}, \boldsymbol{U}) \right) && (61) \\ &= \mu_{\mathrm{hyd}i} + V \left(\frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial n^\circ_i} \right)_{V^\circ, \hat{\boldsymbol{\varepsilon}}^\circ, T^\circ, n^\circ_{j \neq i}} && (62) \end{aligned}$$

The second term on the RHS of Equation 62 can be expanded using Equation 47:

$$\begin{aligned} \mu_{\hat{\boldsymbol{\varepsilon}}i} = \mu_{\mathrm{hyd}i} &- V_{\mathrm{mol}} 1_i \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \ln V_{\mathrm{mol}}} + V_{\mathrm{mol}} \left(\delta_{ij} - 1_i p_j \right) \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial p_j} \\ &+ V_{\mathrm{mol}} \left(1_i \left(\hat{\varepsilon}_{pq} - \frac{\delta_{pq}}{3} \right) - \left(\delta_{ij} - 1_i p_j \right) \frac{\partial \varepsilon_{pq}}{\partial p_j} \right) \frac{\partial \mathcal{F}_{\rho\mathrm{el}}}{\partial \left(\ln_{\mathrm{M}} \boldsymbol{U} \right)_{pq}} \end{aligned} \tag{63}$$

None of the terms in Equation 63 are a function of n, so as expected, the non-hydrostatic chemical potential is independent of system size. In addition, all the partial derivatives are linear or quadratic in non-hydrostatic strain $\ln_{\mathrm{M}} \boldsymbol{U}$ (see Equations 26, 27 and 28). Thus, under hydrostatic conditions (where $\ln_{\mathrm{M}} \boldsymbol{U} = \boldsymbol{0}$), the chemical potential (Equation 63) reduces to the standard hydrostatic form.

The only difference between all of the chemical potentials is the single term involving $\hat{\varepsilon}$ in Equation 63. Therefore, any chemical potential can be related to any other via the expression:

$$\Delta\mu_{\hat{\varepsilon}i} = \left(1_i V_{\text{mol}} \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}}\right) \Delta\hat{\varepsilon}_{pq} \tag{64}$$

$$= \left(1_i V_{\text{mol}} (\ln_{\text{M}} \boldsymbol{U})_{rs} \mathbb{C}_{\text{T,hyd}rspq}\right) \Delta\hat{\varepsilon}_{pq} \tag{65}$$

where the substitution is from Equation 28.

3.4.2 The "isotropic strain" chemical potential

The "isotropic strain" chemical potential $\mu_{\boldsymbol{M}i}$ can be obtained by substituting

$$\hat{\varepsilon}_{\boldsymbol{M}pq} = \frac{\delta_{pq}}{3} \tag{66}$$

into Equation 63:

$$\begin{aligned} \mu_{\boldsymbol{M}i} = \mu_{\text{hyd}i} - V_{\text{mol}} 1_i \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \ln V_{\text{mol}}} \\ + V_{\text{mol}} \left(\delta_{ij} - 1_i p_j\right) \left(\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial p_j} - \frac{\partial \varepsilon_{pq}}{\partial p_j} \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}}\right) \end{aligned} \tag{67}$$

This expression can be simplified considerably for one component solids:

$$\mu_{\boldsymbol{M}} = \mu_{\text{hyd}} - V_{\text{mol}} \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \ln V_{\text{mol}}} \tag{68}$$

3.4.3 Interfacial chemical potentials

Using Equation 64, interfacial chemical potentials can be defined relative to the isotropic strain chemical potential:

$$\mu_{\hat{\boldsymbol{n}}i} = \mu_{\boldsymbol{M}i} + 1_i V_{\text{mol}} \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \left(\ln_{\text{M}} \boldsymbol{U}\right)_{pq}} \left(\hat{n}_p \hat{n}_q - \frac{\delta_{pq}}{3}\right) \tag{69}$$

By comparison with Equation 60, the relationship between the two chemical potentials is dependent only on the molar volume, orientation and deviatoric stress:

$$\mu_{\hat{\boldsymbol{n}}i} = \mu_{\boldsymbol{M}i} + 1_i V_{\text{mol}} \hat{n}_k \tau_{kl} \hat{n}_l \tag{70}$$

This expression for the interfacial chemical potential, which governs phase growth and dissolution at phase boundaries, resembles that proposed by Wheeler (2014). The dependence of interfacial chemical potential on the normal stress explains a number of experimental observations (Wheeler, 2020). However, it is important to note that $\mu_{\boldsymbol{M}i}$ is not generally equal to $1_i \left(\mathcal{F}_{\text{mol}} - P V_{\text{mol}}\right)$ as suggested by Wheeler (2014), but is given instead by Equation 67.

