Macroscopic Flow Potentials in Swelling Porous Media

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ABSTRACT

In swelling porous media, the potential for flow is much more than pressure, and derivations for flow equations have yielded a variety of equations. In this paper we show that the macroscopic flow potentials are the electro-chemical potentials of the components of the fluid and that other forms of flow equations, such as those derived through mixture theory or homogenization, are a result of particular forms of the chemical potentials of the species. It is also shown that depending upon whether one is considering the pressure of a liquid in a reservoir in electro-chemical equilibrium with the swelling porous media, or the pressure of the vicinal liquid within the swelling porous media, a critical pressure gradient threshold exists or does not.

Key Words porous media, swelling porous media, threshold pressure gradient, flow, thermodynamics

1 Introduction

Swelling porous materials are ubiquitous - they occur in soils such as swelling clays (montmorillonite), biotissues (cartilage), and in drug delivery systems such as Aleve (swelling polymers). Experiments are performed at the microscale (scale at which the solid and liquid or adsorbed liquid can be distinguished) and at the macroscale (scale at which the swelling porous media appears to be homogeneous, i.e. one cannot distinguish between the phases). The concept of pressure at each of these scales are often confused and interchanged. Example of terms used include 'disjoining pressure', 'osmotic pressure', and 'swelling pressure' and are attributed to the double-layer forces, van der Waals dispersion forces, osmotic forces, and surface hydration forces.

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In addition, it is unclear which microscopic forces are dominant to macroscopic behavior. For example, although direct measurements indicate surface hydration is considered to have short-range effects (up to 4 monolayers of water entering between layers of montmorillonite clay) [34, 12], experiments by Low [28, 27] indicate that the macroscopic affects of these interactions can explain the osmotic swelling of montmorillonite soils in which the swelling is due to 100’s of layers of water.

Several upscaling approaches have been used to arrive at a macroscopic model for flow through a swelling porous media, and with these approaches a variety of definitions of macroscopic flow potentials. It is the purpose of this paper to propose a macroscopic form for flow, derived from a hybrid mixture theory formulation [8, 9], and demonstrate how the form involving electrochemical potentials is a generalization of equations derived using homogenization [30], and is consistent with a Lagrangian mixture theoretic approach [23, 20]. In the process we illustrate that a pressure gradient threshold may exist, depending upon how the pressure is measured.

For simplicity we assume that the swelling porous medium is composed of a solid and liquid phase (i.e. no gaseous phase). The solid phase (polymer, montmorillonite) is assumed to be negatively charged and the fluid contains cations, ions, and a neutral liquid. We will refer to the liquid phase as vicinal fluid to distinguish it from the bulk phase (liquid unaffected by its vicinity to the solid phase, or reservoir fluid).

In the first section we review the microscale forces. We next review macroscopic quantities: osmotic repulsion, surface hydration, and disjoining pressure. We derive the flow equation in terms of chemical potentials from hybrid mixture theory results and discuss pressure gradient thresholds. Then we illustrate how the potential form of the flow equation can be used to derive forms derived via homogenization (Moyne and Murad [30]) used to model swelling montmorillonite, and is consistent with the mixture theory approach of Huyghe and Janssen [23] used to model swelling biotissues [20]. Although the models appear quite different, we show they can be derived from the potential form under particular assumptions on the chemical potentials of the species.

2 Microscale Forces

At the microscale there are various forces, some attractive and some repulsive, that cause a swelling porous medium to swell (repulsive forces dominate) or shrink (attractive forces dominate). In this section we summarize some of the forces considered to be dominant for determining the behavior at the macroscale. We note that these different categories of forces are ambiguous and not disjoint.

**Electrostatic repulsion:** Due to the solid phase being e.g. negatively charged, the cation and anion fields at the microscopic scale in the vicinal fluid are neither equal nor uniform, and as a result, there is a microscopically varying electric field. One could solve for the electrostatic condition coupled with diffusion of ions (Poisson-Boltzmann equation [31, 34]), but for practical
situations, the complexity of the microstructure makes this a difficult task. The repulsion forces become significant when the increased cation/anion concentrations near each surface (the double layer consisting of first the cation dominant layer and then the anion dominant layer) begin to interact (double-layer overlap) due to the proximity of the two surfaces. These are considered to dominate at long-range scales.

**Van der Waals attraction:** This is an attractive force acting between all atoms and molecules, regardless of whether they are charged or uncharged [25]. The current trend is to label any additional non-pressure forces not attributed to electrostatic forces as Van der Waals: London forces, dispersion forces, charge-fluctuation forces, and induced-dipole induced-dipole forces [25]. Although some of these listed forces may be repulsive forces, the net Van der Waals forces are considered to be attractive and act on a shorter spatial scale than electrostatic but not as short as surface hydration forces [34].

DLVO theory, named after its founders, Derjaguin, Landau, Verwey, and Overbeek [18, 35] incorporates electrostatic double-layer forces and van der Waals dispersion and was developed to describe particle interactions [12]. This model has been criticized [29]. Although both forces contributing to DLVO (electrostatic and van der Waals) are static in nature, these two forces often equilibrate rapidly relative to other forces and so this assumption is appropriate for many systems [25].

### 3 Macroscale Forces

Many experiments are performed at the macroscale, i.e. scale at which one cannot distinguish between the liquid and solid phases. Terms used at this scale include osmotic repulsion, surface hydration, and disjoining pressure.

**Osmotic Repulsion:** Osmotic repulsion is the force that measures how different species interact, and is usually measured through the osmotic pressure experiment. For example, consider a solution (e.g. water and sugar) separated by a semipermeable membrane that allows water but not sugar to pass through. There is a difference in height and this is related to the osmotic pressure (technically one has to take into account the effect of the membrane but for the purposes of this paper we will consider it to be the difference in height). The osmotic pressure, \( \pi \), is the pressure that must be applied to the mixture to stop the influx of solvent [2, 14]. This definition holds whether one species is charged or not.

We can derive an expression for the osmotic pressure. In an osmotic pressure experiment, the chemical potential on either side of the membrane is equal at equilibrium. For a component of a liquid solution which behaves as an ideal gas in the gaseous phase, the chemical potential is given by [2] (see also Appendix B):

\[
\mu_j^{(l)}(T, p, C_j^{(l)}) = \mu_j^{(g)}(T, p) + \frac{RT}{m_j} \ln \left( \frac{p_j^{(g)}}{p_{j,m}^{(g)}} \right),
\]  

(1)
where \( \mu_{lj} \) is the mass chemical potential (energy per mass) of species \( j \) in the liquid phase, \( C_{lj} \) is the mass concentration of species \( j \) in the mixture, \( \mu_{lj}^{jp} \) is the mass chemical potential of pure species \( j \) at the same temperature and pressure in the liquid phase, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( m^j \) is the molar mass (mass of one mole of \( j \)), \( p^g_j \) is the partial pressure of species \( j \) in the gaseous phase in equilibrium with the mixture, and \( p^g_{jm} \) is the maximum partial pressure of species \( j \) in the gaseous phase obtained when in equilibrium with pure species \( j \) in the liquid phase. The activity, \( a_{lj} \) is defined as the ratio of these two partial pressures, \( a_{lj} = \frac{p^g_j}{p^g_{jm}} \).

Let’s assume that on one side of the membrane the mixture is pure solvent (e.g. water), which we label the \( N \)th component, and does not contain species \( j \) and on the other side the mixture contains species \( j \) and solvent. On the side of the mixture the pressure will be higher, by an amount proportional to the osmotic pressure, \( \pi_{lj} \). The chemical potential of the solvent must be equal on both sides and we have

\[
\mu_{lp}^{IN}(T, p + \pi_{lj}) - \mu_{lp}^{IN}(T, p) = RT \rho_{lN} \ln(a_{lj}).
\]

(2)

To evaluate \( \mu_{lp}^{IN}(T, p + \pi) \), we begin with the total differential

\[
d\mu_{lp}^{IN} = \frac{\partial \mu_{lp}^{IN}}{\partial T} dT + \frac{\partial \mu_{lp}^{IN}}{\partial p} dp.
\]

(3)

For a pure substance, \( \frac{\partial \mu_{lj}^{jp}}{\partial p} = 1/\rho_{lj} \) where \( \rho_{lj} \) is the specific density of species \( j \) in the liquid phase with units of mass of \( j \) per volume of \( j \) (see Appendix A, or \([2, 14]\)). Integrating at constant temperature from the state at pressure \( p \) to the state where pressure is \( p + \pi \) we get

\[
\mu_{lp}^{IN}(T, p + \pi_{lj}) - \mu_{lp}^{IN}(T, p) = \int_p^{p + \pi_{lj}} \frac{1}{\rho_{lN}} dP.
\]

(4)

Using this expression in (2b) to eliminate \( \mu_{lp}^{IN}(T, p + \pi_{lj}) \) and then subtracting \( \mu_{lp}^{IN}(T, p) \) from both sides gives:

\[
\int_p^{p + \pi_{lj}} \frac{1}{\rho_{lN}} dP = -\frac{RT}{m^N} \ln(a_{lj}).
\]

(5)

If the density of the solvent, \( \rho_{lN} \), is constant, then we have

\[
\frac{1}{\rho_{lN}} \pi_{lj} = -\frac{RT}{m^N} \ln(a_{lj}),
\]

(6)

and further if we have an ideal solution \([2, 14]\), then

\[
\pi_{lj} = -\frac{RT\rho_{lN}^N}{m^N} \ln(x_{lj}^N),
\]

(7)
where $x^{lN}$ is the molar fraction of solvent, given by moles of solvent per moles of mixture. If the solution is dilute, so that $x^{lN} = 1 - x^l$ where $x^l$ is small, then $\ln(x^{lN}) \approx -x^l$ and approximating the number of moles of $N$ as being equal to the moles in the solution, we get

$$\pi^l \approx RT C_m^l$$  \hspace{1cm} (8)

where $C_m^l$ is the molar concentration of $j$ (moles of $j$ per moles of solution), which is known as the van’t Hoff equation.

