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Non-equilibrium liquid-gas phase change in hygroscopic porous media.

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Introduction

When focusing on the drying of hygroscopic materials (soil, wood, gel ...), liquid-gas phase change is the key phenomenon that enables the complete dewatering. Evaporation is often considered instantaneous when compared to other transport phenomena, what is expressed by the *local equilibrium assumption*. However, a volatilisation retardation time has been observed at the macroscopic scale under certain conditions [1, 3].

At the microscopic scale, the water phase is partially adsorbed on grains surface, and it cannot be considered in a “free” state, where classical thermodynamics applied. In such situations, water displacement induced by pressure gradient is not conceivable and evaporation requires higher energy exchange. At this scale, the phase change phenomenon is generally represented by the Hertz-Knudsen law [4], derived from the kinetic theory for ideal gases.

Trying to upscale this relation confronts itself to various interrogations such as the way the phase change flux depends on hygroscopic effects, on liquid-gas interface curvature, on material composition and texture. In that complex framework, macroscopic phase change descriptions have been proposed, generally based on a first-order kinetic associated with a mass exchange coefficient. This linearization should be valid close to equilibrium conditions, whereas the validity domain has not yet been investigated.

To revisit these issues, a macroscopic formulation of liquid-gas phase change has been developed. It is derived from the TIP ideas (Thermodynamics of Irreversible Processes), by referring to the chemical potential difference taken as the thermodynamic “driving force”. This approach introduced a phenomenological coefficient that must be experimentally determined. An original experimental device has been designed allowing us to explore the complete range of water content, temperature, gas pressure. This leads us to differentiate two domains, a linear behaviour close to equilibrium and a non-linear one far from equilibrium. Eventually, this modelling is confronted to experimental drying kinetics of soil columns.

Phenomenological phase change formulation

As long as the water phase is continuous, the capillary pressure is defined and can be used. However, in the pendular or hygroscopic domain, water is partially adsorbed on the solid surface and the concepts of pressure field and capillary potential are meaningless [6]. In these situations, the chemical potential becomes the key parameter that governs the water transport. Developing the mass,

momentum, energy and entropy balances in a tri-phasic porous medium leads to express the internal production rate of entropy as [2, 3]:

$$\sigma = -J \left(\frac{\mu_v - \mu_l}{T} \right) \geq 0$$

where J is the volumetric phase change flux, μ_l and μ_v are respectively the chemical potentials of water and its vapour. To be used in practical applications, the chemical potential must be expressed as a function of an experimentally measurable quantity, like the vapour pressure. In the framework of linear TIP, the thermodynamic flux is expressed as a linear function of the thermodynamic force by [3, 7]:

$$J = -L \frac{R}{M} \ln \left(\frac{P_v}{P_{veq}} \right)$$

where P_v is the partial pressure of vapour, and P_{veq} is the partial pressure of vapour in equilibrium conditions. For hygroscopic materials, it depends on the activity of the liquid phase and on the saturating vapour pressure through:

$$P_{veq} = a(w) P_{vs}(T)$$

The activity can be determined from experimental desorption isotherms.

This relation introduces a phenomenological coefficient L that depends on the state variables, such as the water content w , the temperature T ... The next section focuses on the experimental determination of this coefficient.

Materials and Methods

The porous media used is a natural soil (clayey silty sand), in which the clayey fraction (10%) causes its hygroscopic nature (the hygroscopic domain spreads until a water content of 7%). The principle of experiments consists in creating a thermodynamic non-equilibrium in a soil sample and, then, analysing the return to equilibrium. For that purpose, the gas pressure is lowered by connecting the sample pore network to a vacuum pump during 3 seconds. This operation aims to decrease the vapour pressure below its equilibrium value. Under these conditions, the phase change occurs until the equilibrium vapour pressure is attained. A sensor inside the cell provides a continuous recording of the variations in the total gas pressure and the temperature of the sample. For indication, the time required to get back to equilibrium ranges from 20 to 100 minutes, emphasizing the slowness of phase change in these situations.

From these measurements combined with mass balance equations, the phenomenological coefficient L can be determined. For a typical experiment at fixed temperature

and water content, this coefficient is plotted as a function of a non-equilibrium criterion: the ratio of the vapour pressure divided by its equilibrium value (Fig. 1).

