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Yield stress fluids method to determine the pore size distribution of a porous medium

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ABSTRACT

In this paper a new method is presented in order to determine the pore size distribution in a porous medium. This original technique uses the rheological properties of some non-Newtonian yield stress fluids flowing through the porous sample. This technique is based on the capillary bundle model (like the other classical methods) which, despite its apparent simplicity, is capable of properly characterizing the percolating pore size distribution. Then this distribution can be simply obtained from the measurement of the total flow rate as a function of the imposed pressure gradient. The present technique is successfully tested analytically and numerically for usual pore size distributions such as the Gaussian mono and multimodal distributions, using Bingham and Casson fluids. The technique can also be extended to any yield stress fluid and any kind of distribution.

1. Introduction

Porous media are found literally everywhere around us [1–4], in living matter, in Nature and in various technological applications. The need in porous media will keep on growing in the future because of the increase in the price of energy and because of environmental challenges; let us cite for example the recent application of heat storage in granular porous media for solar collectors [5]; another instance concerns heat storage for human housing using porous phase change materials [6]; the continuous decrease in conventional oil and gas reserves implies a high level of investments for tertiary recovery techniques [7]; the storage and the behavior of pollutants in porous matter (hazardous wastes, CO_2 sequestration...) are today an important challenge; they are also used in some biological processes (dialysis, membrane transport) [8]... These numerous applications make them the object of abundant studies and are topics for which it is essential to have an in-depth knowledge and an accurate characterization.

Since the early work of Darcy [9], the transport phenomena in general and particularly the flow through porous media generated an important research activity which is today still relevant. In fact, all the porous media are made of networks of pores delimited by a solid. Among the pores constituting this network we are particularly interested in the percolating conduits excluding the isolated pores, the dead ends and the finite clusters which do not carry any flow. In these conditions the characterization of the percolating pore size distribution (PSD) of these porous media is a crucial goal [10]. In fact the strong dependence of the transport properties in porous media with the size of their pores and their polydispersity constitute a challenge in many scientific areas. Various techniques have been developed to characterize the network of such porous solids, and particularly their pore size distribution. Among the most popular techniques, we can quote: the mercury intrusion porosimetry (MIP) [1–3,11] consisting into the injection of mercury in the porous medium. This technique is based on the existence of a threshold below which the pores cannot be invaded. Indeed due to its large surface tension mercury does not wet most of the materials. A pressure difference ΔP_{lg} must be imposed so that mercury penetrates the pores whose radii r_p are greater than $r_p^* = 2\sigma_{lg}\cos\theta/\Delta P_{lg}$ where σ_{lg} is the liquid/gas interfacial tension and θ the contact angle. The pore size volume distribution is obtained with the derivative of the curve representing the volume of the invaded pores according to the radius of the pores. Because of the toxicity of mercury, this technique is intended to be phased out. Another method to measure the pore-size distributions is the BJH. method [12]. This classical method uses two mechanisms: the isothermal adsorption (of nitrogen at 77 K) on the pore walls and the capillary condensation, due to the molecular Van der Waals interactions between a condensing vapor and the internal surface of the pores. This BJH technique is based on the relationship between the imposed pressure and the radius of a cylindrical pore where the capillary condensation takes place. This is the Kelvin–Laplace equation: $\ln(P/P_0) = -2\sigma_{lg}v_l\cos\theta/NkTr_p$, where P and P_0 are respectively the partial vapor pressure, the saturation vapor pressure at the temperature T, r_p the pore radius, N the Avogadro's number, k the Boltzmann's constant and v_l the liquid phase molar volume. This method consists in measuring the desorption volume

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vs. the relative pressure: P/P_0. Then the pore size distribution is obtained from the derivative of this curve.

An alternative technique rests on the liquid–solid phase transition of the fluid in a porous medium [13,14]. This approach for determining the PSD in porous materials has been suggested by Kuhn et al. [15] and derived later by Brun et al. [16]. The principle of the method is based on the lowering of the triple point temperature of a liquid filling a porous material. It uses a thermodynamical relationship between the reduction of the triple point temperature ΔT of the confined liquid in the pores of radius r_p where the phase transition occurs. It is expressed by the Gibbs–Thomson equation: $\Delta T/T_0 = 2\sigma_{ls}\nu_l/\Delta H_0 r_p$, where σ_{ls} is the liquid/solid interfacial tension, ν_l the liquid phase molar volume, ΔH_0 the molar heat of fusion, r_p the pore radius, and T_0 the triple point temperature of the unconfined liquid. Then the phase transitions (solidification or melting) for a liquid confined within a pore occur at lower temperatures when the pore size decreases. This difference in transition temperature ΔT, between confined and bulk liquid can be measured calorimetrically by DSC thermoporometry (differential scanning calorimetry) [17] or cryoporometry using nuclear magnetic resonance (NMR) [18]. Notice that all the techniques mentioned above and developed in order to measure the pore size distribution are based on the existence of a threshold. The first one is due to the capillary pressure; the two others are due to the phase change phenomena. Finally let us quote destructive techniques such as stereology [19] or non-destructive methods such as Small Angle Neutron (SANS) or X-Ray Scattering (SAXS) [20,21]. Unfortunately all these techniques can give quite different results; moreover they are very expensive and require complex equipment. Therefore in this study we propose a new alternative, simpler and cheaper technique, in order to characterize the PSD of a porous medium.