**Surface Hydration:** These are short-range bonding forces between the solid surface and the water that causes one to ten layers of water to be held tightly [25, 34]. These forces perturb the vicinal liquid, so that it behaves differently from its bulk-phase counterpart (water free of adsorptive forces) [28, 21]. Experiments by Low [28] indicate that the macroscopic effects of these interactions can qualitatively completely account for many macroscopic experimental results.

If one considers the solid-liquid mixture as a mixture itself, then the hydration forces can be thought of as the osmotic force of the solid particles. In fact the reverse osmotic swelling pressure experiment is precisely what was done by Low [28] for montmorillonite soils. In this experiment (see Figure 1), the liquid mixture and liquid mixture with well-layered clay minerals were separated by a semipermeable membrane which did not allow the clay minerals to penetrate, and the pressure required to keep the clay mixture from swelling was measured. In this case, the quantity of clay mineral was measured in terms of the distance separating the clay platelets ($\lambda$) which represents the concentration of the clay mineral. In this case, the hydration pressure was determined experimentally to be exponentially related to the clay mineral concentration. If $\lambda_s$ is the thickness of the clay plates then [28]

$$\pi = p_0 e^{\lambda_s} - p_0,$$  \hspace{1cm} (9)

where $p_0$ is the reference (atmospheric) pressure. Equation (9) was also obtained via hybrid mixture theory, [1]. Note that this result is quite different from a pure liquid mixture in which the osmotic pressure is proportional to the log of the concentration, (7), but they have the same general shape - as the moisture goes to zero, the swelling pressure goes to infinity, and as the moisture content goes to 1 ($\lambda_s = 0$), the swelling pressure goes to zero.

**Disjoining pressure:** is a concept traditionally used in the field of foams (gas-liquid dispersions) and emulsions (liquid-liquid dispersions), where the stability of the system relies on the stability of the thin liquid films [12]. If two interfaces (in the case of foams, air-liquid and liquid-air) are separated by a distance $h$, then if $h$ is small enough there is no portion of the interlayer (i.e. liquid film) which possesses the properties of the bulk fluid (see Figure 2). In such a case, Derjaguin and Churaev [17] state

in mechanical equilibrium the disjoining pressure, $\pi(h)$, is equal to the difference existing between the component, $P_{zz}$ of the pressure
tensor in the interlayer and pressure, $P_B$, set up in the bulk of the phase from which it has been formed by thinning out:

$$\pi(h) = P_{zz} - P_B = P_N - P_B.$$  \hspace{1cm} (10)

In the simplest case of a one-component liquid phase, mechanical equilibrium under isothermic conditions implies thermodynamic equilibrium. In that case the disjoining pressure is a single-valued function of the interlayer thickness, $h$...

This definition has been extended so that it applies to curved surfaces by Kralchevsky and Ivanov [26]. This mechanical definition is thought to be equivalent to the thermodynamic definition in terms of the Gibbs free energy, $G$, as [12, 19]

$$\pi(h) = - \frac{\partial G}{\partial h} \bigg|_{T,P,A,N_i}.$$  \hspace{1cm} (11)

where the variables held fixed while taking the partial derivative include temperature, $T$, pressure, $P$, the area of the interface, $A$, and the number of moles of each constituent making up the thin film, $N_i$.

According to Bereron [12], the disjoining pressure is thought to be due to many forces: electrostatic double-layer, van der Waals dispersion forces, short-range structural forces such as hydration, and other forces. In the field of thin liquid soaps, most treat these forces as being additive, although it is not clear that this is a valid assumption [3, 4]. More than one author has come to the conclusion that the swelling pressure and average disjoining pressure are the same, e.g. [18] (p. 282).
We begin with a formulation developed using hybrid mixture theory (HMT) [5, 6]. In this approach, the microscale field equations (conservation of mass, linear and angular momenta, energy, and electroquasistatic form of Maxwell’s equations) are volume averaged to produce macroscopic quantities and equations, and then macroscopic constitutive equations are obtained by assuming a set of constitutive variables are a function of the same set of (macroscopic) independent variables and then exploiting the entropy inequality in the spirit of Coleman and Noll [15]. This approach has the advantage of developing constitutive equations directly at the macroscale, however coefficients in the macroscopic constitutive equations are not directly linked to microscopic quantities. In what is presented here, the only geometric information retained at the macroscale is the volume fraction, although this approach can be expanded to incorporate e.g. interfacial surface density [7, 22]. In [9] the independent variables included

\[ \varepsilon^l, T, \rho^{\alpha j}, \mathbf{v}^{l,s}, \mathbf{E}^s, E, z^{\alpha j}, \nabla \varepsilon^l, \nabla T, \nabla \rho^{\alpha j}, \ldots \] (12)

where \( \varepsilon^l \) is the volume fraction of the liquid phase, \( T \) is temperature, \( \alpha \) represents the phase (\( \alpha = l \) for liquid and \( \alpha = s \) for solid), \( \rho^{\alpha j} \) is the density of the \( \alpha \)-phase (mass of species \( j \) in the \( \alpha \) phase per unit volume of the \( \alpha \) phase), \( \mathbf{v}^{l,s} \) is the velocity of the liquid relative to the solid phase, \( \mathbf{E}^s \) is the strain of the macroscopic (smeared out) solid phase, \( E \) is the electric field, and \( z^{\alpha j} \) is the fixed charge density associated with species \( j \) of phase \( \alpha \).

The thermodynamic definition of liquid pressure is given by

\[ p^l = \sum_j \rho^l \rho^l_j \left. \frac{\partial \psi^l}{\partial \rho^l_j} \right|_{\varepsilon^l, \ldots} \] (13)

where \( \psi^l \) is the intensive (per unit mass) Helmholtz potential. One can either enforce electroneutrality with a Lagrange multiplier, \( \Lambda \), or include an electric field. In the former approach, \( \Lambda \) is the streaming potential. In [6] it is shown that \( p^l + q^l_e \Lambda \) where \( q^l_e \) is the charge density and \( \Lambda \) is a streaming potential, is related to one third the trace of the macroscopic liquid cauchy stress tensor - thus the thermodynamic definition is related to what is physically measured [11].

Another pressure, the “swelling pressure”, is thermodynamically defined as:

\[ \pi^l = \varepsilon^l \rho^l \left. \frac{\partial \psi^l}{\partial \varepsilon^l} \right|_{\rho^l, \ldots} \] (14)

where \( \varepsilon^l \) is the liquid volume fraction and where the partial derivative is evaluated keeping the other independent variables (density, concentrations, temperature) fixed. It is defined so that it is a positive quantity for a swelling mixture. Clearly this is a macroscopic form of the thermodynamic definition of the disjoining pressure, and in fact, if the solid phase is structured so that it

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does not support stress (e.g. parallel platelets), it can be shown [11] that for a single component liquid,

\[ \pi^l = -\varepsilon^l \frac{\partial p^l}{\partial \varepsilon^l} \bigg|_{\varepsilon^l = \varepsilon^l} \]  

where the partial derivative is evaluated keeping the Gibbs potential (chemical potential) fixed, which is exactly the reverse-osmotic swelling potential experiment used to measure the osmotic force. Note that if the material is not swelling, then the energy of the liquid phase would not change with liquid content and the swelling pressure is zero.

It can be shown that \( p^l \) and \( \pi^l \) are related via a third thermodynamic property which is related to the change in Helmholtz potential with respect to volume keeping the mass fixed [11]:

\[ p^l = -\varepsilon^l \rho^l \frac{\partial \psi^l}{\partial \varepsilon^l} + \pi^l \]  

Equation (16) is mathematically exact (no assumptions), and if one converts to extensive variables one can show that this new quantity is the traditional thermodynamic definition of pressure: change in energy with respect to volume keeping the mass fixed. Thus the pressure in the liquid phase has two components: one which is the ‘classical’ pressure for a bulk fluid, and the other the swelling pressure [11]. If the swelling pressure is zero, then the traditional thermodynamic pressure is the same as one third the trace of the Cauchy stress tensor of a liquid.