3.4.4 The "chemical strain energy" tensor

Equation 70 demonstrates that there is a tensorial relationship between all interfacial chemical potentials. A third order tensor Ξ concisely describes this relationship:

$$\mu_{\hat{\boldsymbol{n}}i} = \hat{n}_j \Xi_{ijk} \hat{n}_k \tag{71}$$

$$\Xi_{ijk} = \delta_{jk} \mu_{\boldsymbol{M}i} + V_{\text{mol}} 1_i \tau_{jk} \tag{72}$$

$$= \delta_{jk} \left(\mu_{\boldsymbol{M}i} + V_{\text{mol}} P \right) + V_{\text{mol}} 1_i \sigma_{jk} \tag{73}$$

The tensor Ξ, which is here termed the "chemical strain energy" tensor, has units of chemical potential (J/mol), and describes the relationship between chemical strain and the resulting energy added to the domain. Note the similarity between Equation 71 and the relationship between the stress and normal stress to the interface:

$$\sigma_{\hat{\boldsymbol{n}}} = \hat{n}_j \sigma_{jk} \hat{n}_k \tag{74}$$

Any material in local chemical and mechanical equilibrium should have continuous interfacial chemical potentials $\mu_{\hat{\boldsymbol{n}}i}$ along any vector $\hat{\boldsymbol{n}}$. Therefore, by Equation 71, Ξ should also be continuous.

4 DISCUSSION

4.1 Gibbs' thought experiment

Let us return to Gibbs' thought experiment (Section 2.2). He deduced that "fluids in equilibrium with [a one-component] solid are all supersaturated with respect to the substance of the solid, except when the solid is in a state of hydrostatic stress; so that if there were present in any one of these fluids any small fragment of the same kind of solid subject to the hydrostatic pressure of the fluid, such a fragment would tend to increase.". In equation form:

$$\mu_{\text{fluid}}(P_{\text{fluid}}, T) \geq \mu_{\text{hyd,solid}}(P_{\text{fluid}}, T) \tag{75}$$

Alternatively, using our definition for the interfacial chemical potential (Section 3.4.3) the same expression is:

$$\mu_{\hat{\boldsymbol{n}}\text{solid}}(P_{\text{solid}}, T, \boldsymbol{\tau}_{\text{solid}}, \hat{\boldsymbol{n}}) - \mu_{\text{hyd,solid}}(P_{\text{fluid}}, T) \geq 0 \tag{76}$$

Taylor expanding μ_{hyd} about (P_{solid}, T):

$$\begin{aligned}
\mu_{\text{hyd,solid}}(P_{\text{fluid}}, T) &= \mu_{\text{hyd,solid}}(P_{\text{solid}}, T) + \frac{\partial \mu_{\text{hyd}}}{\partial P}(\Delta P) + \frac{1}{2}\frac{\partial^2 \mu_{\text{hyd}}}{\partial P^2}(\Delta P)^2 + \mathcal{O}((\Delta P)^3) && (77)\\
\frac{\partial \mu_{\text{hyd}}}{\partial P} &= V_{\text{mol,hyd,solid}}(P_{\text{solid}}, T) && (78)\\
\frac{\partial^2 \mu_{\text{hyd}}}{\partial P^2} &= -V_{\text{mol,hyd,solid}}(P_{\text{solid}}, T)\beta_{\text{RT}} && (79)\\
\Delta P &= P_{\text{fluid}} - P_{\text{solid}} && (80)
\end{aligned}$$

and also expanding the interfacial chemical potential (Equations 68 and 69):

$$\begin{aligned}
\mu_{\hat{\boldsymbol{n}}\text{solid}} &= \mu_{\text{hyd, solid}}(P_{\text{solid}}, T) - V_{\text{mol,hyd,solid}}\frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \ln V_{\text{mol}}} + V_{\text{mol,hyd,solid}}\hat{n}_u \tau_{uv} \hat{n}_v && (81)\\
&= \mu_{\text{hyd, solid}}(P_{\text{solid}}, T) + V_{\text{mol,hyd,solid}}(P_{\text{solid}}, T)\left(\Delta P - \frac{\partial \mathcal{F}_{\rho\text{el}}}{\partial \ln V_{\text{mol}}}\right) && (82)
\end{aligned}$$

