Physics Letters A ••• (••••) •••–•••

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Fluctuations of the number of neighboring pores and appearance of multiple nonergodic states of a nonwetting liquid confined in a disordered nanoporous medium

Vladimir D. Borman, Anton A. Belogorlov *, Alexey M. Grekhov, Vladimir N. Tronin

National Research Nuclear University MEPhI, Kashirskoe sh. 31, Moscow, 115409, Russia

ARTICLE INFO

Article history:
Received 25 July 2014
Accepted 31 July 2014
Available online xxxx
Communicated by V.M. Agranovich

Keywords:
Disordered nanoporous medium
Nonwetting liquid
Nonergodic states
Fluctuations

ABSTRACT

Multiple nonergodic states have been observed for nonwetting liquid in the Fluka100 C18 and Fluka100 C8 porous media with broad pore size distributions having different widths. The dispersion transition where the volume of confined liquid depends critically on the degree of filling of the porous medium and temperature is observed in the temperature range 293–343 K under study for the Fluka100 C18 porous medium and is not observed for the Fluka100 C8 porous medium. A mechanism of the appearance of multiple nonergodic states has been proposed. It has been shown that fluctuations of the number of the nearest neighbors in the disordered system are mainly responsible for the features of confinement of nonwetting liquid and nonergodic states of nonwetting liquid in the nanoporous media under investigation with wide pore size distributions.

1. Introduction

A disordered system of pores of a porous medium can be filled with a nonwetting liquid at a pressure that can be estimated by the Laplace formula at porosity above the percolation threshold [1]. After the removal of excess pressure, the state of nonwetting liquid becomes unstable and this liquid should flow out of the porous medium. However, it is known [2–14] that for many porous media and liquids, a liquid after complete filling can partially or completely remain in a porous medium after the removal of excess pressure. This means that nonwetting liquid passing to a dispersed state of an ensemble of liquid nanoclusters at disordered confinement becomes effectively “wetting”. The volume of confined liquid depends critically on the degree of filling of the porous medium and temperature [2]. This phenomenon was called in [2] the dispersion transition.

Within the physical mechanism and statistical description proposed in [15,16], the observed transition of the system of nanoclusters of nonwetting liquid at confinement to a metastable state in a narrow range of degrees of filling and temperatures [16] is attributed to the appearance of a potential barrier owing to fluctuations of the collective “multiparticle” interaction between liquid nanoclusters in neighboring pores with various sizes on the shell of a fractal percolation cluster of filled pores. This makes it possible to explain the confinement of a nonwetting liquid (mercury) in a nanoporous glass for months [17]. According to this mechanism, local metastable configurations of filled pores appear in the porous medium and the decay of the metastable state because of the extrusion of the liquid through pores of the infinite percolation cluster is the process of transition from a nonergodic state to an ergodic state of the empty medium. Ergodic states of a system are states for which the time average of a physical quantity is equal to its mean over an ensemble as an integral over the entire phase space of the system [34,35]. However, the space of all states of the system in the usual ferromagnetic Ising model below the transition point is divided into halves if the average magnetization of a certain sign is separated. In this case, only states from one half of the phase space contribute to observables. These two equal halves are separated by an infinite (in the limit of the infinite number of particles N) free-energy barrier. This phenomenon can be called breaking of ergodicity [21]. Systems where ergodicity is broken are called nonergodic [21]. The phase space of the system under consideration is the phase space in the fractal percolation cluster of filled pores. It is divided into a phase space in which the liquid is in a metastable state and a phase space in which the liquid is unstable and fast outflowing is observed [37].

This mechanism gives the observed dependence of the volume of confined liquid on the temperature, size of granules, and observation time [18–20]. The energy of the nonergodic metastable state of various configurations of clusters of confined liquid in neighboring pores has a potential relief in the space of the medium with numerous maxima and minima [15,16]. Because of the

* Corresponding author.

http://dx.doi.org/10.1016/j.physleta.2014.07.045
0375-9601/

confinement of nonwetting liquid in the disordered nanoporous medium, this system can be referred to nonergodic systems such as glass, spin glass, and sol–gel system [21–27]. To describe the properties of these systems, phenomenological approaches are now considered; in one of them, fluctuation-induced shear transformation zones (STZs) serve as local metastable configurations [22–26].

In this model, the energy of interaction between liquid clusters is defined as a decrease in the surface energy of a liquid cluster after the appearance of another liquid cluster in a neighboring connected pore. The interaction energy is equal to the surface energy of a meniscus disappearing in this case in a throat connecting two pores. A decrease in the surface energy of two clusters in neighboring pores is equivalent to the attraction energy. A consequence of such attraction can be "condensation" of clusters in confinement. However, the magnitude and sign of change in the energy of the total "multiparticle" interaction of all neighboring clusters at the extrusion of the liquid from a pore obviously depend on the number of filled neighboring pores and their size on a nonsmooth fractal shell and inside the percolation cluster. This is indicated by the observed critical dependence of the volume of confined liquid on the volume of initially filled pores [15].

The volume of confined liquid was calculated in [15,16] within analytical percolation theory for the degenerate ground state of the system consisting of the liquid and porous medium with the infinite percolation cluster of filled pores in the case of a narrow pore size distribution with the relative width $\Delta R/R \ll 1$ under the assumption of a constant number z of the nearest neighbor pores. In this case, capture of liquid to a metastable nonergodic state is determined by fluctuations of the number of filled neighboring pores with various sizes on the shell of the infinite percolation cluster. However, for a disordered medium, the random field of the potential barrier of metastable states can also appear because of fluctuations of the number of nearest neighbors in the disordered medium with a wide pore size distribution with the relative width $\Delta R/R \sim 1$.