Assuming: (i) terms involving the polarization vector field are negligible, (ii) the gravitational term is negligible, (iii) isothermal conditions, (iv) sufficient moisture so that the liquid phase does not support shearing forces, (v) the charge associated with each species, \( z^j \), is fixed, and (v) not assuming charge neutrality, the resulting Darcy’s law using Hybrid Mixture Theory is given by [9]

\[ \mathbf{R} \cdot \mathbf{v}^{l,s} = -\varepsilon^l \nabla p^l - \pi^l \nabla \varepsilon^l + \varepsilon^l q^l e - \sum_{j=1}^{N} r^{lj} v^{lj,l} \]  

\[ = -\varepsilon^l \rho^l \nabla \psi^l + \sum_{j=1}^{N} \varepsilon^l (\rho^l)^2 \frac{\partial \psi^l}{\partial \rho^l} \nabla C^{lj} + \varepsilon^l q^l e - \sum_{j=1}^{N} r^{lj} v^{lj,l} \]  

where \( q^l e \) is the charge density of the liquid phase, \( \psi^l = \psi^l - p^l / \rho^l \) is the Gibbs potential for the liquid phase, \( C^{lj} \) is the mass concentration (mass of species \( j \) in the liquid phase per mass of liquid phase), and \( v^{lj,l} = v^{lj} - v^l \) is the diffusive velocity. The last term involving the diffusive velocities captures the effects of ion hydration and relative friction between the mass-averaged velocity and species velocity. If the diffusive velocities \( (v^{lj,l}) \) are small then this term may be neglected. Note that in (17) there are no terms directly involving chemical potential or concentrations of species that contribute to flow.
Changing the concentrations of the species making up the liquid phase changes the pressure through (13) and through relative velocities. The generalized version of Fick’s law for diffusion is given by

\[ \mathbf{v}^{l,j} = \mathbf{Q}^{l,j} \cdot \nabla \mu^{\alpha_j} \] (19)

where \( \mathbf{Q}^{l} \) is a diffusion coefficient tensor which may be a function of volume fraction, temperature, and densities so that

\[ R \cdot \mathbf{v}^{l,s} = -\varepsilon^l \nabla p^l - \pi^l \nabla \varepsilon^l + \varepsilon^l q^l_e E - \sum_{j=1}^{N} r^{l,j} \mathbf{Q}^{l,j} \cdot \nabla \mu^{l,j} \] (20)

\[ = -\varepsilon^l \rho^l \nabla G^l + \sum_{j=1}^{N} \varepsilon^l (\rho^l)^2 \frac{\partial \psi_j^l}{\partial \rho_j^l} \nabla C_j^l + \varepsilon^l q^l_e E \]

\[ - \sum_{j=1}^{N} r^{l,j} \mathbf{Q}^{l,j} \cdot \nabla \mu^{l,j,l} \] (21)

From equation (20) we see that if \( \pi^l \) is not zero we have a pressure gradient threshold - i.e. gradient in the volume fraction can offset the pressure in the liquid pressure until \( \pi^l \nabla \varepsilon^l \) is maximum, and then further increasing the pressure gradient will induce flow \[32, 36, 33\]. An analogy between this and concentration gradients can be made - flow is induced by a “concentration” gradient of the solid phase.

Next we express the flow equation in terms of liquid chemical potentials because the electro-chemical potentials are continuous between vicinal and bulk fluids and because it may be more useful for numerical solutions \[30, 24, 23\]. Within HMT, the chemical potential is given by \[13, 10\]:

\[ \mu^{\alpha_j} = \frac{\partial (\rho^\alpha \psi^\alpha)}{\partial \rho^{\alpha_j}} \] (22)

whereas the electrochemical potential \[31\] is given by

\[ \widetilde{\mu}^{\alpha_j} = \mu^{\alpha_j} + z^{\alpha_j} \phi \] (23)

where \( \phi \) is the electric field potential and \( z^{\alpha_j} \) is the charge density (per unit mass) for species \( j \) in phase \( \alpha \).

We consider two cases: one in which the liquid (and bulk) phase is composed of only one constituent, and then a multi-constituent liquid phase.

First consider a liquid phase which is composed of only one constituent. The relationship between the Gibbs potential and chemical potentials is given by \[13\]:

\[ G^\alpha = \sum_{j=1}^{N} C^{\alpha_j} \mu^{\alpha_j} \quad \alpha = l, B. \] (24)
So for a single component phase, the concentration is 1 and $\nabla C^l_j = 0$. Thus all diffusion velocities are zero, and the Gibbs potentials for the vicinal and bulk phases are equal up to the Lorentz term: $G^l + q^l_e \phi = G^B$ where we assume the bulk phase fluid is charge neutral ($\nabla \phi^B = 0$). Using the relationship between the Gibbs potential and the Helmholtz potential, $G^l + q^l e \phi = G^B$, we get that the right-hand side of Darcy’s equation (21), not including the hydration terms, is given by:

$$-\varepsilon^l \rho^l \nabla G^B + \varepsilon^l q^l_e E$$

(25)

$$= -\varepsilon^l \rho^l \nabla \psi^B + \varepsilon^l \rho^l \frac{p^B}{(\rho^B)^2} \nabla \rho^B - \varepsilon^l \rho^l \frac{1}{\rho^B} \nabla p^B + \varepsilon^l q^l_e E.$$  (26)

Now assume the bulk phase Helmholtz potential is only a function of density. Then using the thermodynamic definition of pressure, (13), the flow equation can be written as

$$\mathbf{R} \cdot \mathbf{v}^l,^s = -\varepsilon^l \rho^l \frac{\partial \psi^B}{\partial \rho^B} \nabla \rho^B + \varepsilon^l \rho^l \frac{p^B}{(\rho^B)^2} \nabla \rho^B - \varepsilon^l \rho^l \frac{1}{\rho^B} \nabla p^B + \varepsilon^l q^l_e E.$$  (27)

$$= -\frac{\varepsilon^l \rho^l}{\rho^B} \nabla p^B + \varepsilon^l q^l_e E.$$  (28)

and we see that if we write the flow equation in terms of potentials of the vicinal fluid as in equation (17), we have both a pressure and volume fraction potential, but if the flow equation is written as the bulk phase we have only a pressure potential. This implies that if one is measuring a vicinal pressure, there may be a pressure gradient threshold, but if one is measuring pressure of the bulk phase, there is no pressure gradient threshold.

Now consider a multi-component liquid phase. Beginning with the right-hand side of Darcy equation (21) and using (24) we have:

$$-\varepsilon^l \rho^l \sum_{j=1}^{N} \nabla (C^l_j \mu^l_j) + \sum_{j=1}^{N} \varepsilon^l (\rho^l)^2 \frac{\partial \psi^l_j}{\partial \rho^l_j} \nabla C^l_j + \varepsilon^l q^l_e E - \sum_{j=1}^{N} r^l_j Q^l_j \cdot \nabla \mu^l_j.$$  (29)

Using (22) for the thermodynamic definition of the chemical potential to eliminate $\frac{\partial \psi^l_j}{\partial \rho^l_j}$ we have (29) is equivalent to

$$-\varepsilon^l \rho^l \sum_{j=1}^{N} C^l_j \nabla \mu^l_j - \varepsilon^l \rho^l \sum_{j=1}^{N} \mu^l_j \nabla C^l_j + \sum_{j=1}^{N} \varepsilon^l \rho^l (\mu^l_j - \psi^l_j) \nabla C^l_j$$

$$+ \varepsilon^l q^l_e E - \sum_{j=1}^{N} r^l_j Q^l_j \cdot \nabla \mu^l_j.$$  (30)

Noting that $\sum_{j=1}^{N} C^l_j = 1$ so that the second part of the third term on the right side is zero and that the electrochemical potentials between the vicinal phase
and bulk phases are equal, we can rewrite the flow equation as:

\[ R \cdot v^{l,s} = -\varepsilon^l \rho \sum_{j=1}^{N} C^l_j \nabla \mu^l_j + \varepsilon^l q^l E - \sum_{j=1}^{N} r^l_j Q^l_j \cdot \nabla \mu^B_j \]

\[ = -\sum_{j=1}^{N} \varepsilon^l \rho^l_j \nabla \mu^B_j + q^l E - \sum_{j=1}^{N} r^l_j Q^l_j \cdot \nabla \mu^B_j. \quad (32) \]

So in a multi-component fluid, it is the electrochemical potentials of the liquid phase species, \( \tilde{\mu}^l_j = \mu^l_j + z^l_j \phi \), that are the primary potential for fluid flow.

To get one final form of this equation, consider the form of chemical potential for a liquid to be (see Appendix B):

\[ \mu^l_j = \mu^l_j(T, p_0) + \frac{1}{\rho^l_j} (p^l - p_0) + \frac{RT}{m^l_j} \ln a^j, \quad (33) \]

where \( \rho^l_j \) is the specific density of species \( j \) in the liquid phase (mass of \( l_j \) per volume of \( l_j \)) and it is assumed that each component of the liquid phase is incompressible. Then flow equation (32) in terms of bulk variables can be written as:

\[ R \cdot v^{l,s} = -\nabla p^B - \sum_{j=1}^{N} \varepsilon^l \rho^l_j \frac{RT}{m^l_j a^j} \nabla a^j + q^l E - \sum_{j=1}^{N} r^l_j Q^l_j \cdot \nabla \mu^B_j. \quad (34) \]

where we used the fact that \( \sum_{j=1}^{N} \frac{\varepsilon^l \rho^l_j}{\rho^l_0} = 1 \). So in the reservoir bulk fluid the primary driving forces are the activities (which are closely related to concentrations) and just as we had for a single-component fluid, the bulk phase pressure. Hydration of ions is an additional component whose magnitude for many problems has yet to be determined.

