PHYSICAL REVIEW E **88**, 052116 (2013)

Kinetics of the dispersion transition and nonergodicity of a system consisting of a disordered porous medium and a nonwetting liquid

Vladimir D. Borman,[*] Anton A. Belogorlov, Victor A. Byrkin,[†] and Vladimir N. Tronin
Department of Molecular Physics, National Research Nuclear University MEPhI, Moscow, Russia

(Received 3 September 2013; published 11 November 2013)

An approach has been proposed for the description of the dispersion transition of a nonwetting liquid in confinement. This approach describes intrusion and extrusion processes for the ground state of a disordered porous medium, which is characterized by the formation of a fractal percolation cluster. The observed transition of the system of liquid nanoclusters in confinement to a metastable state in a narrow range of degrees of filling and temperatures has been explained by the appearance of a potential barrier owing to fluctuations of the collective "multiparticle interaction" of liquid nanoclusters in neighboring pores of different sizes on the shell of the fractal percolation cluster of filled pores. The energy of the metastable state forms a potential relief in the space of the porous medium with many maxima and minima. The volume of the dispersed liquid in the metastable state has been calculated within the analytical percolation theory for the ground state with the infinite percolation cluster. The extrusion-time distribution function of pores has been calculated. It has been found that the volume of the nonwetting liquid remaining in the porous medium decreases with time according to a power law. Relaxation in the system under study is a multistep process involving discontinuous equilibrium and overcoming of many local maxima of the potential relief. The formation of the metastable state of the trapped nonwetting liquid has been attributed to the nonergodicity of the disordered porous medium. The model reproduces the observed dependence of the volume of the dispersed liquid both on the degree of filling and on the temperature.

DOI: 10.1103/PhysRevE.88.052116 PACS number(s): 64.60.My, 47.56.+r, 71.45.Gm

I. INTRODUCTION

The intrusion of a liquid into a porous medium is accompanied by the dispersion of the liquid, and a system of clusters in connected pores is formed in the porous medium. If the liquid is nonwetting, intrusion requires excess pressure, which can be estimated as the Laplace pressure. When the pressure vanishes, the nonwetting liquid should flow out of the porous medium. However, it is known [1–12] that, for many porous media and liquids such as water, aqueous solutions of salts and organic materials, and liquid metals, a part of a liquid or the entire liquid after complete filling can remain in the porous medium after the reduction of pressure. This means that the nonwetting liquid passing to the dispersed state becomes "wetting." The stable dispersed state was observed when studying the hysteresis of the intrusion (extrusion) of the liquid into (from) disordered porous media such as modified silicagels PEP100 C8(C18), KSK-G, Libersorb 23, and Fluca 60C8 [1–12]. Studies of the transition of the liquid to the dispersed state have not yet been reported, but it was shown in [13,14] that the volume of the liquid remaining in the porous medium can be from 1% to 100% and this volume remains unchanged in the observation time from several hours to several months for various systems [13,14]. The entrapment of the nonwetting liquid was observed for disordered porous media with various porosities, wide and narrow pore size distributions, and various surface energies of the liquid and interfaces between the liquid and the frame of the porous medium. It was also found that the volume of the trapped liquid depends on the size of granules [15] and the observation time [16]. It was revealed in [17] that the dispersion of the liquid in the porous medium after removal of the pressure critically depends on the initial degree of filling and the temperature. Consequently, the dispersion of the liquid is a threshold phenomenon and can be described taking into account correlation effects at the "interaction" between the liquid clusters in neighboring connected pores. For this reason, the entrapment of the liquid can not be explained under the assumptions on intrusion (extrusion) into (from) individual "noninteracting" pores.

The authors of [15,18] assumed that entrapment occurs because the disordered porous medium includes configurations of pores consisting, e.g., of a large pore surrounded by smaller pores connected to the large pore. Then, after the first filling of the porous medium and the subsequent reduction of excess pressure to the Laplace pressure, small pores become empty and the liquid from the large pore can not be extruded because possible paths for its extrusion are broken. The authors of [15] attributed the observed entrapment of the liquid at fragmentation and the reduction of the sizes of granules of the porous medium to the existence of such configurations. The correlation effects of the interaction between liquid clusters in neighboring pores were considered in [16,19–21]. The authors of [16] introduced the Hamiltonian of the lattice gas, which contains two sets of the occupation numbers to describe the intrusion-extrusion hysteresis and entrapment after the complete filling. One set describes occupation of a site of the lattice by either a pore or a frame. The other set corresponds to an empty or liquid-filled pore. This Hamiltonian with various relations between its parameters allows the calculation of intrusion-extrusion dependencies in a variant similar to diluted magnets or in the variant of the mean field, taking into account a random distribution of pores in neighboring sites of the lattice. The authors of [16,20,21] believe that the intrusion of liquid and its extrusion can be described as the diffusion transport of vapor for which it is unnecessary to take into account transport