Finally, using Equation 26 and truncating the series expansion at second order in ΔP, Gibbs' statement is equivalent to:

$$\frac{1}{2}V_{\text{mol,hyd,solid}}\left(\beta_{\text{RT}}(\Delta P)^2 - (\ln_{\text{M}} \boldsymbol{U})_{pq}\frac{\partial \mathbb{C}_{\text{T,hyd}pqrs}}{\partial \ln V_{\text{mol}}}(\ln_{\text{M}} \boldsymbol{U})_{rs}\right) \geq 0 \qquad (83)$$

As materials always have positive compressibilities, the first term is always positive. The whole left hand side is thus expected to be negative as long as $\partial \mathbb{C}_{\text{T,hyd}pqrs}/\partial \ln V_{\text{mol}}$ is negative semi-definite. Thus the inequality, and therefore Gibbs' statement, is usually expected to be true.

4.2 By how much does deviatoric stress affect chemical equilibria?

There have been a number of arguments over how much non-hydrostatic stresses modify chemical potentials. Some argue for large effects (Wheeler, 2014), while others argue for much smaller effects Fletcher (2015); Hobbs & Ord (2015); Powell et al. (2018) or a large effect only when mixing is non-ideal (Hess et al., 2022). An in-depth review of these arguments is beyond the scope of this study. Instead, let us briefly investigate the magnitude of the change in chemical potential due to non-hydrostatic stress in the Gibbs thought experiment. The left hand side of Equation 83 represents this change. For an elastically isotropic material, the elastic stiffness tensor can be reexpressed in terms of the two Lamé parameters, λ and G:

$$\frac{\partial \mathbb{C}_{\text{T,hyd}pqrs}}{\partial \ln V_{\text{mol}}} = \frac{\partial \lambda}{\partial \ln V_{\text{mol}}}\delta_{pq}\delta_{rs} + \frac{\partial G}{\partial \ln V_{\text{mol}}}\left(\delta_{pr}\delta_{qs} + \delta_{ps}\delta_{rq}\right) \qquad (84)$$

By also approximating $\beta_{\text{RT}} \sim -\Delta \ln V_{\text{mol}}/\Delta P$, Equation 83 can be reexpressed as

$$\frac{1}{2}V_{\text{mol,hyd,solid}}K_{\text{RT}}\left((\Delta \ln V_{\text{mol}})^2 + 2\frac{\partial G}{\partial P}(\ln_{\text{M}} \boldsymbol{U})_{pq}(\ln_{\text{M}} \boldsymbol{U})_{pq}\right) \geq 0 \qquad (85)$$

Typical geological minerals have values of $V_{\text{mol}}K_{\text{TR}}$ on the order of 10^6 J/mol-atom. The pressure dependence on the shear modulus is of order 1 (Stixrude & Lithgow-Bertelloni, 2011). Typical non-hydrostatic strains in minerals rarely exceed 1%, and are often only 0.1% before inducing brittle failure, and so the difference in chemical potential between hydrostatic and non-hydrostatically stressed states will be of order 1-100 J/mol-atom. Entropies of melting are on the order of R (8.3145) J/K/mol-atom (Stishov, 1988), and so even very large deviatoric stresses will only affect melting temperatures by at most a few degrees Kelvin. This result agrees, at least qualitatively, with previous works based on Larché & Cahn (1985) (Sekerka & Cahn, 2004; Powell et al., 2018; Hess & Ague, 2021). This does not mean that non-hydrostatic stresses are not important drivers of reaction, but rather that pressure and temperature under/overstepping is likely to play the dominant role in geological systems conducive to thermobarometry (e.g. Powell et al., 2018).

4.3 Comparison with previous studies and a resolution of controversies

In this work, I have shown that there is a scalar chemical potential, $\mu_{\boldsymbol{M}i}$, that represents the energy required to add component i to a volume by isotropically compressing preexisting material. This chemical potential should be used in total derivatives of the Helmholtz energy (Sections 2.1 and 3.4.2; Equation 13), and is suited to modelling thermodynamic disequilibrium in continuum simulations (e.g. Mianroodi et al., 2022). However, it is not the only possible chemical potential, and there is an entire class of chemical potentials that correspond to different ways of squeezing the material inside a volume $\mu_{\hat{\boldsymbol{\varepsilon}}i}$ (Sections 2.3, 3.4.1). An important subclass is the set of interfacial chemical potentials $\mu_{\hat{\boldsymbol{n}}i}$ that can be used to define equilibrium between phases across an interface (Section 3.4.3).