Next we illustrate the insight that can be obtained by writing the equations in terms of the chemical potential. Consider Figures 3, 4, and 5, where we have a reverse osmotic swelling potential experimental set up where the two bulk phases are separated from a swelling porous material such as montmorillonite clay mixture by a semipermeable membrane. Across the membrane the electrochemical potentials are continuous \([13, 31]\). Assume the chemical potential of the bulk phase is determined solely by the bulk phase pressure and the chemical potential of the liquid in the clay mixture is determined by the pressure and the liquid volume fraction (i.e. gradients in liquid concentrations and macroscale electric fields are negligible). In Figure 3 there is no gradient in the chemical potential of the liquid phase, so there is no flow. The swelling pressure, \( \pi \), is proportional to the difference in height of the mixture and the bulk fluid. In Figure 4 a pressure is applied to the clay mixture. If the clay mixture is well-layered then (up to the hydrostatic pressure) the applied pressure is equal to liquid pressure, \( p^l \). However in this case the gradient in the applied pressure is
offset by a gradient in volume fraction, and because the chemical potentials in the bulk phase (which is in chemical equilibrium with the vicinal phase) are the same, there is no net flow. In 5 a pressure is applied to the left side, changing its chemical potential. This applied pressure causes the clay to swell more on the left side and because there is an overall chemical potential gradient the liquid flow is induced. We could recreate these same pictures for a multi-component liquid by keeping the pressure fixed and changing the concentrations.

5 Comparison with Other Models

In this section, we show how the chemical potential formulation for flow is a generalization of several other models, including that derived using homogenization (Moyne and Murad [30]), and a mixture theoretic derivation of Huyghhe and Janssen [23].

5.1 Model of Moyne and Murad

In [30], Moyne and Murad use homogenization to upscale microscopic field (conservation laws and Maxwell equations) and constitutive equations to the macroscale. This approach provides first-order equations with precise expressions for coefficients in terms of solutions to the microscale equation on a periodic structure. The microscopic equations include: an incompressible liquid phase (composed of a liquid, a cation and anion) and a linear elastic solid phase; the conservation of momentum with the Lorentz term added ($q_c E$ where $q_c$ is the charge of the liquid (solvent) and $E$ is the electric field); Gauss’ law assuming polarization is negligible ($\bar{\varepsilon} \bar{\varepsilon}_0 \nabla \cdot E = q_c^l$, where $\bar{\varepsilon}$ is the relative dielectric constant of the solvent and $\bar{\varepsilon}_0$ is the vacuum permittivity); the conservation of mass for each ion, $j$, $\partial n^j / \partial t + \nabla \cdot j^j = 0$ with the ion flux given by $j^j = n^j v - D n^j / (kT) \nabla \mu^j$ where $\mu^j$ is the chemical potential of $j$ (per molecule $j$), $n^j$ is the volumetric concentration of ion $j$, $k$ is the Boltzmann’s constant, and $T$ is absolute temperature (assumed constant). In addition, electroneutrality is enforced.

The solid phase is assumed to be platelet shaped (as in, e.g. montmorillonite). Before upscaling, a change of variables is performed to replace variables which may change very rapidly between the platelets (vicinal fluid) to variables that

![Figure 3: equal chemical potentials](image)

![Figure 4: $p^j$ is a function of $x$](image)

![Figure 5: higher chemical potential on side 1](image)
are more smoothly varying. With this in mind, instead of using the chemical potentials of the ions in the vicinal liquid, the chemical potential of the ions in the bulk fluid in thermodynamic equilibrium, \( \mu_B^j \), is used. The apparent "bulk" phase fluid is a hypothetical fluid in electrochemical equilibrium with the vicinal fluid [16]. The relationship between \( \mu_B^j \) and \( \mu^j \) is obtained assuming the charged particles satisfy the Boltzmann distribution, which itself assumes a single flat double layer. Similarly, the liquid pressure is replaced by a form of the "disjoining pressure":

\[
\pi = P_b - p
\]

where \( p \) is the pressure of the vicinal fluid, and

\[
P_B = \rho \mu_w = p + \int_0^\phi q(\phi) \, d\phi
\]

is the "local apparent bulk phase pressure", and where \( \rho \) is the density of the liquid, \( \mu_w \) is the chemical potential of the water in the liquid phase (per unit mass), and \( \phi \) is the electric potential. Note that \( \nabla P_b = \nabla p - q_e E \) so that \( P_b \) incorporates the Lorentz term. Because the relationship between \( p \) and \( P_B \) are assumed, it is not clear at this point whether \( \pi \) is the same as the mechanical definition of the disjoining pressure as defined previously. After homogenizing, the resulting Darcy-type law is

\[
\nu_D^0 = -K \nabla_x p_b^0 - K_+ \nabla_x n_b^{0+} - K_- \nabla_x n_b^{-0}
\]

(37)

where \( K, K_-, K_+ \) are second-order tensors, \( \mu_w^0 \) is the chemical potential of the water in the liquid phase defined so that \( \rho \mu_w = p_b^0 \), and a superscript 0 denotes the first term in a series expansion of orders \( \varepsilon \). In this case \( p_b^0 \) incorporates the first-order approximation of the Lorentz term and the remaining terms come from second-order terms (fluctuations within the vicinal layer) and their relationship to the Boltzmann distribution.

We now show that these results are a special case of (32) Beginning with (1) and proceeding as we did to derive (4) we have

\[
\mu^{B_j}(T, p^B, C_{B_j}) = \mu_p^{B_j}(T, p) + \frac{RT}{m^j} \ln a^{B_j}
\]

\[
= \mu_p^{B_j}(T, p) + \frac{1}{p_0^{B_j}}(p^B - p_s) + \frac{RT}{m^j} \ln a^{B_j},
\]

(39)

where \( p_s \) is the standard reference pressure (1 bar) and where we assumed the specific densities, \( p_0^{B_j} \), are constant. At constant temperature we thus have

\[
\nabla \mu^{B_j} = \frac{1}{p_0^{B_j}} \nabla p^B + \frac{RT}{m^j a^{B_j}} \nabla a^{B_j}.
\]

(40)

Let us consider that we have three species: water, \( j = w \), cations, \( j = + \), and anions, \( j = - \). If the solution is dilute then it is reasonable that the solvent,
water, will follow Raoult’s law very well, so that \( a^w \approx x^B_w \approx 1 \), so that we have from (32)

\[
R \cdot v^{l,s} = - \sum_{j=1}^{N} \varepsilon^j l \rho^j \nabla \mu^{B_j} = - \sum_{j=1}^{N} \left[ \frac{\varepsilon^j l \rho^j}{\rho_0} \nabla p^B + \frac{\varepsilon^j l \rho^j RT}{m^j a^{B_j}} \nabla a^{B_j} \right]
\]

\[
= -\nabla p^B - \sum_{j=+,-} \frac{n^{B_j} RT}{a^{B_j} V} \nabla a^{B_j}, \tag{41}
\]

where \( V \) is the volume of the Representative Elementary volume and \( n^B_j \) is the number of moles of \( j \) in \( V \). If Raoult’s law applies \((a^B_j = x^B_j)\), then (41) has the same form as (37).

Comparing the two approaches through equations (38) and (32), we see the results are the same up to the definition of coefficients if we make the following observations/assumptions: (i) in (32) neglect the effects of hydration in the HMT approach, (ii) in (38) recall that the definition of \( P_b \) incorporates the Lorentz term (36), (iii) in equation (32) we can assume the bulk chemical potential is primarily a function of the concentrations so that \( \nabla \mu^{B_j} \approx \frac{\partial \mu^{B_j}}{\partial C^{B_j}} \nabla C^{B_j} \), and (iv) the coefficients \( K \) in (38) are a function of the microscopic geometry and so are a function of the volume fraction.

5.2 Model of Huyghe and Janssen

In [23], Huyghe and Janssen use a mixture theoretic approach in a Lagrangian framework to develop equations subsequently used in biological applications e.g. [20].

They label their model the Quadriphasic model because they treat the system as consisting of four phases: cations (+), anions (-), a charged solid (s), and a fluid (f). Each “phase” is considered incompressible, and that the volume fraction of the anions and cations are negligible relative to the volume fraction of the solid and fluid phases. Chemical interactions are neglected and electroneutrality is enforced. A work energy function is assumed with independent variables consisting of the Green strain, Lagrangian form of the volume fraction of the fluid and ions, and the Lagrangian form of the relative velocities. The generalized Darcy law derived by exploiting the entropy inequality, neglecting inertial and gravitational terms is (equation (6) from [20] or equations (52) and (53) from [23]):

\[
\varepsilon^l v^{l,s} = -F \cdot K \cdot F^T \cdot \left[ \nabla (p^I - \pi) + n^+ \nabla \tilde{\mu}^+ + n^- \nabla \tilde{\mu}^- \right] \tag{42}
\]

where \( F \) is the deformation tensor used to convert between eulerian and Lagrangian frameworks, \( p^I \) is the hydrodynamic pressure, \( \pi \) is the osmotic pressure of the ions, \( \tilde{\mu}^\alpha \) is the electrochemical potential incorporating the streaming potential, and \( n^\alpha \) is the volumetric concentration of phase \( \alpha \). Here the osmotic pressure, \( \pi \) is defined to be \( p^I - p^B \), is assumed to be due to concentrations of cations and anions and is assumed to have a modified form of
the van’t Hoff equation \( (8) \),
\[
P^l - p^B = RT\phi(c^+ + c^-) + \pi_0\]
where \( \phi = \frac{\partial(\ln a^w)}{\partial(\ln x^w)} \),
a^w is the activity of the water or solvent, \( x^w \) is the molar concentration of the water, and \( c^j \) are the moles of ions per volume of fluid in porous material.