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[*] VDBorman@mephi.ru
[†] VAByrkin@mephi.ru

paths through a certain system of filled pores. In the performed Monte Carlo studies of entrapment with the Glauber-Kawasaki algorithm, it was also assumed that the liquid flows from a filled pore to a neighboring empty pore. In these approximations, extrusion at the reduction of the pressure is represented as the decay of a nonequilibrium state and the volume of the trapped liquid is determined by the ratio of the observation time to the characteristic transport time. The dependence of the volume of the trapped liquid on the observation time was determined in [16] for the mercury-Vycor system. The performed calculations qualitatively describe the observed increase in the volume of mercury trapped in pores for Controlled Pore Glass (CPG) and Vycor glasses with reduction of the experiment time. However, it is noteworthy that the assumption of transport through gas diffusion contradicts the observed liquid extrusion time after the removal of excess pressure in the experiments with water and the L23 porous medium [22]. For the system studied in [22], this extrusion time is ~ 0.1 s. In the case of mercury, the time of diffusion transport of vapor is several orders of magnitude longer than that for water because the density of saturated vapor is much lower than the density of water.

In [1,2], entrapment after complete filling was considered in the framework of statistical theory of fluctuations [23]. It was assumed that the liquid remains in pores where the spontaneous extrusion condition is not satisfied. This condition for the extrusion fluctuation probability is determined by the competition between the energy of the frame-liquid surface and the energy spent on the formation of the liquid-gas surface in the formed menisci in throats connecting the drained pore with the surrounding filled pores. The spontaneous extrusion condition makes it possible to calculate the volume of the nonwetting liquid remaining in the porous medium. The inclusion of these correlation effects and transport of the liquid through filled pores of the infinite cluster makes it possible to calculate and explain [19] thermal effects and temperature dependencies of the intrusion-extrusion pressure. It is assumed in [19] that all pores of the porous medium have the same radius. For this reason, the dispersion transition and critical character of entrapment after arbitrary intrusion can not be described within this approach because the pressure varies at arbitrary filling and pores with different radii are filled. Thus, the mechanism of the entrapment of the nonwetting liquid in the disordered nanoporous medium remains unclear. This study is devoted to theoretical research of the kinetics of dispersion transition.

Our approach is as follows. We consider granules of the porous medium with the size $L \gg \bar{R}$ ($\bar{R}$ is the average size of pores) with a known pore size distribution that are immersed in a nonwetting liquid. The porosity φ of the porous medium exceeds the percolation threshold so that the system of connected pores is formed in the granules. The state of the porous medium is described by the N-particle distribution function, depending on the coordinates of the pores, their sizes, and filling factors (0, 1) of the pores with the liquid (Sec. II). This approach allows the description of extrusion entrapment for the ground state of the disordered porous medium, which is characterized by the formation of a fractal percolation cluster. Since pores in the percolation cluster are connected to each other, paths for the extrusion of the liquid from granules appear when pores are filled. It is assumed that the medium can be described in the model of randomly distributed polydisperse overlapping spheres. In this section, the single-particle distribution function and the correlation function of the mutual arrangement and overlapping of neighboring pores with various sizes are calculated in order to determine the condition of spontaneous extrusion of the liquid. These functions make it possible to determine an extrusion-induced change in the surface energy of the interaction between the liquid and the frame of the porous medium in a pore and the surface energy of the interaction between the liquid cluster in a pore with the liquid clusters in neighboring pores. The calculation of these energies is based on the analytical percolation theory. The sizes of the pores and the number of the liquid clusters in neighboring pores are random variables in the problem. According to the condition of extrusion through pores in the infinite cluster of filled pores, the energy is calculated for filled pores in the bulk and on the shell of the fractal percolation cluster with a random number of filled neighboring pores. This method makes it possible to calculate the distribution function of pores in the time of extrusion, to reveal a power law of relaxation of the system, and to calculate the volume of the trapped liquid (Sec. III). The dependence of this volume on the initial degree of filling obtained in this section allows the description of the critical character of the dispersion transition and the dependence on the degree of filling taking into account the independently measured porosity φ, average size of the pores $\bar{R}$, half-width of the pore size distribution, and the surface tension coefficients of the liquid at the liquid-gas and liquid-frame interfaces, as well as the dependence of this volume on the observation time and on the size of the granule of the porous medium. Within this approach, the formation of the dispersed state of the liquid can be considered as a process with discontinuous equilibrium that is due to numerous activated transitions through barriers that are spatially distributed in the porous medium and have various heights for pores of various radii and various numbers of neighbors of filled pores at various places on the rough shell of the fractal percolation cluster of filled pores. Another established reason for entrapment is the decomposition of the percolation cluster with the formation of localized clusters of filled pores. Paths for the extrusion of the liquid are absent in pores of such clusters, and this case corresponds to the nonergodic behavior of the system with the infinitely high barrier separating the dispersed state of the liquid in these localized clusters. In view of the revealed properties of entrapment and dispersion transition, the system consisting of the disordered porous medium and nonwetting liquid is similar in properties to spin glass [24] and other nonergodic systems [25–32]. In contrast to a similar problem for spin glasses, the problem for this system with the short-range interaction between liquid clusters in neighboring pores can be solved under accepted assumptions owing to the introduction of the ground state of the disordered porous medium with the infinite percolation cluster of filled pores.

