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 here defined as the change in Helmholtz energy on adding a single chemical component to a material while locally preserving total volume, temperature and the shape of the domain. The paper demonstrates that an entire class of chemical potentials can be defined given different boundary conditions. Total derivatives of the Helmholtz free energies use a chemical potential defined by imposing isotropic compression of existing material, while crystal growth and dissolution is governed by interfacial chemical potentials, defined by imposing uniaxial compression of existing material normal to the crystal surface. A chemical equivalent of the conservation of linear momentum (Cauchy’s first law) is provided that encapsulates the concept of chemical equilibrium under non-hydrostatically stressed states. The derived chemical potentials are valid for all phases; both solid and liquid, crystalline and amorphous, and do not depend on rheology. They are discussed in the context of previous results, resolving several points of controversy in the literature.

Key words:  Equations of state – Elasticity – Thermodynamics

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1 INTRODUCTION

Finite non-hydrostatic stress states 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 relationships between chemical diffusion, reaction and deviatoric stress.

The mathematical treatment of chemical equilibrium and disequilibrium under non-hydrostatic stress states has a long history. The first treatment by Gibbs (1878) is universally considered to be correct (Kamb, 1961; Larché & Cahn, 1973; Mullins & Sekerka, 1985; Hobbs & Ord, 2016; Powell et al., 2018; Wheeler, 2020), but is limited to diffusionless systems with two 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 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 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; that the total internal energy of a system is minimised at constant entropy and temperature, and that chemical equilibrium can be assessed via compositional derivatives of a thermodynamic energy - so-called (relative) chemical potentials.

There are a number of subtle disagreements in the papers discussing chemical potentials (see, for example, Truesdell, 1984; Cahn, 2013; Hirth, 2014; Tajčmanová et al., 2021). One could probably spend a lifetime reading through and digesting the literature. 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 differences between the papers boil down to the following issues:

- The mathematical definition of chemical potential, including whether it exists under non-hydrostatic stress states, exists only as a relative value, only when diffusion is possible, or only when a crystal lattice is present.
- The relationship between this definition of chemical potential and physical phenomena under non-hydrostatic conditions.
- The veracity of the mathematical derivations relating the definition of chemical potential to mate-
rial state (stress, strain, temperature, entropy) and properties (especially molar volume and the isothermal stiffness tensor).

None of these papers provide a definition of chemical potential under non-hydrostatic stress states that is a direct generalisation of the hydrostatic definition, that is, (i) definable everywhere based only on local state, (ii) the energy conjugate of the number of moles of chemical component, (iii) constant everywhere at equilibrium, and (iv) related to a chemical property that is continuous under the assumption of local equilibrium. A definition satisfying these requirements would be useful as input to continuum models of diffusion, reaction and textural evolution in materials. In this paper, I show how such a definition may be derived.

2 DEFINING CHEMICAL POTENTIALS

2.1 Chemical potentials under hydrostatic and non-hydrostatic states

Under hydrostatic conditions, the chemical potential $\mu_i$ of a component $i$ is defined as the partial derivative of internal energy (or Helmholtz energy) with respect to the number of moles of that component at fixed domain volume $V$, entropy $N$ (or temperature $T$), and number of moles of other components ($n_j \neq i$):

$$\mu_{\text{hyd}}_i = \left( \frac{\partial E_{\text{hyd}}}{\partial n_i} \right)_{V,N,n_j \neq i} = \left( \frac{\partial F_{\text{hyd}}}{\partial n_i} \right)_{V,T,n_j \neq i}$$

(1)

Under non-hydrostatic conditions, the volume, entropy (temperature) and chemical composition are insufficient to completely define the energy of the domain, as the material within the domain can be elastically strained at constant volume, entropy and mole number. One might think that fixing the shape of the domain would then be sufficient to define a useful chemical potential given an initial state of elastic strain. However, an ambiguity remains: the positions of the atoms in the domain must change to accommodate the extra amount of component $i$, and there are several non-unique ways of doing this. For example, a cubic domain could have material added by squeezing existing material uniaxially in any direction, or by squeezing the material in multiple directions at once. If the material is initially hydrostatically stressed, the resulting change in energy does not depend on how existing material is squeezed. This is why a unique chemical potential can be defined under hydrostatic stress states (i.e., in inviscid fluids). In contrast, 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.