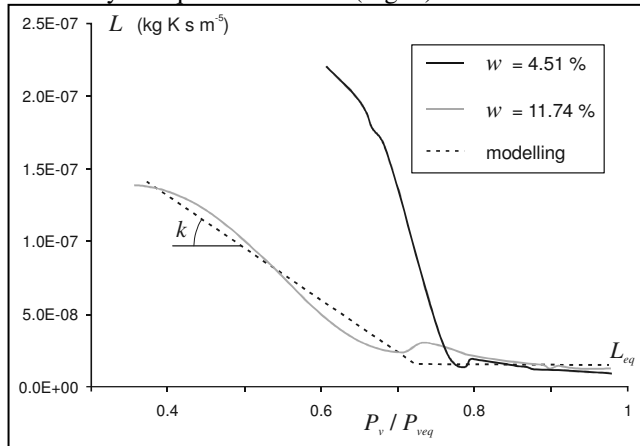


Fig 1: Phase change coefficient L as a function of the ratio of the vapour pressure divided by its equilibrium value.

This figure clearly shows two domains. Close to equilibrium, where the ratio of vapour pressure is close to 1, the phase change behaves as a linear phenomenon with a constant mass exchange coefficient L_{eq} . This defines the limit of validity in the framework of linear TIP. Beyond this limit as the non-equilibrium increases, a non-linear behaviour is observed, what is not surprising. The matter is that this situation is regularly encountered in practical drying application since the vapour pressure can easily drop far below its equilibrium value, especially when venting techniques are involved. As a first approximation, the phase change coefficient variation can be represented through the slope k .

For a set of environmental parameters (temperature, pressure, porosity), the phase change coefficient close to equilibrium L_{eq} is determined as a function of the water content (Fig. 2). This is done for various total gas pressures by regulating the vacuum pump used to extract the gas phase. The third curve corresponding to atmospheric pressure is carried out by “completely” removing the gas phase and connecting the pore network with dry air.

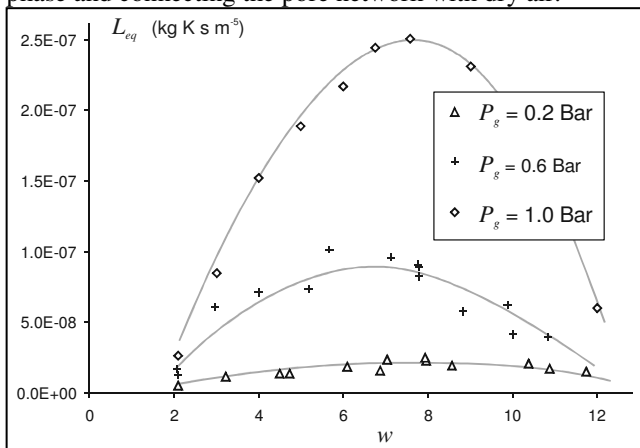


Fig 2: Phase change equilibrium coefficient L_{eq} as a function of the water content w .

For each gas pressure, the variation of L_{eq} reaches a maximum around 7%, which is roughly the upper limit of the hygroscopic domain. Above this maximum, the phase change velocity decreases since the liquid-gas interface is getting lower. For water content greater than 12%, the gas phase is occluded and phase change cannot be activated.

Below the maximum, when hygroscopic effects become predominant, the intensity of solid-liquid interactions increases in the adsorbed layers. The supplementary energy requires for water desorption decreases the phase change velocity, leading to a lower coefficient L_{eq} . The influence of these micro-scale interactions have also been shown by adding a mass fraction of calibrated sand to the original material. The presence of sand, weakly hygroscopic, manifests itself through shifting the maximum to the left and increasing the phase change coefficient.

The perfect gases theory is unable to predict the influence of gas pressure experimentally observed. At the interface scale, evaporation is predominantly stimulated by shocks with gas phase molecules [5]. This confirms the greater phase change coefficient resulting from higher gas pressure as shown in figure 2.

In order to illustrate the interests of such investigation, macroscopic drying experiments have been conducted. 30 cm soil columns prepared at 8% water content were placed in a temperature- and moisture-regulated atmosphere. Drying kinetics were established through differential weighing of the column while water content profiles were measured by destructive uptakes. Numerical simulations of water transport were performed in which the phenomena taken into account are liquid-gas phase change and vapour diffusion. In this simple case without gas convection, the vapour pressure computed drops far below its equilibrium value, justifying a non-equilibrium description. When compared to experimental kinetics, a fair agreement is obtained, while some discrepancies are observed on the upper side of the column. At the interface with the atmosphere, phase change is highly activated and do not behaves as inside the sample. Further investigations are needed to develop accurate boundary conditions.

Conclusion

A macroscopic modelling of liquid-gas phase change in porous media has been developed from thermodynamics principles. In non-equilibrium conditions, the chemical potential appears to be the key parameter that governs the mass transport. This phenomenon has been experimentally characterized, emphasizing that hygroscopic effects have a significant influence by lowering the phase change velocity. Further microscopic thermodynamics developments should bring some essential physical descriptions of phase change.

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