II. PHYSICAL PICTURE OF THE DISPERSION TRANSITION

Let a porous body be formed by a solid frame inside which pores form a spatial structure as polydisperse overlapping spheres. This model of the porous medium is a generalization of the model of randomly distributed spheres that is widely used to describe porous media [33]. The pores in the real media do not have spherical symmetry and the surface tension discussed in the paper depends on the surface shape of the pores. Actually, the average value of surface tension σ, $\delta\sigma$ in nonspherical pore surface is used in the paper. Such an approach makes it possible to use the model of a porous medium in the form of randomly distributed spheres. Within the framework of this model, analytical results and a qualitative description of the observed phenomena could be obtained. In the model of randomly distributed spheres, a unit pore is a spherical void with cuts (throats). In this model, a "quantum" of the change in the volume of the liquid in the medium at intrusion (extrusion) is intrusion-extrusion for one pore. It is suggested that the volume of throats is negligibly small as compared to the volume of pores. When the liquid is intruded into a pore and is extruded from it, menisci of the liquid are formed in these throats. Let the half-width δR of the pore size distribution satisfy the inequality $\delta R/\bar{R} < 3$, which guarantees that the percolation threshold through connected pores is independent of the radius of pores [34].

Pores can be filled only when they are connected to each other through throats and with the surface of the porous medium. This is the case if the porosity of the medium is such that the system of pores in it is above the percolation threshold $\varphi > \varphi_c$. For various models of the porous medium, the percolation threshold is $\varphi_c = 0.16 \div 0.3$ [33,35,36] and is characteristic of the porous medium. The connection of pores with each other is a result of the appearance of an infinite (geometric) cluster consisting of such pores at $\varphi = \varphi_c$. At a given pressure, only pores whose radii are larger than a certain value can be filled; therefore, the filling of the disordered porous medium at $\varphi > \varphi_c$ is the filling of the percolation cluster consisting of interconnected pores with various radii.

The extrusion of the liquid from a pore becomes possible under the following two conditions:

(1) Its extrusion should be energetically favorable. Negative work should be spent on the extrusion of the liquid from a pore owing to the change in the energy of the (porous medium-liquid) interface and to the formation of menisci in throats of neighboring pores.

(2) Since the liquid can flow only through a connected system of filled pores, geometric paths for the outflow of the liquid from a given pore should exist.

For this reason, the extrusion of the liquid from the pore in this medium after the reduction of excess pressure can be considered as a result of the depletion of the pore belonging to the percolation cluster of connected pores with various sizes filled with the liquid.

The entrapment of the liquid in this medium can be explained by the geometric reason when the porous medium contains clusters with a finite number of filled pores for which paths for extrusion are absent and the energy reason when the liquid in pores remains in the stable state at the vanishing of the pressure because positive work is necessary for the extrusion of the liquid. To estimate the critical degree of filling θ_{cr} and the critical temperature T_{cr} at which the nonwetting liquid can remain in the porous medium at excess pressure $p = 0$, we assume that paths for the extrusion of the liquid from the pores under consideration exist and use the statistical theory of fluctuations. We consider the change in the state of the (liquid-porous medium) system at the extrusion of the liquid from the pore surrounded by empty and filled pores at partial filling. These surrounding pores are connected to the pore under consideration through throats in the mouths of which a meniscus appears if one of two connected pores are not filled with the liquid. According to [23], the probability w of the change in the state of the system in unit time at the extrusion of the liquid from the pore under consideration under the action of fluctuations in the system is determined by the change in the entropy of the system ΔS at the extrusion of the liquid from the pore: $w \sim \exp(\Delta S)$. The proportionality coefficient in this relation is determined by the extrusion dynamics of the liquid. Consequently, the entrapment of the liquid in this medium can be due, first, to the geometric reason, when the porous medium contains clusters with a finite number of filled pores for which paths for extrusion are absent and, second, to the energy reason associated with the change in ΔS. We consider the second reason. We suggest that the change in the temperature of the system can be neglected in this process. This corresponds to the experimentally observed small thermal effect [8,37]. Then, the probability can be written in the form