This relationship between non-hydrostatic stress, material deformation and energy change has led to different responses in the academic literature. Some have argued that chemical potentials of
individual chemical components cannot be defined under non-hydrostatic conditions (Kamb, 1961; Larché & Cahn, 1973, 1985; Wheeler, 2018; Powell et al., 2018; Hess et al., 2022), while others claim that chemical potential can still be usefully defined (McLellan, 1980; Mullins & Sekerka, 1985; Hobbs & Ord, 2016), or that chemical potential becomes tensorial in nature (Rusanov, 2005). These studies differ in what they consider to be the defining characteristic of a chemical potential, and what they choose to be the natural variables of the system.

From a mathematical perspective, Equation 1 can be generalised (non-uniquely) to non-hydrostatic states by fixing the extensive cell tensor $M$, a tensor describing the local parallelepiped shape of the unit cell and having the volume of the material ($M = n^{\frac{3}{2}}M_{\text{unit}}$):

$$\mu_{M_i} = \left( \frac{\partial \mathcal{E}}{\partial n_i} \right)_{M,N,n_j\neq i} = \left( \frac{\partial F}{\partial n_i} \right)_{M,T,n_j\neq i}$$

Equation 2 implies that the natural variables of the Helmholtz energy are $\{M, T, n\}$, but the total derivative of the Helmholtz energy is often written:

$$d\mathcal{F} = P dV - \tau_{ij} d\bar{\varepsilon}_{ij} + T dS + \mu_k d\eta_k$$

where $\tau$ is a strictly deviatoric stress and $\bar{\varepsilon}$ is a small isochoric strain:

$$\bar{\varepsilon}_{ij} = \varepsilon_{ij} - \frac{1}{3} \delta_{ij} \delta_{kl} \varepsilon_{kl}$$

Writing the independent variables $V$ and $\bar{\varepsilon}$ as functions of $M$, $\mu_{M_i}$ can be used as the corresponding chemical potential:

$$d\mathcal{F} = P dV - \tau_{ij} d\bar{\varepsilon}_{ij} + T dS + \mu_{M_k} d\eta_k$$

$$V = \det M$$

$$d\bar{\varepsilon}_{ij} = d\varepsilon_{ij} - \left( \frac{1}{3} \delta_{ij} \delta_{kl} \right) d\varepsilon_{kl}$$

$$d\varepsilon = \frac{1}{2} \left( dM_{ik} M_{kj}^{-1} + dM_{jk} M_{ki}^{-1} \right)$$

Although $\mu_{M_i}$ is a natural choice for a chemical potential, it is not the only valid definition of a chemical potential, just as the volumetric heat capacity $c_V$ is not the only valid definition of a heat capacity ($c_P$, $c_\sigma$ and $c_\varepsilon$ represent isobaric, isostress and isometric heat capacities (Nye et al., 1985)). Nor is $\mu_{M_i}$ as directly connected to thermodynamic phenomena in the same way as $\mu_{\text{hyd}}$ under hydrostatic conditions. In the following section, I will use a thought experiment from Gibbs (1878) to demonstrate
that $\mu_{M_1}$ is not spatially continuous under the assumption of local equilibrium. I will use this to motivate the definition of a general class of chemical potentials, and a related tensor whose components are spatially continuous under local equilibrium.

### 2.2 Continuity and discontinuity in measures of disequilibrium

In isolated systems, progress towards equilibrium is governed by the second law of thermodynamics, which dictates that entropy must continuously increase. This increase in entropy is related to and concurrent with the reduction of spatial gradients in stress, temperature and chemical potential, and also reductions in deviatoric stress and chemical affinity. 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. Chemical affinities and deviatoric stresses might be quite large. The law governing stress continuity is the conservation of linear momentum (Cauchy’s First Law), which is, in a Lagrangian reference frame:

$$\frac{\partial \sigma_{ij}}{\partial x_j} + \rho (b_i - a_i) = 0_i$$

(9)

where $b$ is a body force such as gravity and $a$ is the acceleration (units of both are N/kg or m/s$^2$). If this law is to hold, the stress must be finite and spatially continuous.

Depending on the system, the reduction of gradients in stress, temperature and chemistry may be coupled. For example, in baro- and thermodiffusion, differences in pressure and temperature can drive chemical diffusion. Gradients in deviatoric stress and chemical potential are rarely considered together, partially because of the complications involved with defining chemical potential under non-hydrostatic stress states (Section 2.1). But clearly, if the second sentence of this subsection is to hold under deviatoric stresses, there should be some measure of chemical potential that is spatially continuous at local equilibrium.