Using \( \pi = P^l - p^B \) in equation \( (42) \) we see that \( P^l - \pi \) is the bulk phase pressure. This form of the equation can be derived from \( (32) \) if one uses \( (33) \) for the chemical potential of the liquid phase, assumes the density of water is one, and neglects the hydration of ions.

There is some question as to how well the “osmotic pressure”, \( P^l - p^B \), which is physically the swelling pressure, can be approximated by the van’t Hoff equation which is used for species (and not swelling) osmotic pressure.

### 6 Summary

In this paper we show that the most general way to write Darcy’s law for swelling soils is in terms of gradients of chemical potentials, see equation \( (32) \). In this way one can float between using variables such as pressure and moisture content and electro-chemical potentials of either the vicinal fluid or a bulk fluid in electro-chemical equilibrium. Using this formulation tells us more easily the assumptions used for other models, e.g. Moyne and Murad \[30\] and Huyghe and Janssen \[23\].

One clear consequence of this formulation is determining when a pressure threshold gradient may exist. This is the pressure gradient that must be exceeded before flow is observed. A pressure gradient has been shown to exist when whetting a previously dry sample, \[36, 33\], or for swelling soils such as clay \[32\]. In this paper, we demonstrated that concentration gradients are negligible, if the pressure is the pressure of a reservoir in electro-chemical equilibrium with the swelling porous media, \( P^B \), then there is no pressure threshold gradient. However if the pressure is of the vicinal liquid within the porous media, \( P^l \), then a threshold gradient may exist - depending upon whether the swelling potential, \( \pi \) is nonzero. See equations \( (20) \) and \( (28) \) and the discussion directly following them.

This has implications in measuring the pressure - if one measures the pressure within a swelling porous media with a device which takes in (any) amount of fluid, then the fluid which is no longer affected by the presence of the charged solid phase becomes a bulk-phase fluid and is no longer at the same pressure as the fluid within the swelling porous media. Using such a device will not indicate a critical pressure gradient. One way that one can obtain the pressure within a swelling porous material is by measuring the overburden pressure - if the solid phase supports no portion of the stress (i.e. it is at the same pressure as the fluid) then the overburden pressure is the pressure in the fluid and also in the solid - see for example, Figures 3, 4, and 5.
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Appendix A: The change in chemical potential with respect to pressure

In this appendix we go through the calculations to show that the partial derivative of the chemical potential with respect to pressure while holding concentrations and volume fraction fixed is constant if the specific densities of each component is fixed. We first show this is valid in terms of extensive variables and then verify the result with our definition of chemical potential in terms of intensive variables.

In this section we suppress the notation for phase, $\alpha$, as the definitions involved do not directly depend on which phase or the volume fraction of the phase. We assume there are $N$ constituents making up the phase, and we define $C^j$ to be the mass fraction of component $j$ with units (mass of $j$)(mass of phase).

Extensive Variables

Let $G$ be the extensive Gibbs potential, $G = G(T, p, M^j, X)$ where $p$ is pressure, $M^j$ is the mass of species $j$, and $X$ is any other variable upon which the Gibbs potential depends, such as the volume of the porous media. We note that normally we write $G$ as a function of the number of moles of species $j$, $N^j$,
but the ratio of $M^j$ and $N^j$ is the molecular weight of $j$ (with units of mass of $j$ per mole of $j$), and since the molecular weight is a constant this does not change the following results.

The thermodynamic definition of chemical potential in units of energy per unit mass is given by

$$\mu^j = \frac{\partial G}{\partial M^j} \Bigg|_{T,p,X} \quad (A.1)$$

Before deriving a Maxwell relation we use the total differential to determine $\frac{\partial G}{\partial p}$:

$$dG = d(U - TS + pV)
   = \left. dU - TdS - SdT + pdV + V dp \right|_{M^j}
   = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum_{j=1}^{N} \frac{\partial U}{\partial M^j} dM^j + \frac{\partial U}{\partial X} dX - TdS - SdT + pdV + V dp
   = \left. TdS - pdV + \sum_{j=1}^{N} \frac{\partial U}{\partial M^j} dM^j + \frac{\partial U}{\partial X} dX - TdS - SdT + pdV + V dp \right|_{M^j}
   = \sum_{j=1}^{N} \frac{\partial U}{\partial M^j} dM^j + \frac{\partial U}{\partial X} dX - SdT + V dp \quad (A.2)$$

where we used $T = \frac{\partial U}{\partial S}$, and $\frac{\partial U}{\partial V} = -p$ \[13\].

Now taking the partial of both sides with respect to $p$ keeping the appropriate variables fixed we have:

$$\frac{\partial G}{\partial p} \Bigg|_{T,M^j,X} = V. \quad (A.3)$$

Now let’s assume that the function $G$ is smooth enough so that mixed partials commute. Using (A.3) we have

$$\frac{\partial^2 G}{\partial p \partial M^j} = \frac{\partial^2 G}{\partial M^j \partial p}
   \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial M^j} \right) = \frac{\partial}{\partial M^j} \left( \frac{\partial G}{\partial p} \right)
   \frac{\partial \mu^j}{\partial p} \Bigg|_{T,M^k,X} = \frac{\partial V}{\partial M^j} \Bigg|_{T,p,M^k(k\neq j),X} \quad (A.4)$$

Equation (A.4) tells us that the partial of the chemical potential with respect to pressure is related to how the volume changes with the quantity of $j$.

Recall that our goal is to show that if the intensive densities of the species (so the mass of species $j$ per volume of species $j$) are constant then so is $\frac{\partial \mu^j}{\partial p}$. The units of $\rho^j$ are mass of $j$ per volume of mixture. So let’s define the intensive density to be $\rho^j_0$, which has units of mass of species $j$ per volume of species $j$. 

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We use a subscript 0 to emphasize the fact that it is not equal to \( \rho^j \) and that in what follows we consider \( \rho^j_0 \) to be a constant.

Let \( V = V^1 + V^2 + \cdots + V^N \) be the volume of the mixture, where \( V^j \) is the volume of species \( j \). Then we have \( M^j = \rho^j_0 V^j \). With this, (A.4) gives:

\[
\frac{\partial \mu^j}{\partial p} \bigg|_{T, M^k, X} = \frac{\partial V}{\partial M^j} \bigg|_{T, p, M^l \ (l \neq j), X} = \sum_{k=1}^{N} \frac{\partial V^k}{\partial M^j} \bigg|_{T, p, M^l \ (l \neq j), X} = \sum_{k=1}^{N} \frac{1}{\rho^j_0} \frac{\partial V^k}{\partial V^j} \bigg|_{T, p, V^l \ (l \neq j), X} = \frac{1}{\rho^j_0}.
\]

So if the specific densities for every component is fixed then the dependence of the chemical potential upon pressure is linear. Note that if only one species is incompressible, then we would need the additional assumption that the density of species \( j \) is independent of the quantity (volume) of all species (including \( j \)), in order for (A.5) to hold.

**Intensive Variables**

We now go through the same argument in terms of intensive variables. Since the definition of chemical potential is relatively new, [10], we go through the calculations in detail to verify the same result holds. The chemical potential as defined in this paper in terms of the Helmholtz potential, (22), is written with assumed independent variables, \( T, \rho^j, X \), where \( X \) could be any other variable. We would like to determine the definition of chemical potential in terms of the Gibbs potential, \( \tilde{\psi}(T, \rho, C^j) \). To do this we first look at the definition of chemical potential in terms of \( \psi = \tilde{\psi}(T, \rho, C^j, X) \).