$$w = w_0 \exp(-\delta A/kT). \tag{1}$$

Here, w_0 is the preexponential factor taking into account the extrusion dynamics of the liquid from the porous medium and δA is the isothermal work that should be spent on the extrusion of the liquid from the pore. This work serves as a potential barrier for extrusion in the case under consideration. The quantity δA should include the work pV done by the system for an increase in its volume by the volume V of the pore at the pressure p and the change in the surface energy ΔE of the liquid in the pore. In the initial state, the surface energy of the liquid in the pore E_i consists of the energy E_{isl} of the [solid- (frame-) liquid] interface and the surface energy E_{ilg} of the liquid-gas interface summed in all mouths connecting the pore under consideration with surrounding empty pores. We assume that the state of the liquid in surrounding pores remains unchanged at the extrusion of the liquid from the pore under consideration. Consequently, the surface energy E_f in the final state consists of the energy E_{fsg} of the solid-gas interface and the energy E_{flg} of the liquid-gas interface, which appears in the mouths of the throats connecting the empty pore under consideration with the surrounding filled pores. We represent the work δA spent on an increase in the volume of the system and on the change in the surface energy in the form of the difference between the energy of the interface in the pore near the surface of the frame and the difference between the total surface energy of menisci in the mouths of all throats connecting the pore with the neighboring pores in the final and initial states after and before extrusion. In this case,

$$\begin{aligned} \delta A &= pV + \Delta E, \quad \Delta E = \Delta E_s + \Delta E_l, \\ \Delta E_s &= E_{fsg} - E_{isl}, \quad \Delta E_l = E_{flg} - E_{ilg}. \end{aligned} \tag{2}$$

Let the number of neighboring pores be z, including n filled pores and $z - n$ empty pores before extrusion, so that the number of menisci in the mouths of throats is $z - n$. After extrusion, the number of menisci becomes n, which is the number of neighboring filled pores. Then,

$$\begin{aligned} \Delta E_s &= (\sigma_{sg} - \sigma_{sl})(s - s_m z) = -\delta\sigma(s - s_m z), \\ \Delta E_l &= \sigma s_m[k - (z - k)] = \sigma s_m(2k - z). \end{aligned} \tag{3}$$

Here, $\delta\sigma = |\sigma_{sg} - \sigma_{sl}|$ is the change in the specific surface energy of the solid (frame of the porous medium) at the extrusion of the liquid (for the nonwetting liquid, $\sigma_{sg} < \sigma_{sl}$) and s and s_m ($s_m z < s$) are the surface areas of the pore and meniscus in the mouth of the throat connecting two neighboring pores, respectively.

According to Eqs. (2) and (3), the extrusion potential barrier decreases with the pressure p. In the described experiment, the fraction of the trapped liquid is determined after removal of excess pressure, i.e., at $p = 0$. In this case, the potential barrier $\delta A(p = 0)$ is determined by the sum $\Delta E_s + \Delta E_l$, where $\Delta E_s < 0$ according to Eq. (3) and ΔE_l changes sign when the number of neighboring filled pores is $n = z/2$. At $n < z/2$ and, correspondingly, according to Eq. (3), at $\Delta E_l < 0$, the extrusion potential barrier is negative and the nonwetting liquid can not remain in the porous medium after removal of excess pressure. If the number n of the neighboring filled pores is larger than half of the number of neighbors $n > z/2$, the extrusion potential barrier can be both positive and negative, depending on the relation between ΔE_s and ΔE_l. Thus, the nonwetting liquid can remain in the porous medium at $p = 0$ if the extrusion-induced change ΔE_l in the energy of the liquid in the mouths of the throats connecting the pore with neighbors exceeds the change $|\Delta E_s|$ in the energy of the boundary of the frame in the pore.

At $\delta A = 0$, the spontaneous extrusion of the nonwetting liquid should occur owing to thermal fluctuations in the system. This condition can be used to estimate the critical degree of filling θ_{cr} at which the nonwetting liquid can remain in the porous medium at excess pressure $p = 0$.

The degree of filling θ in the mean-field approximation defines the fraction of filled pores in a macroscopically small volume of the porous medium. Hence, the critical degree of filling in this approximation can be estimated as the fraction (n/z) of filled pores neighboring for the pore under consideration, i.e., $\theta \approx n/z$, and the condition $\delta A(p = 0) \approx 0$ in view of Eq. (3) can be represented in the form

$$\delta\sigma\left(1 - \frac{z s_m}{s}\right) = \sigma\frac{z s_m}{s}(2\theta_{\mathrm{cr}} - 1). \tag{4}$$