A famous demonstration of discontinuities in the standard hydrostatic chemical potential was presented by Gibbs (1878) (Chapter IX, his pages 343-360). In the example Gibbs envisaged an isothermal system containing a fluid and a crystal (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. The fluid is 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.

By the law of conservation of linear momentum (Equation 9), the stress normal to each crystal
**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).

face must be equal to the pressure of the fluid. The fluid pressure must therefore be different in the fluid pools adjacent to each face. As the chemical potential in the fluid is a function of the pressure, the chemical potential must also be different in each fluid pool. There is therefore no way for any single scalar chemical potential to be continuous across both fluid-crystal interfaces.

Gibbs’ thought experiment is in apparent contradiction with the opening paragraph of this section. 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? The next section resolves this paradox by considering the effect of boundary conditions on mechanical equilibrium.

### 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 the thought experiment of Gibbs (1878), 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 also strains existing material on both sides. Let us here define the “squeeze” applied to existing material as more material is added to the
Figure 2. Visual representation of shape changes in the domain (top panels) and extensive cell tensor $M$ (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 10). The squeeze shown in the center panel is for addition of material along a vector $\hat{n}$. 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.

phase as:

$$\hat{\varepsilon}_{jk} = \left( \frac{\partial \varepsilon_{jk}}{\partial \ln V_{mol}} \right)$$  \hspace{1cm} (10)

The molar volume $V_{mol}$ is itself a function of the strain, so $\hat{\varepsilon}$ must obey the following constraint:

$$\text{Tr}(\hat{\varepsilon}) = 1$$ \hspace{1cm} (11)

At the same time that existing material is squeezed, the domain is refilled with new material, such that the domain preserves its original volume and shape. 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 it isotropically increases the extensive cell tensor. A graphical representation of the two components of elastochemical strain (squeeze and fill) are shown in Figure 2.

A general class of chemical potentials can be defined for different normalised strains $\hat{\varepsilon}$:

$$\mu_{\hat{\varepsilon}_i} = \left( \frac{\partial E}{\partial n_i} \right)_{V,\hat{\varepsilon},N,n_{j\neq i}} = \left( \frac{\partial F}{\partial n_i} \right)_{V,\hat{\varepsilon},T,n_{j\neq i}}$$ \hspace{1cm} (12)

If material is only added across a single interface with unit normal $\hat{n}$, the strain is equal to $\hat{n} \otimes \hat{n}$:

$$\hat{\varepsilon}_{jk} = \hat{n}_j \hat{n}_k$$ \hspace{1cm} (13)

Chemical equilibrium across an interface is therefore achieved when the “interfacial” chemical poten-
3.1 Introduction

The theoretical development in the previous section is only of practical use when combined with an equation of state. In this section, I will derive expressions for the “isotropic compression” chemical potential and the “chemical diffusion potential tensor” using a hyperelastic equation of state based on a previous anisotropic equation of state (Myhill, 2022).

3.2 A hyperelastic equation of state

\[ F(V_{\text{mol}}, T, p, n, U) = nF_{\text{hyd}}(V_{\text{mol}}, T, p) + (nV_{\text{mol}})F_{\rho \text{el}}(V_{\text{mol}}, T, p, U) \]  

(15)

\[ M_{ij}(V_{\text{mol}}, T, p, n, U) = U_{ik}F_{kl}(V_{\text{mol}}, T, p)M_{lj}(p, n) \]  

(16)

\[ F_{\rho \text{el}}(V_{\text{mol}}, T, p, U) = \frac{1}{2} \ln M_U \]  

(17)

For small deviations from a hydrostatic state, \( U = I + \bar{\varepsilon} \), where \( \bar{\varepsilon} \) is an infinitesimal, isochoric strain tensor. Under finite deviations from hydrostaticity, \( U \) is an finite, isochoric, rotation-free deformation gradient:

\[ \det U = 1, \quad U = U^T \]  

(18)

A small change in \( \ln M_U \) with respect to isochoric strain is:

\[ \delta(\ln M_U) = \ln M_U \left( \left( I + \frac{1}{2} \delta \bar{\varepsilon} \right) U \right) - \ln M_U \left( \left( I - \frac{1}{2} \delta \bar{\varepsilon} \right) U \right) \]  

(19)

If \( \delta \bar{\varepsilon} \) and \( U \) commute (for example, under hydrostatic conditions, when \( U = I \)),

\[ \frac{\partial(\ln M_U)_{kl}}{\partial \bar{\varepsilon}_{mn}} = \delta_{km}\delta_{ln} \]  

(20)

If \( \delta \bar{\varepsilon} \) and \( U \) do not commute, the partial derivative must be calculated numerically.