Claim:

\[
p = \sum_{j=1}^{N} \rho \rho^j \frac{\partial \tilde{\psi}}{\partial \rho^j} \bigg|_{T, \rho^l \ (l \neq j), X} = \rho^2 \frac{\partial \tilde{\psi}}{\partial \rho} \bigg|_{T, C^l \ (l=1, \ldots, N-1), X}.
\]

To show this result we begin with the equivalencies of the total differential of the Helmholtz potentials:

\[
\tilde{\psi}(T, \rho, C^j, X) = \psi(T, \rho^k, X)
\]
\[
d\tilde{\psi}(T, \rho, C^j, X) = d\psi(T, \rho^k, X)
\]
\[
d\tilde{\psi}(T, \rho, C^j, X) = \frac{\partial \psi}{\partial T} dT + \sum_{k=1}^{N} \frac{\partial \psi}{\partial \rho^k} d\rho^k + \frac{\partial \psi}{\partial X} dX.
\]
Now taking the partial with respect to $\rho$ on both sides keeping the concentrations (and $T$ and $X$) fixed we have:

\[
\frac{\partial \tilde{\psi}}{\partial \rho} \bigg|_{T,C^j(j=1,\ldots,N-1),X} = \sum_{k=1}^{N} \frac{\partial \psi}{\partial \rho^k} \bigg|_{C_j} \cdot \frac{\partial \rho^k}{\partial \rho} \bigg|_{C_j}
\]

\[
= \sum_{k=1}^{N-1} \frac{\partial \psi}{\partial \rho^k} \frac{\partial (C^k \rho)}{\partial \rho} \bigg|_{C_j} \left[ \frac{\partial \tilde{\psi}}{\partial \rho^N} \right]^{C_j} - \frac{\partial \psi}{\partial \rho^N} \bigg|_{C_j} \left[ (1 - \sum_{l=1}^{N-1} C^l \rho) \right]^{C_j}
\]

\[
= \sum_{k=1}^{N-1} C^k \frac{\partial \psi}{\partial \rho^k} + C^N \frac{\partial \psi}{\partial \rho^N}
\]

\[
= \sum_{k=1}^{N} C^k \frac{\partial \psi}{\partial \rho^k}.
\]

Multiplying both sides by $\rho^2$ and using the fact that $C^k \rho = \rho^k$ we get (A.6).

**Claim:** The chemical potential in terms of the Helmholtz potential, is given by

\[
\mu^j = \frac{\partial (\rho \psi)}{\partial \rho^j} \bigg|_{\rho^k(k \neq j)} = \psi + \frac{p}{\rho} - \sum_{k=1}^{N-1} C^k \frac{\partial \tilde{\psi}}{\partial C^k} \bigg|_{T,\rho,C^i(l \neq k),X} + \frac{\partial \tilde{\psi}}{\partial X} (1 - \delta^jN),
\]

where $\delta^jN$ is one if $j = N$ and zero otherwise.

We begin as we did in the previous claim by equating the two functions of Helmholtz potential, $\psi = \tilde{\psi}$ and looking at the total differential. We will then use the thermodynamic definition of chemical potential given by (22),

\[
\mu^j = \frac{\partial (\rho \psi)}{\partial \rho^j} \bigg|_{\rho^k(k \neq j)}.
\]

\[
d\psi = d\tilde{\psi} = \frac{\partial \tilde{\psi}}{\partial T} dT + \frac{\partial \tilde{\psi}}{\partial \rho} d\rho + \sum_{k=1}^{N-1} \frac{\partial \tilde{\psi}}{\partial C^k} dC^k + \frac{\partial \tilde{\psi}}{\partial X} dX.
\]

Taking the partial derivative of both sides with respect to $\rho^j$ we have

\[
\frac{\partial \psi}{\partial \rho^j} \bigg|_{T,\rho^l(l \neq j),X} = \frac{\partial \tilde{\psi}}{\partial \rho^j} \bigg|_{\rho^k(\neq \rho^j)} + \sum_{k=1}^{N-1} \frac{\partial \tilde{\psi}}{\partial C^k} \frac{\partial C^k}{\partial \rho^j} \bigg|_{\rho^l(\neq \rho^j)}.
\]

We now need to evaluate the terms $\partial \psi/\partial \rho^j$ and $\partial C^k/\partial \rho^j$:

\[
\rho = \sum_{k=1}^{N} \rho^k \Rightarrow \frac{\partial \rho}{\partial \rho^j} \bigg|_{\rho^l(\neq \rho^j)} = 1.
\]
Also:

\[ j = k : \quad \frac{\partial C_j}{\partial \rho_j} = \frac{\partial}{\partial \rho_j} \left( \frac{\rho_j}{\rho} \right) = \frac{\rho_j - \rho_j^0}{\rho^2} = \frac{1}{\rho} - \frac{C_j}{\rho} \]

\[ j \neq k : \quad \frac{\partial C_k}{\partial \rho_j} = \frac{\partial}{\partial \rho_j} \left( \frac{\rho_k}{\rho} \right) = -\frac{\rho_k}{\rho^2} = -\frac{C_k}{\rho} \]

Substituting these results into (A.8) we get:

\[
\left. \frac{\partial \psi}{\partial \rho_j} \right|_{T,\rho^i(l \neq j),X} = \frac{\partial \tilde{\psi}}{\partial \rho_j} + \sum_{k=1}^{N-1} \frac{\partial \tilde{\psi}}{\partial C_k} \left( -\frac{C_k}{\rho} \right) + \frac{\partial \tilde{\psi}}{\partial C_j} \frac{1}{\rho} (1 - \delta_{jN})
\]

So

\[
\mu^j = \left. \frac{\partial (\rho \psi)}{\partial \rho^j} \right|_{\rho^k} = \psi + \rho \left. \frac{\partial \psi}{\partial \rho_j} \right|_{T,\rho^i(l \neq j),X} + \frac{\partial \tilde{\psi}}{\partial C_j} (1 - \delta_{jN})
\]

\[
= \psi + \rho \left. \frac{\partial \tilde{\psi}}{\partial \rho_j} \right|_{T,\rho^i(l \neq j),X} - \sum_{k=1}^{N-1} C_k \left. \frac{\partial \tilde{\psi}}{\partial C_k} \right|_{T,\rho^i(l \neq j),X} + \frac{\partial \tilde{\psi}}{\partial C_j} (1 - \delta_{jN}), \quad \text{(A.10)}
\]

where we used (A.6) and is the result of this claim. In the above we note that \( \psi = \tilde{\psi} \) as these represent the same quantities and we can choose the functional form of the Helmholtz potential.

Also note that we have

\[
\mu^j - \mu^N = \left. \frac{\partial \tilde{\psi}}{\partial C_j} \right|_{T,\rho^i(l \neq k),X} \quad \text{(A.11)}
\]

which is the relationship derived using an exploitation of the entropy inequality in [10].

Claim: The chemical potential in terms of the Gibbs potential is given by

\[
\mu^j = g - \sum_{k=1}^{N-1} C_k \left. \frac{\partial g}{\partial C_k} \right|_{T,\rho^i(l \neq k),X} + \frac{\partial g}{\partial C_j} (1 - \delta_{jN}), \quad j = 1, \ldots, N \quad \text{(A.12)}
\]

where \( \delta_{jN} \) is one if \( j = N \) and zero otherwise.

We first derive the intensive equivalent to (A.3) by beginning with the relationship between the Gibbs potential and the Helmholtz potential,

\[
g = \tilde{\psi} + \frac{p}{\rho}
\]
where \( g = g(T, p, C^k, X) \) for \( k = 1, \ldots, N - 1 \). Taking the total differential of both sides:

\[
dg = d\tilde{\psi} + \frac{1}{\rho} dp - \frac{p}{\rho^2} d\rho
\]

\[
= \frac{\partial \tilde{\psi}}{\partial T} dT + \frac{\partial \tilde{\psi}}{\partial p} dp + \sum_{k=1}^{N-1} \frac{\partial \tilde{\psi}}{\partial C^k} dC^k + \frac{\partial \tilde{\psi}}{\partial X} dX + \frac{1}{\rho} dp - \frac{p}{\rho^2} d\rho
\]

\[(A.13)\]

where we used (A.6) to cancel two terms in the last step.

To get the equivalent of (A.3) take the partial with respect to \( p \) on both sides and we have

\[
\frac{\partial g}{\partial p} \bigg|_{T,C^j(j=1,...,N-1),X} = \frac{1}{\rho}
\]

\[(A.14)\]

which is consistent with (A.3) in the sense that if we divide both sides of (A.3) by the total mass (and the total mass is fixed) we get (A.14). This remark just shows consistency.

To get the chemical potential in terms of the Gibbs potential begin with (A.13),

\[
\frac{\partial g}{\partial C^j} \bigg|_{T,p,C^k(k\neq j),X} = \frac{\partial \tilde{\psi}}{\partial C^j} \bigg|_{T,\rho,C^k(k\neq j),X},
\]

\[(A.15)\]

and use the result from the previous claim, (A.7), to get (A.12).

Two checks can be made on this result. If there is only one component \((N = 1)\) then the chemical potential of the phase should be the Gibbs potential, and the sum of the weighted chemical potentials should be the Gibbs potential:

\[
\sum_{j=1}^{N} C^j \mu^j = g.
\]

A few algebraic steps shows that both of these results hold.

Further, letting \( j = N \) in (A.12), we get

\[
\mu^N = g - \sum_{k=1}^{N-1} C^k \frac{\partial g}{\partial C^k} \bigg|_{T,\rho,C^l(l\neq k),X}.
\]

\[(A.16)\]

Claim: If each component of the phase is incompressible, then the partial derivative of the chemical potential with respect to pressure is constant.