We introduce the cosine of the wetting angle $|\cos\psi| = \delta\sigma/\sigma$, and the parameter $\eta = \frac{z s_m}{s}$ determining the geometric connectivity of pores through the mouths of neighboring pores. To estimate the number of the neighboring pores in the disordered porous medium, we use the model of randomly distributed overlapping spheres [33,38]. In this model, pores are represented in the form of randomly distributed overlapping spheres with the same radius R. The area s_m of the mouths of the throats connecting two neighboring pores and the average number z of the nearest neighbor pores in this model depend on the porosity φ and are given by the formulas [33,38]

$$z = -8\ln(1 - \varphi), \quad s_m = \frac{9\pi^2}{256}R^2. \tag{5}$$

Condition (4) for the critical degree of filling can be written in the form

$$\theta_{\mathrm{cr}} = \frac{1}{2}\left[1 + |\cos\psi|\left(\frac{1 - \eta}{\eta}\right)\right]. \tag{6}$$

According to the data reported in [2,17,22], the porosity for the system consisting of the L23 porous medium and water is $\varphi \approx 0.5$ and, according to Eqs. (5), the number of the nearest neighbors is $z = 6$ and the area of the mouths of pores is $s_m =$ 13 nm^2. For this system, $|\cos\psi| \approx 0.2$ [19]. Then, according to Eq. (6), the critical degree of filling at which the nonwetting liquid can be trapped in the porous medium at zero excess pressure is $\theta_{\mathrm{cr}} = 0.7$. This value is consistent with the value $\theta_{\mathrm{cr}} = 0.9$ experimentally determined at $T = 290$ K [17].

According to Eqs. (2)–(4), the potential barrier at degrees of filling smaller than θ_{cr} is negative [$\delta A(p = 0) < 0$] and the characteristic time of extrusion $\tau \sim w^{-1}$ is determined by the hydrodynamic time $\tau_0 \sim w_0^{-1}$ of the motion of the liquid in the porous medium. The quantity τ_0 was determined experimentally [22] and is $\tau \approx 10^{-1}$ s for the systems studied in [17]. According to Eqs. (2)–(4), the potential barrier at degrees of filling larger than θ_{cr} is positive [$\delta A(p = 0) > 0$] and increases with θ. In particular, $\delta A \approx 1$ eV at $\theta = 1.1\theta_{\mathrm{cr}}$. As the temperature increases, σ decreases [39], whereas $\delta\sigma$ and $|\cos\psi|$ increase [19,40]. For this reason, according to Eq. (6), the critical degree of filling at a certain critical temperature T_{cr} becomes larger than unity and the liquid should not remain in the porous medium.

The estimates of θ_{cr} show that the entrapment of the nonwetting liquid can be attributed to the formation of the potential barrier as a result of fluctuations in the number of menisci in the mouths of the throats connecting the neighboring filled pores and the pore from which the liquid flows at the degree of filling $\theta < \theta_{\mathrm{cr}}$. At these degrees of filling and extrusion observation time smaller than the fluctuation decay time of the state of the system, a long-lived metastable state of the nonwetting liquid appears in the form of the ensemble of liquid nanoclusters in pores (dispersed liquid).

We now discuss a physical reason for the transition of the nonwetting liquid to a metastable dispersed state at confinement. The surface energy of the system of liquid clusters in completely filled pores is not reduced to the sum of the surface energies of all independent liquid clusters. Clusters can contact with each other in neighboring pores connected through throats. The mouths of these throats are free of the liquid-gas surface if the pore is connected through throats with neighboring filled pores. This means that the surface energy of two clusters in neighboring pores is lower than the surface energy of two independent clusters by the energy of the liquid-gas surface in the mouth of the throat connecting these filled pores. A decrease in the surface energy can be considered as the negative energy of the interaction between two liquid clusters, i.e., as the effective attraction between interacting clusters. This is the physical meaning of the energy ΔE_l introduced in Eqs. (2) and (3). It takes into account the "multiparticle interaction" of the liquid cluster in the pore with clusters existing in neighboring connected pores. The interaction between liquid clusters can be responsible for the situation where the total energy of "the multiparticle attractive interaction" at the degree of filling $\theta > \theta_{\mathrm{cr}}$ becomes higher [see Eq. (4)] than the energy of the liquid-solid interface. In this case, extrusion is energetically unfavorable after removal of excess pressure. The probability of extrusion w (1) can be smaller than the inverse observation time and the system of clusters becomes "condensed."