3.3 Variable sets and partial derivatives

The Helmholtz energy and cell tensor in the previous section are defined as a function of the variables \( \{V_{\text{mol}}, T, p, n, \ln M_U\} \). In contrast, material properties are defined as a function of the variables \( \{\varepsilon^*, T^*, n^*\} \) and the class of chemical potentials in Section 2.3 as a function of the variables \( \{V^\circ, \hat{\varepsilon}^\circ, T^\circ, n^\circ\} \) (where the superscripts 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.

Starting with any function

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

partial derivatives with respect to strain can be written:

$$\frac{\partial}{\partial \varepsilon_{ij}^*} = \frac{\partial \ln V_{mol}}{\partial \varepsilon_{ij}^*} \frac{\partial \ln V_{mol}}{\partial \varepsilon_{ij}^*} + \frac{\partial \ln (U_{mn})}{\partial \ln (U_{mn})} \frac{\partial}{\partial (\ln M U)_{mn}}$$

Similarly, starting with:

$$X = X(V_{mol}(V^o, n^o), T(T^o), p(n^o), n(n^o), \ln M U(V^o, \varepsilon^o, T^o, n^o))$$

partial derivatives with respect to composition can be written:

$$\frac{\partial}{\partial n_i^o} = \frac{\partial \ln V_{mol}}{\partial n_i^o} \frac{\partial \ln V_{mol}}{\partial n_i^o} + \frac{\partial p_j}{\partial n_i^o} \frac{\partial p_j}{\partial n_i^o} + \frac{\partial n_i}{\partial n_i^o} \frac{\partial n_i}{\partial n_i^o} + \frac{\partial (\ln M U)_{pq}}{\partial (\ln M U)_{pq}} \frac{\partial}{\partial (\ln M U)_{pq}}$$

The partial derivative in the last term can be derived from the definition of the chemical potential, that states that the domain does not change volume or shape on changing composition, and so \( \varepsilon = 0 \).

Substituting \( \varepsilon \) into the above expression:

$$\frac{\partial \varepsilon_{kl}}{\partial n_i^o} = 0_{kl} - \frac{1}{n} \frac{\partial \varepsilon_{kl}}{\partial n_i^o} + \left( \frac{\delta_{ij} - 1}{n} \frac{\partial \varepsilon_{kl}}{\partial p_j} \right) + \frac{1}{n} \frac{\partial \varepsilon_{kl}}{\partial n_i}$$

then rearranging:

$$\frac{\partial \varepsilon_{kl}}{\partial n_i^o} = \frac{1}{n} \varepsilon_{kl} - \left( \frac{\delta_{ij} - 1}{n} \frac{\partial \varepsilon_{kl}}{\partial p_j} \right) + \frac{\partial \varepsilon_{kl}}{\partial n_i}$$

$$\frac{\partial \varepsilon_{kl}}{\partial n_i^o} = \frac{1}{n} \left( \varepsilon_{kl} - \frac{\delta_{kl}}{3} \right) - \left( \frac{\delta_{ij} - 1}{n} \frac{\partial \varepsilon_{kl}}{\partial p_j} \right)$$
3.4 Stress and pressure

The true stress (Cauchy stress) is defined as

\[ \sigma_{ij} = \frac{1}{V} \frac{\partial F}{\partial \varepsilon_{ij}^*} \]  (33)

Splitting the Helmholtz energy into hydrostatic and non-hydrostatic parts (Equation 15) and using Equation 23:

\[ \sigma_{ij} = \delta_{ij} P_{hyd} + \delta_{ij} \left( \frac{\partial F_{\rho \text{el}}}{\partial \varepsilon_{ij}^*} \right) \]  (34)

\[ = \delta_{ij} \left( \frac{1}{2} (\ln M U)_{kj} \frac{\partial C_{T,hyd,snn}}{\partial \varepsilon_{kl}} (\ln M U)_{mn} - P_{hyd} \right) \]  (35)

\[ + (\ln M U)_{rs} C_{T,hyd,snn} \frac{\partial (\ln M U)_{mn}}{\partial \varepsilon_{kl}} \left( \delta_{ik} \delta_{jl} - \frac{\beta_{T,hyd}}{\beta_{T,hyd}} \delta_{ij} \right) \]  (36)