The dispersion transition was detected in [2] for the system of water and the L23 porous medium with a narrow pore size distribution with the relative width $\Delta R/R < 0.1$.

In this work, multiple nonergodic states are observed for liquid in the Fluka 100 C18 and Fluka 100 C8 porous media with wide pore size distributions with different relative widths $\Delta R/R \sim 1$. The dispersion transition of nonwetting liquid (water) to the metastable nonergodic state is observed in the temperature range 280–370 K under study for the Fluka 100 C18 porous medium is not observed for the Fluka 100 C8 porous medium. A mechanism of the appearance of multiple nonergodic states at confinement of nonwetting liquid is proposed on the basis of allowance for fluctuations of the number of neighboring pores in the disordered nanoporous medium. It is shown that fluctuations of the number of the nearest neighbors are mainly responsible for the features of confinement of nonwetting liquid and nonergodic states of nonwetting liquid in nanoporous media with wide pore size distributions under investigation.

2. Materials and methods

The Fluka 100 C8 and Fluka 100 C18 nanoporous hydrophobized media have the same material of the frame and are produced by Sigma-Aldrich Co. The Fluka 100 C8 medium was obtained in one of two produced variants and is silica gel 100 C_8, reversed phase # 60759-50G (Sigma-Aldrich Co.), whose surface is modified with 8-alkylsilane. The Fluka 100 C18 medium (silica gel 100 C_{18} – reversed phase # 60756-50G, Sigma-Aldrich Co.) is modified with 18-alkylsilane.

The characteristics of the porous media were determined by the gas pycnometry method with a Micro-Ultrapyc 1200e helium pycnometer (Quantachrome Instruments, USA) and by the nitrogen gas adsorption method with a Nova 1200e instrument (Quantachrome Instruments, USA). The real density ρ, specific volume of pores V_p, specific area of the surface of pores S_p, average radius $\langle R\rangle$, and relative width of the pore size distribution $\langle \Delta R\rangle/\langle R\rangle$ are presented in Table 1 in comparison with the characteristics of the L23 silica gel similarly hydrophobized and previously studied in [2]. According to the table, the media under study have the same average radius of pores, but the specific surface, volume of pores, and porosity for the Fluka 100 C18 medium are smaller than the respective quantities for the Fluka 100 C8 medium. The porosity of these media is smaller than that for L23.

Table 1
Characteristics of the porous media.

	Fluka 100 C8	Fluka 100 C18	L23(C8)
ρ, g/cm^3	1.7603 ± 0.0034	1.6125 ± 0.0025	1.7798±0.0016
V_p, cm^3/g	0.56 ± 0.02	0.46 ± 0.02	0.66±0.02
S_p, m^2/g	267 ± 10	183 ± 6	212±7
$\langle R\rangle$, nm	3.9 ± 0.2	3.9 ± 0.2	4.9±0.2
$\langle \Delta R\rangle/\langle R\rangle$	0.9	0.75	0.1
ϕ	0.49 ± 0.02	0.42 ± 0.02	0.66±0.02

The pore size distribution functions $f(R)$ for the porous media under study were determined from nitrogen desorption isotherms by the BJH method [17,28].

The aim of the experiments was to determine the dependence of the volume fraction θ_2 of pores filled with the confined liquid on the volume fraction θ_1 of pores previously filled with the liquid. The method of the study was similar to the method used in mercury [17] or water [29] porometry. A high-pressure bench previously described in [29] was used in the experiments. The (nonwetting liquid–porous medium) system was placed in a constant-temperature high-pressure chamber. The system was aged at a given temperature for 1–1.5 h before the measurements. The temperature was maintained with an accuracy of 0.2 K. The pressure in the chamber was recorded by a CWH-T2 tensiometric dynamometer (Dacell, South Korea) with the measurement range from 0.1 to 20 kN with an accuracy of 0.04%. Readings from the dynamometer and slide-wire gauge were recorded with a frequency of 1 kHz through an analog-to-digital converter on a computer.

The method based on the repeated filling of the porous medium [29] was used to determine the quantity θ_2. Excess pressure was reduced to zero in 20–60 s. The time of fixation of the volume of the liquid remaining in pores was 60 s. The cycle of an increase and a decrease in pressure in the system lasted from 60 to 300 s depending on the fraction of the filled volume of pores. The time interval between cycles was 60 s. It was found that the fraction of the remaining liquid did not change within the error at several (ten) repetitions of the second cycle. After each experiment, the porous medium was dried in vacuum at $T = 353$ K for 3 h until the sample reached its initial mass and was repeatedly used in studies. Measurements showed that such a drying recovered the characteristics of the samples.

3. Results

Fig. 1 shows the dependences $\theta_2(\theta_1)$ for the Fluka 100 C18–water system at temperatures of (a) 293, 303, and 313 K and (b) 323, 333, and 343 K. It was found that the dependences $\theta_2(\theta_1)$ for temperatures from 293 to 313 K are linear within the measurement error. When the temperature increases from 313 to 323 K, a linear dependence changes to "stepwise". At the latter temperature, the volume fraction of pores filled with the confined liquid changes abruptly at the degree of preliminary filling $\theta_1 = \theta_{cr} \approx 0.63$. The same singularity is observed in the dependence $\theta_2(\theta_1)$

Please cite this article in press as: V.D. Borman et al., Fluctuations of the number of neighboring pores and appearance of multiple nonergodic states of a nonwetting liquid confined in a disordered nanoporous medium, Phys. Lett. A (2014), http://dx.doi.org/10.1016/j.physleta.2014.07.045