The above estimates of the probability of extrusion w were based on the assumptions that the disordered porous medium is homogeneous and isotropic and that the local geometric configuration consisting of the liquid cluster in the completely filled pore and its nearest liquid clusters in connected neighboring pores is identical throughout the volume of the porous medium. However, there are several reasons for which various spatially inhomogeneous geometric configurations consisting of the liquid cluster in the pore and its environment appear in the disordered porous medium. Such an inhomogeneity can appear according to the model of randomly distributed overlapping spheres at $R = \text{const}$ [33,38] in the case of spatially nonuniform porosity. According to Eqs. (5), the number of the nearest neighbor pores and, as a result, variation of the potential barrier and the probability of extrusion of the liquid from the pore, are inhomogeneous in this case. Another reason can be the dependence of the connectivity parameter η of the pores [see Eq. (6)] on the radius of the pore if the porous medium contains pores of different sizes. In this case, for example, a larger pore can be surrounded by smaller pores or by a smaller number of neighboring pores. As a result, spatial variations appear in geometric configurations of the pore and its environment. This situation appears at various degrees of filling because larger pores are filled at smaller degrees of filling requiring lower pressures.

An additional reason for the variation of the local configuration of the pore and its environment [36] when the porosity φ is above the percolation threshold φ_c is that the fractal percolation cluster of pores connected to each other and with the surface of the porous medium appears in the porous medium, disordered or with a lattice of pores. This fractal cluster with the size l has a nonsmooth strongly rough shell [36] with the area $S \sim l^{2.4}$ and volume $V \sim l^{2.4}$. Connection between pores in the percolation cluster ensures its filling and the extrusion of the liquid from it. For this reason, filling is accompanied by the formation of a percolation cluster of filled pores inside this percolation cluster of pores. The percolation cluster of filled pores appears at the degree of filling $\theta > \theta_c = \varphi_c$. Because of the fractality of the percolation cluster, filled pores on the shell of this cluster at a given degree of filling can have different numbers of neighboring filled (or empty) pores, and, according to Eq. (3), different extrusion potential barriers. Thus, within the percolation theory, variations of the local configurations of the pore and its environment can be taken into account and the extrusion of the liquid from the porous medium can be adequately described. Variations of the local configurations of the pore and its environment at the extrusion of the liquid from the pore can lead to the decomposition of the infinite cluster of filled pores and to the formation of clusters containing a finite number of filled pores for which paths for extrusion are absent. Consequently, to describe the dispersion transition, it is necessary to calculate the change in the volume and energy of the liquid in the disordered porous medium taking into account a possible break of paths for the extrusion of the liquid, to describe the porous medium filled with the nonwetting liquid, and, using this description, to calculate the volume of the liquid trapped in the porous body after removal of the pressure, which is due to the above two reasons.

III. ENERGY AND FLUCTUATIONS IN THE EXTRUSION BARRIER FOR THE NONWETTING LIQUID, DISPERSED IN THE DISORDERED NANOPOROUS MEDIUM

We consider a spatially disordered porous medium consisting of N pores with various random radii R_i that has the porosity φ and is filled to the degree of filling θ. Each pore that has the radius R_i and is located at the point $\vec{r}_i$ can be either filled or empty. We introduce the number n_i that is unity and zero if the pore with the radius R_i at the point $\vec{r}_i$ is filled with the liquid and is empty, respectively. The phase space of this system is the $5N$-dimensional space of the coordinates of the pores, their radii, and filling factors n_i of all N pores. Let $F(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N,n_1,n_2\ldots n_N)$ be the N-particle distribution function of pores in their coordinates $\vec{r}_i$, radii R_i, and filling factors n_i. The function $F(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N,0_1,0_2\ldots 0_N)$ is the N-particle distribution function of empty pores and $F(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N,1_1,1_2\ldots 1_N)$ is the distribution function of pores in the completely filled porous medium. At $\theta < 1$, various geometric configurations of filled and empty pores can correspond to the state of the porous medium. Consequently, for the porous medium filled to the degree of filling θ, the multiparticle distribution function of empty and filled pores $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ is degenerate and can be obtained from $F(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N,n_1,n_2\ldots n_N)$ by summing over these configurations $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N) = \sum_{k=1}^{N_\theta} F(\vec{r}_1,R_1\ldots\vec{r}_N,R_N\{n_i\}_\theta^k)$. The distribution function $F(\vec{r}_1,R_1\ldots\vec{r}_N,R_N\{n_i\}_\theta^k)$ corresponds to $\{n_i\}_\theta^k$ configurations of empty and filled pores such that the total relative volume of filled pores is θ, the index $k = 1,\ldots,N_\theta$ enumerates these configurations, and N_θ is the maximum number of degenerate configurations. In particular, in the case of nonoverlapping pores, the multiparticle distribution function of empty and filled pores $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ for the porous medium with the degree of filling θ has the form $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N) = \sum_{\{n_i\}} F(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N,\{n_i\})\delta(\frac{\sum_{i=1}^N n_i V_i}{\sum_{i=1}^N V_i} - \theta)$, where V_i is the volume of the ith pore.

