Physica A 457 (2016) 391–405

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Anomalously slow relaxation of the system of strongly interacting liquid clusters in a disordered nanoporous medium: Self-organized criticality

V.D. Borman, V.N. Tronin *

Department of Molecular Physics, National Research Nuclear University "MEPhI", Kashirskoye shosse 31, Moscow, 115409, Russian Federation

HIGHLIGHTS

- The relaxation of the system is a self-organized criticality process.
- The relaxation characterized by waiting for fluctuation.
- The interaction between configurations is an internal feedback initiating the SOC.

ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form 25 February 2016
Available online 6 April 2016

Keywords:
Disordered nanoporous medium
Self-organized criticality

ABSTRACT

It has been shown that changes in the energy of a system of nonwetting liquid clusters confined in a random nanoporous medium in the process of relaxation can be written in the quasiparticle approximation in the form of the sum of the energies of local (metastable) configurations of liquid clusters interacting with clusters in the connected nearest pores. The energy spectrum and density of states of the local configuration have been calculated.

It has been shown that the relaxation of the state of the system occurs through the scenario of self-organized criticality (SOC). The process is characterized by the expectation of a fluctuation necessary for overcoming a local energy barrier of the metastable state with the subsequent rapid hydrodynamic extrusion of the liquid under the action of the surface buoyancy forces of the nonwetting framework. In this case, the dependence of the interaction between local configurations on the number of filled pores belonging to the infinite percolation cluster of filled pores serves as an internal feedback initiating the SOC process. The calculations give a power-law time dependence of the relative volume of the confined liquid $\theta \sim t^{-\alpha} (\alpha \sim 0.1)$.

The developed model of the relaxation of the porous medium with the nonwetting liquid demonstrates possible mechanisms and scenarios of SOC for disordered atomic systems.

1. Introduction

Anomalously slow relaxation is a common property of many disordered condensed media with various particle sizes from atomic to micron. These media include metallic and molecular glasses, polymers, colloid media, granulated matter, nanocomposites, etc. The relaxation of these media is characterized by the "stretched exponential law"; i.e., a characteristic

* Corresponding author.
E-mail address: vntronin@mephi.ru (V.N. Tronin).

http://dx.doi.org/10.1016/j.physa.2016.03.078
0378-4371/

property depends on the time as $\exp(-(t/\tau_0)^{\beta})$, where τ is the characteristic relaxation time and $\beta < 1$ (see, e.g., Refs. [1,2]). For this reason, anomalously slow relaxation is considered as a cooperative phenomenon [3]. The dynamics of such cooperative phenomena in a nanoconfinement is currently under active numerical investigation [4]. Several phenomenological models have been proposed to describe anomalously slow relaxation. They were analyzed in recent reviews [2,3,5,6]. The key assumption in these models is the assumption of the existence of local configurations of particles that are not detected in experiments on the measurement of the static density correlation function and their energy is not calculated. The connection between anomalously slow relaxation and such local configurations is actively discussed [2,3,5,6].

Disordered nanoporous media (silica gel, etc.) studied in this work are formed at a sol–gel transition in a colloid medium. The random structure of pores and framework of the medium "is frozen" at gelling owing to a chemical reaction between colloid particles. The random structure can be inherited by a liquid that fills the space of pores if pores form a connected system. This occurs at a porosity above the percolation threshold, when the infinite percolation cluster of connected pores is formed in the medium and, thereby, the filling of pores of the medium with the liquid is ensured. The characteristics of the structure of pores such as the specific volume of pores, specific surface of pores, and pore size distribution are studied by the methods of gas adsorption–desorption [7,8] and liquid porometry [9–11]. A nonwetting liquid (e.g., water) filling a porous medium at excess pressure is used in liquid porometry. In this application, the liquid is dispersed and forms an ensemble of interacting clusters. When excess pressure is reduced to zero, the liquid should be extruded from pores under the action of the surface repulsive forces of the hydrophobic framework of the medium.

New information on the disordered structure can be obtained by studying the confinement of the nonwetting liquid in the random structure of pores [12–15]. According to Refs. [14,15], this phenomenon is due to the effective interaction (attraction) between liquid clusters in neighboring pores, which is determined by correlation in the arrangement of pores. An anomalously slow relaxation of the state of the confined liquid was observed in Ref. [16] as the slow extrusion of the liquid from the porous medium. The volume of the confined liquid depends on the time according to an inverse power law with the exponent $\alpha \leq 0.1$. Depending on the properties of the porous medium, nonwetting liquids can remain in it for many days and even months [17–20]. A small change in the temperature or a decrease in the degree of filling near the critical values results in the rapid extrusion of the liquid (dispersion transition) [12].

In this work, analyzing the dynamics of a change in the energy spectrum and the density of states of the set of degenerate local metastable configurations of interacting liquid clusters in neighboring pores, we propose a mechanism of this phenomenon. These local configurations interact with each other through the field of the infinite percolation cluster of filled pores according to the arrangement of pores in the frozen random structure of pores in the porous medium. Since the liquid in the frozen random structure of pores follows this structure, it could be expected that the mechanisms of anomalously slow relaxation of the framework in the processes of gelling and the confinement of the liquid in pores should be the same, but with naturally different time scales.

One of the main results of the numerical experiments on studying the mechanism of anomalous relaxation of random media is the space–time heterogeneity of such media (dynamic heterogeneity (DH) and dynamic facilitation (DF) models [2,3,5,21–23]). The same local space–time heterogeneity follows from the statistical model named mode-coupling theory (MCT) [2,5,6,22,23]. Another property of MCT is the divergence of the characteristic relaxation time τ at the critical temperature predicted in MCT. This divergence is attributed in MCT to blocking of the motion of particles by neighboring particles because of memory effects at their interaction [6]. However, this is observed neither in experiments nor in numerical calculations [5].

In the phenomenological random first-order transition (RFOT) model (a first-order phase transition in a random medium) [1–3,5,6,24,25] of relaxation in the disordered medium, the system of particles with a short-range interaction between them is considered as a system of local regions in different metastable states. The RFOT model was formulated under the assumption of the possible realization of the state of glass with a short-range interaction between particles as a heterogenic state with numerous local configurations similar to the disordered state of spin glass in the Potts model with the p-spin of particles and their long-range (infinite-range) interaction [6]. Because of thermal fluctuations in the RFOT model, the states of these local regions of glass change, they can transform to each other, and large regions can decay into small regions. Thus, a hypothetical "mosaic" structure of the state of disordered glass appears with local regions whose size increases with a decrease in the temperature. It is assumed that the time scale of a transition between the states of local regions coincides with the scale of the characteristic relaxation time depending on the temperature.

This model has not yet been statistically justified, and some numerical studies [26] within the achieved computation time does not confirm the mosaic structure of the state. The calculation of the energy of local metastable configurations would be of a key importance for the confirmation of the RFOT model. This model predicts the existence of the temperature at which the divergence of the characteristic relaxation time should be observed, but it is not observed in fact.

Various variants of local regions in the disordered medium were revealed and studied in numerical experiments [21,27,28]. The relation between geometrical frustrations and static local structures with the characteristic relaxation time was analyzed in Ref. [29]. It was found that geometrical frustrations could be responsible for a change in the scenario of cooperative relaxation. In view of the results of that work, the authors assumed that anomalously slow relaxation could possibly have a noncooperative character.

The above brief review demonstrates that the nature of local heterogenic regions, the reason for their appearance and metastability, their connection with the nature and mechanism of anomalously slow relaxation in disordered glass media remain unclear. It is also unclear whether the experimentally observed properties are equilibrium or kinetic in nature.