The total pressure (“mean” stress) is given by:

\[ P = -\frac{\delta_{ij}}{3} \sigma_{ij} \]  (37)

\[ = P_{hyd} - \frac{1}{2} (\ln M U)_{kj} \frac{\partial C_{T,hyd,snn}}{\partial \varepsilon_{kl}} (\ln M U)_{mn} \]  (38)

Combining these two expressions yields the deviatoric stress tensor:

\[ \tau_{ij} = \delta_{ij} P = (\ln M U)_{rs} C_{T,hyd,snn} \frac{\partial (\ln M U)_{mn}}{\partial \varepsilon_{kl}} \left( \delta_{ik} \delta_{jl} - \frac{\delta_{ij}}{3} \right) \]  (39)

3.5 Chemical potentials

3.5.1 The general class of chemical potentials

The class of chemical potentials \( \mu_{\dot{\varepsilon}_i} \) described in Section 2.3 can be obtained by partial differentiation of Equation 15 at fixed \( \dot{\varepsilon} \):

\[ \mu_{\dot{\varepsilon}_i} = \mu_{\text{hyd}_i} + \nu \ln \varepsilon_{\dot{\varepsilon}_i} \frac{\partial F_{\rho \text{el}}}{\partial \varepsilon_{\dot{\varepsilon}_i}} \]  (40)

Using Equations 26 and 32:

\[ \frac{\partial F_{\rho \text{el}}}{\partial n_i} = -\frac{1}{n} \frac{\partial F_{\rho \text{el}}}{\partial \ln \varepsilon_{\dot{\varepsilon}_i}} + \left( \delta_{ij} - \frac{1}{n} p_j \right) \frac{\partial F_{\rho \text{el}}}{\partial p_j} + \frac{1}{n} \frac{\partial F_{\rho \text{el}}}{\partial n} + \frac{\partial (\ln M U)_{kl}}{\partial n_i} \frac{\partial F_{\rho \text{el}}}{\partial n} \]  (41)

\[ = \frac{1}{n} \left( -1_i \frac{\partial F_{\rho \text{el}}}{\partial \ln \varepsilon_{\dot{\varepsilon}_i}} + \left( \delta_{ij} - \frac{1}{n} p_j \right) \frac{\partial F_{\rho \text{el}}}{\partial p_j} \right) \]  (42)
where

\[
\frac{\partial F_{\text{pel}}}{\partial \ln V_{\text{mol}}} = \frac{1}{2} \left( \ln M U \right)_{pq} \frac{\partial C_{T,\text{hyd}pqrs}}{\partial \ln V_{\text{mol}}} (\ln M U)_{rs} \tag{43}
\]

\[
\frac{\partial F_{\text{pel}}}{\partial p_j} = \frac{1}{2} \left( \ln M U \right)_{pq} \frac{\partial C_{T,\text{hyd}pqrs}}{\partial p_j} (\ln M U)_{rs} \tag{44}
\]

\[
\frac{\partial F_{\text{pel}}}{\partial (\ln M U)_{kl}} = (\ln M U)_{rs} C_{T,\text{hyd}rskl} \tag{45}
\]

Note that all the terms in Equation 42 are inversely proportional to \( n \), suggesting that, just as for hydrostatic chemical potential, the non-hydrostatic chemical potential is independent of system size. In addition, all the terms are linear or quadratic in \( \ln M U \). Thus, under hydrostatic conditions (where \( \ln M U = 0 \)), the chemical potential (Equation 40) reduces to the standard hydrostatic form.

The only difference between all of the chemical potentials is the single term involving \( \hat{\varepsilon} \) in Equation 42. Therefore, combining Equations 40, 42 and 45, any chemical potential can be related to any other via the expression:

\[
\Delta \mu_{\hat{\varepsilon}i} = \left( 1, V_{\text{mol}}(\ln M U)_{rs} C_{T,\text{hyd}rskl} \frac{\partial (\ln M U)_{kl}}{\partial \varepsilon_{mn}} \right) \Delta \varepsilon_{mn} \tag{46}
\]