The total thermodynamic potential, which is the energy of the porous medium filled to the degree of filling θ, can be represented in the form

$$E = \int \sum_{k=1}^{N_\theta} \varepsilon\left(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N\{n_i\}_\theta^k\right) \times F_\theta\left(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N\{n_i\}_\theta^k\right) d\Gamma. \quad (7)$$

We calculate the change δE in the energy of the system at the extrusion of the liquid from a randomly chosen filled pore in the porous medium. Let this pore have the radius R_1 and be at the point $\vec{r}_1$. We assume that the state of the remaining multiparticle system, except for the chosen pore, remains unchanged in this process; this assumption corresponds to the mean-field approximation in the description of the extrusion of the liquid from pores of the porous medium. In this case, the multiparticle distribution function of empty and filled pores in the porous medium can be represented in the form

$$\begin{aligned} &F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)\\ &\quad = f(\vec{r}_1,R_1)F_\theta(\vec{r}_2,R_2\ldots\vec{r}_N,R_N). \end{aligned} \tag{8}$$

Here, $f(\vec{r}_1,R_1)$ is the single-particle distribution function of filled pores normalized to the total number of filled pores in the porous medium filled to the degree of filling θ. In view of Eqs. (7) and (8), the change ΔE in the energy in Eq. (2) can be represented in the form

$$\delta E = \int \delta\varepsilon(\vec{r}_1,R_1)f(\vec{r}_1,R_1)d\vec{r}_1dR_1. \tag{9}$$

Here, $\delta\varepsilon(\vec{r}_1,R_1)$ is the change in the energy of the system at the depletion of one pore

$$\begin{aligned} &\delta\varepsilon(\vec{r}_1,R_1)\\ &\quad = \int d\vec{r}_2\ldots d\vec{r}_{N-1}dR_2\ldots dR_{N-1}\\ &\qquad \times \delta\varepsilon(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N),\\ &\delta\varepsilon(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\\ &\quad = \sum_{k=1}^{N_\theta}\delta\varepsilon\big(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N\{\Delta n_1 = 1,n_2\ldots n_{N-1},\}_\theta^k\big)\\ &\qquad \times F_\theta\big(\vec{r}_2,R_2\ldots\vec{r}_{N-1},R_{N-1}\{n_2\ldots n_{N-1}\}_\theta^k\big). \end{aligned} \tag{10}$$

The quantity $\delta\varepsilon(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ in Eqs. (10) is the sum of the energy $\delta\varepsilon_1(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ of the (porous medium-liquid) interface and the energy $\delta\varepsilon_{\text{int}}(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ necessary for the formation of menisci in the throats of neighboring pores. It is assumed that the chemical potential of the liquid remains unchanged at its dispersion. This is valid for pores with sizes $R > 1$ nm [13]. Including the work pV spent on an increase in the volume of the system V, the expressions for energies $\delta\varepsilon_1(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ and $\delta\varepsilon_{\text{int}}(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ can be represented in the form

$$\begin{aligned} &\delta\varepsilon(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\\ &\quad = pV(\vec{r}_1,R_1) - \delta\sigma[1-\eta(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)]S(\vec{r}_1,R_1),\\ &\eta = \frac{S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)}{S(\vec{r}_1,R_1)},\\ &\delta\varepsilon_{\text{int}}(\vec{r}_1,R_1\ldots\vec{r}_N,R_N) = \sigma\delta S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N). \end{aligned} \tag{11}$$

Here, σ is the surface energy of the liquid; $\delta\sigma = (\sigma_{ls} - \sigma_{sg})$ is the difference between the surface energies of the solid-liquid and solid-gas interfaces; $V(\vec{r}_1,R_1)$ and $S(\vec{r}_1,R_1)$ are the volume and surface area of the depleted pore, respectively; $S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ and $\delta S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ are the area of menisci in the pore and the change in the area of menisci at the depletion of the pore, respectively; and p is the pressure of the liquid in the pore. We accept that the area of menisci and the change in the area of menisci at the depletion of the pore are determined only by the nearest environment of the depleted pore. Effects associated with the transport of the liquid to the pores following the nearest environment of the depleted pore without extrusion from the porous medium are neglected. In this case, it follows from Eqs. (8)–(11) that $\delta\varepsilon(\vec{r}_1,R_1)$ can be represented in the form

$$\begin{aligned} &\delta\varepsilon(\vec{r}_1,R_1) = pV(\vec{r}_1,R_1) - \delta\sigma(1-\langle|\eta(\vec{r}_1,R_1)|\rangle)S(\vec{r}_1,R_1)\\ &\qquad + \delta\varepsilon_{\text{int}},\\ &\langle\eta(\vec{r}_1,R_1)\rangle = \frac{\langle S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle}{S(\vec{r}_1,R_1)},\\ &\delta\varepsilon_{\text{int}}(\vec{r}_1,R_1) = \sigma\langle\delta S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle\\ &\qquad = \sigma\langle W(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle. \end{aligned} \tag{12}$$