We adapt the notation from the extensive results and let \( \rho^j_0 \) be the intrinsic density of component \( j \) (mass of \( j \) with respect to volume of \( j \)). For this claim we assume that \( \rho^j_0 \) is constant for \( j = 1, \ldots, N \).
We begin by showing a preliminary results using \( C_j = \rho_j v_j \) where \( v_j \) is the volume of \( j \) per unit mass of the phase material, and is not \( 1/\rho_j \) which has units of mass of \( j \) per unit volume of phase material. Let \( v = 1/\rho = \sum_{j=1}^{N} v_j \). Then

\[
\frac{\partial}{\partial C_k} \left( \frac{1}{\rho} \right) \bigg|_{C_l (l \neq k)} = \frac{\partial}{\partial C_k} (v)
\]

\[
= \frac{\partial}{\partial C_k} \left[ \sum_{j=1}^{N} v_j \right]
\]

\[
= \frac{\partial}{\partial C_k} \left[ \sum_{j=1}^{N} \frac{C_j}{\rho_0} \right]
\]

\[
= \frac{\partial}{\partial C_k} \left[ \sum_{j=1}^{N-1} \frac{C_j}{\rho_0} + \frac{(1 - \sum_{j=1}^{N-1} C_j)}{\rho_0} \right]
\]

\[
= \frac{1}{\rho_0} - \frac{1}{\rho_0^N} \quad (A.17)
\]

Now let’s determine the partial derivative with respect to \( \mu^N \) first. Beginning with (A.16) and using (A.14) we have

\[
\frac{\partial \mu^N}{\partial p} \bigg|_{T,C_k,X} = \frac{\partial g}{\partial p} \bigg|_{T,C_k,X} - \sum_{k=1}^{N-1} C_k \frac{\partial^2 g}{\partial p \partial C_k}
\]

\[
= \frac{1}{\rho} - \sum_{k=1}^{N-1} C_k \frac{\partial}{\partial C_k} \left( \frac{\partial g}{\partial p} \right)
\]

\[
= \frac{1}{\rho} - \sum_{k=1}^{N-1} C_k \frac{\partial}{\partial C_k} \left( \frac{1}{\rho} \right)
\]

\[
= \frac{1}{\rho} - \sum_{k=1}^{N-1} C_k \left[ \frac{1}{\rho_0} - \frac{1}{\rho_0^N} \right]
\]

\[
= \frac{1}{\rho} + \frac{1 - C^N}{\rho_0^N} - \sum_{k=1}^{N-1} \frac{C_k}{\rho_0}
\]

\[
= \frac{1}{\rho} + \frac{1}{\rho_0^N} - C^N - \sum_{k=1}^{N-1} \frac{v_k}{\rho_0}
\]

\[
= \frac{1}{\rho} + \frac{1}{\rho_0^N} - v^N - (v - v^N)
\]

\[
= \frac{1}{\rho_0^N}, \quad (A.18)
\]

where we used result (A.17).

Now the rest is easy if we begin with (A.11) and (A.15): \( \mu^j = \mu^N + \partial g/\partial C^j \)
for $j = 1, \ldots, N - 1$:

$$\frac{\partial \mu^j}{\partial p} \bigg|_{T,C^k,N} = \frac{\partial}{\partial p} \left( \mu^N + \frac{\partial g}{\partial C^j} \right)$$

$$= \frac{\partial \mu^N}{\partial p} + \frac{\partial}{\partial C^j} \frac{\partial g}{\partial p}$$

$$= \frac{1}{\rho_0^N} + \frac{\partial}{\partial C^j} \left( \frac{1}{\rho} \right)$$

$$= \frac{1}{\rho_0^N} + \frac{1}{\rho_0^k} - \frac{1}{\rho_0^N}$$

$$= \frac{1}{\rho_0^k}, \quad (A.19)$$

where we used (A.14) and (A.18) in going from line 2 to line 3, and (A.17) to go from line 3 to line 4.

And so we see that if the specific densities are constant (i.e. do not change too much with the temperature and concentration fluctuations of the particular problem being considered), then the chemical potential changes linearly with the total pressure. This result is generally used for liquids and not for gasses.

**Appendix B: Background Material on Chemical Potential**

This section contains material found in a standard textbook on physical chemistry [2, 14]. It is presented here for easy reference.

The chemical potential has three defining properties (1) it is a scalar quantity representing the energy change as the quantity of species is changed (partial derivative of a potential with respect to quantity), (2) is a quantity which is equal in two different phases at equilibrium, and (3) is the generalized driving force for diffusion.

For a pure substance in a single phase, the chemical potential is equal to the Gibbs potential (per unit mole), $\overline{G}$. We first determine the Gibbs potential for a single component, ideal gas that satisfies $pV = nRT$ where $V$ is the volume, $p$ is the pressure, $n$ is the number of moles, $R$ is the gas constant, and $T$ is the absolute temperature. In this case, the Gibbs potential is only a function of temperature and pressure: $G = G(T, p)$ and [13, 2]

$$d\overline{G} = \frac{\partial \overline{G}}{\partial T} dT + \frac{\partial \overline{G}}{\partial p} dp$$

$$= -SdT + VdP.$$

To determine how the Gibbs potential depends upon pressure, integrate the above relationship from a reference state $\overline{G}_0(T_0, p_0)$ (where $p_0$ is the standard pressure) to a second state at constant temperature and number of moles, $\overline{G}_0(T_0, p)$, and using the ideal gas relationship $p = RT/v_m$ (where $v_m$ is the
molar specific volume with units of volume per mole) we have

\[ G(T, p) = G_0(T, p_0) + \int_{p_0}^{p} v_m dP \]

\[ = G_0(T, p_0) + \int_{p_0}^{p} \frac{RT}{P} dP \]

\[ = G_0(T, p_0) + RT \ln \left( \frac{P}{P_0} \right). \]

If we do not have an ideal gas then we replace the pressure by an effective pressure, called the *fugacity*, \( f \), and we have

\[ G(T, p) = G_0(T, p_0) + \int_{p_0}^{p} v_m dP \]

\[ = G_0(T, p_0) + RT \ln \left( \frac{f}{P_0} \right), \]

and in fact, this is the definition of fugacity.

For a mixture of gases, define the partial pressure of species \( j \) to be \( p_{gj} = x_j p \) where \( x_j \) is the molar fraction of species \( j \) (moles of \( j \) per moles of mixture). For a mixture of perfect gases (each gas ideal and no interactions between species), the partial pressure of species \( j \) would actually be the pressure of species \( j \) if no other species were present (Dalton’s law). Using the definition of partial pressure we have, for a component of a perfect mixture of gases:

\[ \mu_{gj}(T, p, x_j) = \mu_{gj}^0(T, p_0) + RT \ln \left( \frac{p_{gj}}{p_0} \right), \tag{A.1} \]

where \( \mu_{gj} \) is the chemical potential of species \( j \) in units of energy per mole, and \( p_0 \) is the standard pressure (which is 1 if pressure is measured in bars). Using Dalton’s law, we have

\[ \mu_{gj}(T, p, x_j) = \mu_{gj}^0(T, p_0) + RT \ln \left( \frac{x_j p}{p_0} \right), \]

\[ = \mu_j^0(T, p_0) + RT \ln \left( \frac{p}{p_0} \right) + RT \ln x_j. \tag{A.2} \]

Since \( x_j \) is always between 0 and 1, we have that the last term is always negative and so the chemical potential of a component in a mixture is always less than the chemical potential of a pure substance. We should note that the above result is only true for a mixture of ideal gases. This model breaks down if for example, there are chemical reactions, the pressure is high, or there are strong intermolecular forces between (or among) the different species. Water vapor in the atmosphere is usually treated as an ideal gas, with error in e.g. density calculations of less than 0.2% (http://en.wikipedia.org/wiki/Density_of_air). At high pressures the perfect mixture assumption breaks down.
For a mixture of nonideal gases, the partial pressure must be replaced by the fugacity and we have

$$\bar{\mu}_g(j) = \mu_{g0}(T, p) + RT \ln \left( \frac{f_j}{p_0} \right).$$

For a liquid, the chemical potential is determined by using the fact that the chemical potentials of one species in two phases are equal at equilibrium. Thus the chemical potential of a pure liquid of an ideal component, $j$, (the component behaves as an ideal gas in the gaseous state) is:

$$\mu_l(j) = \mu_{g}(j) = \mu_{g0}(T, p_0) + RT \ln \left( \frac{p_g(j)}{p_0} \right),$$

where $\mu_{g}(j)$ is the chemical potential of species $j$ in the gaseous state in equilibrium with the liquid state, $\mu_{g0}(T, p_0)$ is the chemical potential of species $j$ in the gaseous state at the same temperature but at standard pressure (1 bar), $p_g(j)$ is the partial pressure of $j$ in equilibrium with pure $j$ in the liquid phase, and $p_0$ is the standard pressure. Now suppose we have a liquid mixture of ideal species. Let $p_{g0}$ be the partial pressure of species $j$ in the gas phase. Then the chemical potential is:

$$\mu_l(j) = \mu_{g0}(T, p_{g0}) + RT \ln \left( \frac{p_g(j)}{p_{g0}} \right),$$

where we eliminated $\mu_{g0}(T, p_{g0})$ using (A.3) and $a^j = p_g(j)/p_{g0}^j$ is the activity of component $j$. We note that for water, the activity is the relative humidity divided by 100 (i.e. relative humidity not in percent form). Since the partial pressure for a species in a mixture is usually less than the partial pressure in the pure state (i.e. in the case of water, the relative humidity is between 0 and 1), we see that the chemical potential for a species in a mixture is generally lower than the chemical potential of a pure species. The above equation holds whether the liquid solution is ideal or not.