### 3.5.2 The “isotropic compression” chemical potential

The “isotropic compression” chemical potential \( \mu_{M_i} \) can be obtained by substituting

\[
\hat{\varepsilon}_{Mkl} = \frac{\delta_{kl}}{3} \tag{47}
\]

into Equation 42 and then combining it with Equation 40 and Equations 43–45:

\[
\mu_{M_i} = \mu_{\text{hyd}} + \frac{1}{2} V_{\text{mol}}(\ln M U)_{pq} \left( -1, \frac{\partial C_{T,\text{hyd}pqrs}}{\partial \ln V_{\text{mol}}} + (\delta_{ij} - 1, p_j) \frac{\partial C_{T,\text{hyd}pqrs}}{\partial p_j} \right) (\ln M U)_{rs} \tag{48}
\]

\[
- V_{\text{mol}}(\ln M U)_{rs} C_{T,\text{hyd}rskl} \frac{\partial (\ln M U)_{kl}}{\partial \varepsilon_{mn}} (\delta_{ij} - 1, p_j) \frac{\partial \varepsilon_{mn}}{\partial p_j}
\]

For a one component solid:

\[
\mu_M = \mu_{\text{hyd}} - \frac{1}{2} V_{\text{mol}}(\ln M U)_{pq} \left( \frac{\partial C_{T,\text{hyd}pqrs}}{\partial \ln V_{\text{mol}}} \right) (\ln M U)_{rs} \tag{49}
\]

For elastically stable materials, the second term must always be negative, and therefore \( \mu_M \) in a one-component solid is always greater than \( \mu_{\text{hyd}} \).
3.6 The “chemical strain energy” tensor and the conservation of linear momentum

3.6.1 Local chemical equilibrium, revisited

In Section 2.3, I introduced the concept of chemical strain within a domain of fixed volume and shape, and the idea that chemical equilibrium is reached when interfacial chemical potentials $\mu_{\hat{n}i}$ (Equation 14) are equal on both sides of an interface.

In a domain of fixed volume and temperature, the Helmholtz energy should be locally minimized over all potential chemical strains. Let us then introduce a third order tensor that can be used to calculate the chemical potential over all of these strains. Let’s call this the “chemical strain energy tensor” $\Xi$:

$$\mu_{\hat{\varepsilon}i} = \Xi_{ijk}\hat{\varepsilon}_{jk}$$  \hspace{1cm} (50)

$$\mu_{\hat{n}i} = \hat{n}_j\Xi_{ijk}\hat{n}_k$$  \hspace{1cm} (51)

Note the similarity between the second expression and the relationship between the stress and normal stress to the interface, which governs purely mechanical equilibrium:

$$\sigma_{\hat{n}} = \hat{n}_j\sigma_{jk}\hat{n}_k$$  \hspace{1cm} (52)

3.6.2 The chemical strain energy tensor

The general class of chemical potentials can be defined relative to $\mu_{Mi}$ (Equation 46):

$$\mu_{\hat{\varepsilon}i} = \mu_{Mi} + 1_iV_{mol}(\ln_{Mi}U)_{rs}C_{T,\text{hydr}}rskl\frac{\partial(\ln_{Mi}U)}{\partial\hat{\varepsilon}_{mn}}\left(\frac{\hat{\varepsilon}_{mn} - \delta_{mn}}{3}\right)$$  \hspace{1cm} (53)

Equation 53 can be used to construct a form for the “chemical strain energy tensor” $\Xi$ (Equation 50) by recognising that $\hat{\varepsilon}_{uv}\delta_{uv} = 1$, and that $\delta_{mu}\hat{\varepsilon}_{uv}\delta_{nv} = \hat{\varepsilon}_{mn}$:

$$\Xi_{iuv} = \delta_{uv}\mu_{Mi} + V_{mol}1_i(\ln_{Mi}U)_{kl}C_{T,\text{hydr}}rskl\frac{\partial(\ln_{Mi}U)}{\partial\hat{\varepsilon}_{mn}}\left(\delta_{mu}\delta_{nv} - \delta_{uv}\frac{\delta_{mn}}{3}\right)$$  \hspace{1cm} (54)

A simpler expression can be obtained by substitution of the deviatoric stress tensor $\tau$ defined in Equation 39:

$$\Xi_{iuv} = \delta_{uv}\mu_{Mi} + V_{mol}1_i\tau_{uv}$$  \hspace{1cm} (55)

and therefore, interfacial chemical potentials (Equation 51) may be expressed as

$$\mu_{\hat{n}i} = \mu_{Mi} + 1_iV_{mol}\hat{n}_u\tau_{uv}\hat{n}_v$$  \hspace{1cm} (56)

This expression for the interfacial chemical potential, which governs phase growth and dissolution at phase boundaries, resembles that proposed by Wheeler (2014). The dependence on the normal stress at
interfaces can explain the results of a variety of experiments (Wheeler, 2020). The primary difference is that $\mu_{M_i}$ is not generally equal to $1_i(F_{mol} - PV_{mol})$, but is given instead by Equation 48.