2. Objective of the study

Starting from the same principle utilized in the first three thermodynamical methods described above, we develop an approach based on the threshold introduced by a yield stress fluid (which belongs to the class of non-Newtonian viscoplastic fluids without time dependence). These fluids do not flow, before being subject to a minimum shear stress called the flow yield stress τ_0. Many materials such as polymers (carbopol…), foodstuffs (mayonnaise…), cosmetics (beauty cream, toothpaste…), concentrated slurries, electro-rheological fluids (suspensions of very fine conducting particles in an electrically insulating fluid) and magneto-rheological fluids (suspensions of magnetically polarizable micron-sized particles in oil) [22]… have a rheological behavior which is situated between a purely viscous liquid and a plastic solid. These fluids may have a more or less well defined yield stress. This critical stress that accompanies the transition between the solid and the viscous behaviors is related to the internal structure of the network of the material. The magnitude of the yield stress may depend on the concentration of the dissolved substances inducing the threshold and it may also vary with the pH of the solution (like bentonite [23]). A lot of behavior laws are available to describe such complex fluids. In our study we focus only on the classical Bingham fluids [24,25] (drilling muds, oil painting, Laponite [26]…), and Casson fluids (printing ink [27], sludge suspensions and dispersion paint, blood [28]…).

The basic idea is the following: in order to set such fluids into motion, it is necessary to impose between both ends of a pore a pressure gradient (∇P) greater than a critical value depending on the fluid yield stress (τ_0) and the pore radius (r_p). In other words, for the pressure gradient ∇P, only the pores whose radius is greater than the critical radius $r_0 = 2\tau_0/\nabla P$ are invaded. Then it is possible to scan the PSD by increasing the pressure gradient step by step and measuring the corresponding flow rate Q.

3. Models and procedure

3.1. Porous medium and yield stress fluid models

In order to determine the pore size distribution of the percolating pores, the most popular model in all the thermodynamical techniques described above is the capillary bundle model [29,30]. Although it is quite simple, it can account for most of the geometrical properties of the real porous media such as the tortuosity, the permeability and the variation in the pore cross-section as we shall see later. Nevertheless the interconnectivity cannot be modeled. We will use this model to derive the inversion technique which allows us to obtain the PSD from the characteristic curve $Q = f(\nabla P)$ for a given yield stress fluid in non-inertial regimes. The simplest yield stress fluid is described by the Bingham model. Such a fluid obeys the following rheological behavior law:

$$\begin{cases} \underline{\underline{\tau}} = 2\left(\eta + \frac{\tau_0}{\sqrt{2\,\underline{\underline{D}}:\underline{\underline{D}}}}\right)\underline{\underline{D}} & \text{for } \sqrt{\frac{\underline{\underline{\tau}}:\underline{\underline{\tau}}}{2}} > \tau_0 \\ \underline{\underline{D}} = 0 & \text{for } \sqrt{\frac{\underline{\underline{\tau}}:\underline{\underline{\tau}}}{2}} \leqslant \tau_0 \end{cases} \tag{1}$$

with $\underline{\underline{\tau}}$ the shear stress tensor, $\underline{\underline{D}}$ the rate of deformation tensor and η the plastic viscosity of the fluid. For the flow in a tube with circular cross-section, these equations take the simpler form:

$$\begin{cases} \tau_{r'z} = \tau_0 + \eta\left|\frac{\partial u_z}{\partial r'}\right| & \text{for } \tau_{r'z} > \tau_0 \\ \frac{\partial u_z}{\partial r'} = 0 & \text{for } \tau_{r'z} \leqslant \tau_0 \end{cases} \tag{2}$$

where $\tau_{r'z}$ is the shear stress, $(\partial u_z/\partial r')$ the rate of deformation and r' is the radial coordinate.

3.2. Procedure and inversion

Our model is composed of parallel capillaries (Fig. 1) whose radii are distributed according to the unknown probability density function $p(r)$. When a pressure gradient ∇P is imposed on this system, the total flux is calculated from the elementary flow rate $q(\nabla P, r)$ in a single capillary of radius r and from $p(r)$ by the integral:

$$Q(\nabla P) = \int_{r_0=\frac{2\tau_0}{\nabla P}}^{\infty} q(\nabla P, r)p(r)\,dr \tag{3}$$

This integral constitutes a Volterra equation of the first kind. As long as the regime is non-inertial, the kernel of Eq. (3) is given by [31]:

$$q(\nabla P, r) = \begin{cases} \frac{\pi\tau_0 r^4}{4\eta r_0}\left[1 - \frac{4}{3}\left(\frac{r_0}{r}\right) + \frac{1}{3}\left(\frac{r_0}{r}\right)^4\right] & \text{for } r > r_0 \\ 0 \text{ for } r \leqslant r_0 \end{cases} \tag{4}$$

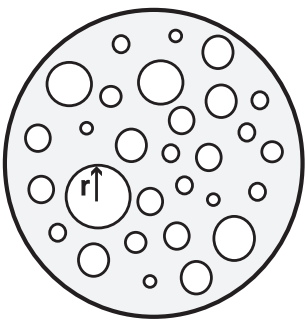

Fig. 1. Capillary bundle model.