Now if we have an ideal liquid solution, then Raoult’s law is satisfied (this is the definition of an ideal solution):

$$p_g(j) = x^j p_p^g,$$

where $p_g(j)$ is the partial pressure of species $j$ in the gas phase in equilibrium with the ideal solution, $x^j$ is the molar volume fraction in the liquid, and $p_p^g$ is the partial pressure of species $j$ in equilibrium with pure liquid $j$. Using this relationship we have

$$\mu_l(j) = \mu_{g0}(T, p_0) + RT \ln x^j,$$

where again, $x^j$ is the molar fraction of species $j$ in the ideal solution. An ideal solution is one in which the liquid molecules in the mixture interact with all other species the same, i.e. there is no difference between how species $i$ interacts
with \(i\) and how species \(i\) interacts with \(j\). This is a much stronger assumption than assuming that the species behaves as an ideal gas in the gaseous phase. Raoult’s law is known to hold for a solvent when it is nearly pure. For real solutions where species \(j\) is at low concentration, instead of \(p^j = x^j p^j_0\) we replace \(p^j_0\) with an empirical constant (measured) so that \(p^j = x^j K^j\) and this is referred to as Henry’s law.

Returning to (A.4) we want to use our knowledge from Appendix A to express the chemical potential of a liquid in terms of pressure. Using the total differential and that \(\mu^j_l = m^j \mu^j_l\) we have:

\[
d\mu^j_l(T, p) = \frac{\partial \mu^j_l}{\partial p} dp + \frac{\partial \mu^j_l}{\partial T} dT,
\]

where no assumptions have been made. Integrating both sides from standard pressure to pressure, \(p\), at a constant temperature we have

\[
\mu^j_l(T, p, x^j) = \mu^j_l(T, p_0) + \frac{m^j}{\rho^j_0}(p - p_0) + RT \ln(\alpha^j).
\] (A.5)

Let’s consider the case where \(j\) is water, the gas phase is atmospheric air, and water is the primary component of the liquid phase. In this case the ratio of pressures in the gas phase is close to 1 (atmospheric pressure is close to 1 bar) and so the pressure term drops. For the liquid phase in which water is the primary component, the activity is approximately the molar concentration which is 1, and the term involving the activity is negligible. Thus we have

\[
\mu^j_l(T, p^g, x^g) \approx \mu^j_l(T, p_0) + RT \ln \left(\frac{p^g}{p_0}\right) + RT \ln x^g.
\] (A.7)

\[
\mu^j_l(T, p^l, x^l) \approx \mu^j_l(T, p_0) + \frac{m^j}{\rho^j_0}(p^l - p_0) + RT \ln(\alpha^j).
\] (A.8)

Let’s consider the case where \(j\) is water, the gas phase is atmospheric air, and water is the primary component of the liquid phase. In this case the ratio of pressures in the gas phase is close to 1 (atmospheric pressure is close to 1 bar) and so the pressure term drops. For the liquid phase in which water is the primary component, the activity is approximately the molar concentration which is 1, and the term involving the activity is negligible. Thus we have

\[
\mu^j_l(T, p^g, x^g) \approx \mu^j_l(T, p_0) + RT \ln x^g.
\] (A.9)

\[
\mu^j_l(T, p^l, x^l) \approx \mu^j_l(T, p_0) + \frac{m^j}{\rho^j_0}(p^l - p_0)
\] (A.10)

that is, the chemical potential of water in the gas phase is primarily determined by the concentration, and the chemical potential of water in the liquid phase is primarily determined by pressure.
If however there is something other than water in the liquid phase, then the chemical potential of a component in the liquid phase is determined by the pressure and the relative humidity in equilibrium with the liquid phase.

Appendix C: Nomenclature

In general, a superscript Greek letter indicates a macroscale quantity from that phase. Superscript minuscules indicate the constituent, so that, e.g. \( \mathbf{v}_\alpha \) is the macroscopic velocity of constituent \( j \) in the \( \alpha \)-phase. Subscript \( b \) refers to the quantity in the bulk or reservoir phase in electrochemical equilibrium with the vicinal fluid.

\[
\begin{align*}
\alpha^j & \quad \text{activity of species } j \text{ defined to be the ratio of pressures } p^g_j / p^p_j, [-] \quad (2) \\
A & \quad \text{area } [\text{length}^2] \quad (11) \\
\rho^{\alpha_j} & \quad \text{mass concentration, } \rho^{\alpha_j} / \rho^\alpha, [-] \quad (1) \\
E & \quad \text{electric field } [\text{force/charge}] \quad (12) \\
\mathbf{E}^* & \quad \text{macroscale strain tensor of solid phase, } [-] \quad (12) \\
F & \quad \text{deformation tensor } [-] \quad (42) \\
G^\alpha & \quad \text{Gibbs free energy, } [\text{energy of } \alpha\text{-phase/mass } \alpha] \quad (11), (24) \\
\mathbf{j}^j & \quad \text{ion flux } [\text{length/time}] \quad \text{Section 5.1} \\
m^j & \quad \text{molar mass } [\text{mass / mole of } j] \quad (1) \\
r^j & \quad \text{volumetric ion concentration } [\text{volume ion } j/\text{volume of solvent}] \quad \text{Section 5.1} \\
N_i & \quad \text{number of moles of species } i \ [\text{moles}] \quad (11) \\
p & \quad \text{pressure } [\text{force/area}] \quad (1) \\
p^\alpha & \quad \text{classical pressure } (1/3 \text{ trace of cauchy stress tensor at rest}), [\text{force/length}^2] \quad (13) \\
p^{g_j} & \quad \text{partial pressure of species } j \text{ in the gas phase} \quad (1) \\
p^{g_j}_P & \quad \text{maximum partial pressure of species } j \text{ in the gas phase} \quad (1) \\
q^\alpha & \quad \text{charge density of phase } \alpha, \sum_{j=1}^N \rho^{\alpha_j} z^{\alpha_j} \ [\text{charge } \alpha/\text{volume } \alpha] \quad (17) \\
\mathbf{Q}^j & \quad \text{coefficient for generalized Fick’s law} \quad (19) \\
r^{l_j} & \quad \text{coefficient for capturing ion hydration effects} \quad (17) \\
R & \quad \text{Universal gas constant, } [\text{Force-length/(degree-moles)}] \quad (1) \\
t & \quad \text{time} \\
T & \quad \text{absolute temperature } [\text{degree}] \quad (1) \\
\mathbf{v}^{\alpha_j} & \quad \text{velocity of } j^{th} \text{ constituent in phase } \alpha, \ (18) \ [\text{length/time}] \\
\mathbf{v}^\alpha & \quad \text{mass-averaged velocity of phase } \alpha, \sum_{j=1}^N C^{\alpha_j} \mathbf{v}^{\alpha_j}, [\text{length/time}] \quad (12) \\
\mathbf{v}^{\alpha_j,\alpha} & \quad \text{diffusive velocity}, \mathbf{v}^{\alpha_j} - \mathbf{v}^\alpha \ [\text{length/time}] \quad (12) \\
\mathbf{v}^{l,s} & \quad \text{velocity of liquid relative to solid phase}, \mathbf{v}^l - \mathbf{v}^s, [\text{length/time}] \quad (12) \\
x^{l_j} & \quad \text{molar fraction of } l^{th} \text{ species in phase } l, [-] \quad (7) \\
z^{\alpha_j} & \quad \text{fixed charge density associated with } \alpha_j, \ [\text{charge } \alpha_j/\text{mass } \alpha_j] \quad (12), (23) \\
\varepsilon^\alpha & \quad \text{volume fraction of } \alpha\text{-phase in Representative Elementary Volume (REV)}, |\delta V_\alpha|/|\delta V|, [-] \quad (12) \\
\tilde{\varepsilon} & \quad \text{dielectric constant of solvent } [-] \quad \text{Section 5.1} \\
\tilde{\varepsilon}_0 & \quad \text{vacuum permittivity } [\text{charge}^2/\text{Force-Length}^2] \quad \text{Section 5.1}
\end{align*}
\]
λs  thickness of montmorillonite clay mineral, [length] (9)
nλ  thickness of vicinal liquid of montmorillonite clay, [length] (9)
μαj chemical potential of jth constituent in phase α
    [energy α/ mass αj] (1), (22)
¯μαj electro-chemical potential of jth constituent in phase α
    [energy α/ mass αj] (23)
ραj chemical potential of jth constituent in phase α
    [energy α/ mole αj] in Appendix B (23)
πl  osmotic pressure, [force/area] (2)
πα  swelling pressure, [force/area] (14)
φ   electric field potential, \( \mathbf{E} = -\nabla \phi \), [force/charge-length] (23)
Ψα  Helmholtz free energy density of α-phase,
    \( e^\alpha - T \eta^\alpha \) [energy α/ mass α] (13)
ραj density of jth constituent in phase α, \( C^\alpha j \rho^\alpha \), [mass αj/ volume α] (12)
ρα specific mass density of phase α, \( \sum_{j=1}^{N} \rho^\alpha j \), [mass α/ volume α] (4)

ρα averaged mass density of phase α, \( \sum_{j=1}^{N} \rho^\alpha j \), [mass α/ volume α] (4)