### 3.6.3 The conservation of linear momentum

If any material is in local chemical equilibrium (not necessarily global equilibrium), that implies that along any vector $\hat{n}$, the interfacial chemical potential $\mu_{\hat{n}i}$ should be continuous. Therefore, by Equation 51, $\Xi$ should also be continuous. By rearranging $\Xi$ (Equation 55), we have:

$$\Xi_{iuv} = \delta_{uv} (\mu_{M_i} + V_{mol}P) + V_{mol}1_i \sigma_{uv}$$  \hspace{1cm} (57)

Taking the derivative with respect to position:

$$\frac{\partial \Xi_{iuv}}{\partial x_v} = \frac{\partial (\mu_{M_i} + V_{mol}P)}{\partial x_v} + V_{mol}1_i \frac{\partial \sigma_{uv}}{\partial x_u}$$  \hspace{1cm} (58)

This gradient in elastochemical energy will be balanced by acceleration of the component:

$$\rho_i a_{iv} = V_{mol}^{-1} \frac{\partial (\mu_{M_i} + V_{mol}P)}{\partial x_v} + 1_i \frac{\partial \sigma_{uv}}{\partial x_u}$$  \hspace{1cm} (59)

Where $\rho_i$ is the density of component $i$. This equation is a statement of the conservation of linear momentum (Equation 9), with the first term on the right hand side taking the role of the body force:

$$\rho_i b_{iv} = V_{mol}^{-1} \frac{\partial (\mu_{M_i} + V_{mol}P)}{\partial x_v}$$  \hspace{1cm} (60)

For an incompressible, hydrostatically stressed fluid, this body force is equal to zero.

### 4 DISCUSSION

#### 4.1 Gibbs’ thought experiment

Let us return to Gibbs’ thought experiment. Using Equations 49 and 56, the equilibrium condition for a one component solid in equilibrium with a (potentially multicomponent) fluid is:

$$\mu_{\text{fluid}} = \mu_{\text{hyd}}(V_{mol}, T) - \frac{1}{2} V_{mol}(\ln_M U)_{pq} \left( \frac{\partial C_{T,\text{hyd},pqrs}}{\partial \ln V_{mol}} \right) (\ln_M U)_{rs} + V_{mol} \hat{n}_u \tau_{uv} \hat{n}_v$$  \hspace{1cm} (61)

where all the terms on the right hand side correspond to properties of the solid. The pressure (mean stress) in the solid, assuming a cubic material, is (Equation 38):

$$P = P_{\text{hyd}} - \frac{1}{2} (\ln_M U)_{kl} \frac{\partial C_{T,\text{hyd},klmn}}{\partial \ln V_{mol}} (\ln_M U)_{mn}$$  \hspace{1cm} (62)

such that

$$\mu_{\text{fluid}} = \mu_{\text{hyd}}(P_{\text{hyd}}, T) + V_{mol}(P - P_{\text{hyd}}) + V_{mol} \hat{n}_u \tau_{uv} \hat{n}_v$$  \hspace{1cm} (63)

$$= \mu_{\text{hyd}}(P_{\text{hyd}}, T) + V_{mol}(P_{\text{fluid}} - P_{\text{hyd}})$$  \hspace{1cm} (64)
Now, because the chemical potential of any pure substance (molar Gibbs energy) is a concave function of pressure, we can state that

\[ \mu_{\text{hyd}}(P_{\text{fluid}}, T) \leq \mu_{\text{hyd}}(P_{\text{hyd}}, T) + V_{\text{mol}}(P_{\text{fluid}} - P_{\text{hyd}}) \]  

whether or not the fluid pressure is greater or lower than the mean stress in the solid. Therefore

\[ \mu_{\text{hyd}}(P_{\text{fluid}}, T) \leq \mu_{\text{fluid}}(P_{\text{fluid}}, T) \]  

This is the fundamental conclusion of Gibbs (1878): “fluids in equilibrium with the 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.”. A corollary of this is that non-hydrostatically stressed solids are less stable than their hydrostatically stressed counterparts (Sekerka & Cahn, 2004).