These different chemical potentials resolve a number of controversies surrounding non-hydrostatic chemical equilibrium. The “interfacial” chemical potentials satisfy the observed relevance of the normal stress for chemical reactions (Wheeler, 2014, 2020), while the “isotropic compressibility” chemical potential $\mu_{\boldsymbol{M}i}$ is a state property of the system, satisfying the requirement of Hobbs & Ord (2015). The chemical strain energy tensor Ξ (Section 3.4.4) encompasses the variety of ways in which preexisting material can be compressed to accommodate new material Rusanov (2005).

A major contribution to the field of thermodynamics under non-hydrostatic conditions was provided by Larché & Cahn (1973, 1978a,b, 1985), and that work has been tested by experiment (e.g. Shi et al., 2018). However, one limitation of the Larché-Cahn models is that they are developed around the concept of a fixed lattice, precluding the creation of defects and formation of subgrain boundaries. The current work does not require a fixed lattice, only a “thermodynamically-averaged lattice” used to define $\boldsymbol{M}$. The current work also defines individual component chemical potentials, a development not trivially achieved within the Larché-Cahn framework.

Another derivation of non-hydrostatic chemical phenomena that does introduce individual chemical potentials was provided by Mullins & Sekerka (1985). However, they used the unit cell tensor $\boldsymbol{q}$

as an independent variable (their Equation 6), rather than the extensive cell tensor $\boldsymbol{M} = n^{\frac{1}{3}}\boldsymbol{q}$. Their chemical potentials are therefore defined for a fixed lattice, which differs from the usual definition given for hydrostatic equations of state. In the current study, the lack of a fixed lattice constraint allows chemical potentials to equal the classical hydrostatic values in the absence of deviatoric stresses.

4.4 The applicability of the thermodynamic model to amorphous and defect-bearing materials

Most papers on non-hydrostatic chemical equilibria make a special distinction between inviscid fluids and solids, the latter being able to support significant deviatoric stresses. This distinction is evident in works such as Gibbs (1878), McLellan (1980) (specifically their equation 21.2.17), Larché & Cahn (1985), and Mullins & Sekerka (1985). These distinctions hinge on time-dependent phenomena, which are typically not a part of classical thermodynamics, except where they influence the ability to achieve a thermodynamic ensemble. In this paper, no distinction is made between fluids and solids, or between amorphous and crystalline solids; chemical potentials are definable throughout any material in any thermodynamic state. This is important, because most fluids are able to support deviatoric stresses on short timescales; this even applies to water when deformation takes place at THz frequencies (Schulz et al., 2020). The theory described here is applicable to glasses and other viscous fluids without a crystalline structure, and to crystalline materials which are able to develop lattice-disrupting dislocations and subgrain boundaries.

5 CONCLUSIONS

This paper was born out of a desire for a formulation for non-hydrostatic thermodynamics that was a straightforward generalisation of hydrostatic thermodynamics. Reading through some of the existing literature cited in this paper, I found it difficult to work out where different derivations were just an alternative description of the same phenomena, and where they were in error. In this paper, I have tried to avoid judging other papers, and have instead focused on a new derivation with only brief mention of commonalities with and differences from other papers.

One of the things which I think is new here is the use of the extensive cell tensor $\boldsymbol{M}$ as a natural variable of the Helmholtz energy. Without it, the concept of chemical potential seems (at least to me) hard to understand, and I think this is why previous strategies such as those of Larché & Cahn (1985) and Mullins & Sekerka (1985) are not obviously compatible with hydrostatic thermodynamics. McLellan (1980) (his Equation 20.1.14) took an alternative approach, and multiplied the infinitesimal strain tensor by the volume, a choice which has no obvious conceptual meaning. This is not to say that those works are wrong, only that the descriptions did not match my expectations from familiar hydrostatic expressions. Another thing that I think is useful in this study is tying the (brief) theoretical development with a concrete equation of state (Myhill, 2022, 2024).

The quantitative framework for chemical potentials provided in this paper provides a framework for continuum modelling of grain scale dynamics (either finite difference, element or volume) that avoids the need to explicitly define and track grain boundaries and their orientations, enabling continuum modelling of defect concentrations and subgrain generation. Particularly useful are the definitions for the Cauchy stress ($\boldsymbol{\sigma}$, Equation 52), "isotropic strain" chemical potential (μ_{Mi}, Equation 67) and chemical strain energy tensor (Ξ, Equation 73).

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