4.2 Comparison with previous studies and a resolution of controversies

In this work, I have shown that there is a scalar chemical potential, \( \mu_{M_i} \), that represents the energy required to add component \( i \) to a volume by isotropically compressing preexisting material. This chemical potential should be used in the total derivative of the Helmholtz energy (Section 2.1, Equation 5), and is therefore suited to modelling thermodynamic disequilibrium. However, it is not the only possible chemical potential, and there is an entire class of different chemical potentials that correspond to different ways of squeezing the material inside a volume \( \mu_{\hat{e}_i} \) (Section 2.3). The entire class of chemical potentials can be described by a third order “chemical strain energy” tensor \( \Xi \). Pre- and post-multiplying this tensor with the unit normal to an interface \( \hat{n} \), and multiplying with the molar volume of the phase produces an “interfacial” chemical potential \( \mu_{\hat{n}_i} \) that can be used to determine equilibrium at interfaces (Section 3.6).

These different chemical potentials and the related tensor \( \Xi \) resolve a number of controversies surrounding non-hydrostatic chemical equilibrium. The “interfacial” chemical potentials satisfy the observed importance of the normal stress on chemical reactions (Wheeler, 2014, 2020), while the “isotropic compressibility” chemical potential \( \mu_{M_i} \) is a state property of the system, satisfying the requirement of Hobbs & Ord (2015). The chemical strain energy tensor \( \Xi \) encapsulates the fundamental symmetries of the class of chemical potentials, and acknowledges the variety of ways in which preexisting material can be compressed to accommodate new material Rusanov (2005). The tensor \( V_{\text{mol}}\Xi \) provides a convenient chemical property that is locally continuous in nonhydrostatically stressed systems (Equation 60).
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). Those studies, however, only defined relative chemical potentials, as a result of requiring a fixed lattice - in other words, inside a preexisting crystal, the Larché models only allow substitution, and preclude the creation of defects and formation of subgrain boundaries. The theory is therefore powerful but not trivially extended to general numerical models of grain scale behaviour (e.g. Mianroodi et al., 2022).

Another derivation of non-hydrostatic chemical phenomena more similar to that in this paper was provided by Mullins & Sekerka (1985). However, they used the unit cell tensor $q$ as an independent variable (their Equation 6), rather than the extensive cell tensor $M = n^{\frac{1}{3}}q$. Their chemical potentials are therefore defined for a fixed lattice, which differs from the usual definition given for hydrostatic equations of state. By explicitly referencing a specific equation of state in this paper (Section 3.2), I hope to have made the connections to usual hydrostatic descriptions clear.

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

Most papers on non-hydrostatic chemical equilibria have made a special distinction between (inviscid) fluids and solids which are able to support significant deviatoric stresses. These include, for example, Gibbs (1878), McLellan (1980) (their equation 21.2.17), Larché & Cahn (1985) and Mullins & Sekerka (1985). These distinctions are based on time-dependent phenomena, which are not considered in classical thermodynamics. In this paper, no distinction is made between fluids and solids; chemical potentials are definable throughout any material under any state of stress. 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).

Another related difference between this paper and most previous works is that the current paper does not require a fixed crystalline lattice (Larché & Cahn, 1973, 1978a,b, 1985; Mullins & Sekerka, 1985). The only thing that is required is a way to define the extensive cell tensor $M$, which describes the strain experienced by an elastic object. The definition of this elastic strain does not require the presence of a lattice. In amorphous materials, the tensor $M$ under hydrostatic conditions is isotropic, i.e., $M_{\text{hyd}} = V_{\text{hyd}}^{\frac{1}{3}}I$. This enables the application of the theory 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 to see a formulation for non-hydrostatic thermodynamics that was a straightforward generalisation of the hydrostatic thermodynamics. Reading through the existing literature cited in this paper, I found it quite 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 some mentions of commonalities with other papers.

One of the things which I think is new here is the use of the extensive cell tensor $M$ 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 perfectly compatible with hydrostatic thermodynamics. McLellan (1980) (his Equation 20.1.14) took an alternative view, and simply multiplied the 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 more familiar expressions restricted to hydrostatic states.

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 should avoid the need to explicitly define grain boundaries and their orientations, enabling continuum modelling of defect concentrations and subgrain generation. Particularly useful are the definitions for $\sigma$ (Equation 36), $\mu_M$ (Equation 48) and $\Xi$ (Equation 55), and the continuity condition (Equation 60).

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References


Gibbs, J. W., 1878. On the equilibrium of heterogeneous substances, American Journal of Science and Arts, 16(96), 441.


Rusanov, A. I., 2005. Surface thermodynamics revisited, Surface Science Reports, 58(5-8), 111–239.


Wheeler, J., 2020. A unifying basis for the interplay of stress and chemical processes in the earth: support from diverse experiments, Contributions to Mineralogy and Petrology, 175(12).

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