Here,

$$\begin{aligned} &\langle S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle\\ &\quad = \int F_\theta(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\sum_{k=1}^{z}s_m(\vec{r}_1,R_1,\vec{r}_k,R_k)\\ &\qquad \times d\vec{r}_2,dR_2\ldots d\vec{r}_N,dR_N\\ &\quad = \int d\vec{x}\,dR_1S_m(\vec{r}_1,R_1,\vec{x},R_2)g_2(\vec{r}_1,R_1,\vec{x},R_2), \end{aligned} \tag{13}$$

and $W(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)$ is the change in the number of menisci at the extrusion of the liquid from the filled pore. In Eq. (13), $g_2(\vec{r}_1,R_1,\vec{x},R_2) = g_2(\vec{r}_1,R_1,\vec{r}_1-\vec{r}_2,R_2) = \int d\vec{r}_3dR_3\ldots\vec{r}_NdR_NF_\theta(\vec{r}_1R_1\ldots\vec{r}_NR_N)$ is the pair correlation function of pores in the porous medium filled to the degree of filling θ; $s_m(\vec{r}_1,R_1,\vec{r}_2,R_2)$ is the area of the meniscus of pores with the radii R_1, R_2 that are located at the points $\vec{r}_1$ and $\vec{r}_2$, respectively; z is the number of pores in the environment of the depleted pore; and integration is performed over the distances $|\vec{x}| < R_1 + R_2$ corresponding to the first coordination sphere. For the spatially isotropic medium, $g_2(\vec{r}_1,R_1,\vec{x},R_2) = g_2(R_1,|\vec{r}_2-\vec{r}_1|,R_2)$.

In the model of randomly distributed spheres, the pair correlation function of pores with the radii R and R_1 whose centers are spaced by the distance $\vec{r}$ has the form [41]

$$g_2(R,R_1,\vec{r}) = \varphi^{\frac{1}{R_1^3}[R^3+R_1^3-3/4x^2(R_1-x/3)-3/4y^2(R-y/3)],}. \tag{14}$$

where $x = \frac{R^2-(|\vec{r}|-R_1)^2}{2|\vec{r}|}$ and $y = R + R_1 - x - |\vec{r}|$. The integration of the pair distribution function given by Eq. (14) over the volume nearest to the depleted pore yields the number $z(R,R_1)$ of the nearest neighbor pores with the radius R_1 to the pore of the radius R:

$$z(R,R_1) = \frac{1}{\varphi V_{\text{pore}}}\int_{|R-R_1|}^{|R+R_1|}g_2(R,R_1,\vec{r})d\vec{r}. \tag{15}$$

Here, V_{pore} is the volume of one pore with the radius R_1 and φ is the porosity. Averaging Eq. (15) with the normalized pore size distribution function $f(R_1)$, we obtain the average number of the nearest neighbors of the depleted pore with the radius R:

$$z(R) = \int_0^\infty dR_1f(R_1)z(R,R_1). \tag{16}$$

Expression (16) for the average number of the nearest neighbors was analyzed in [41].

We assume that the extrusion of the liquid from the pore occurs only when at least one of the pores neighboring to the depleted pore belongs to the infinite cluster of filled pores through which the liquid can be extruded from a granule of the porous medium. In this case, the change in the energy of the pore owing to the change in the number of menisci $\sigma\langle\delta S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle=\sigma\langle W(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\, S_m(\vec{r}_1,R_1\ldots\vec{r}_N,R_N)\rangle$ is nonzero only for the states determined by the distribution function $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ that contain at least one realization of the infinite cluster of filled pores. Only states with the infinite cluster of filled pores should be retained. Many realizations of states of the system containing the infinite cluster can exist, corresponding to degeneracy of the state with the infinite cluster of filled pores. For this reason, such a state can be characterized by the probability $P(\theta)$ that the pore belongs to the infinite cluster of filled pores. In this case, the quantity W in Eq. (12) depends on the probability $P(\theta)$ that the pore belongs to the infinite cluster and the number z of the nearest neighbors of the depleted pore with the radius R:

$$W=W[z(R),P(\theta)]\eta(R). \tag{17}$$

The quantity $W(z,\theta_1)$ is determined as the difference between the average number of menisci before and after the depletion of the pore per nearest neighbor. The product of $W(z,\theta_1)$ by the surface energy of the liquid in the menisci determines the change in the energy of the pore at the extrusion of the liquid from it. This quantity can be interpreted as the energy $\delta\varepsilon_{\text{int}}$ of the interaction between the liquid cluster in the pore with the environment at the transition to an unstable state. It follows from Eqs. (11)–(13) that

$$\begin{aligned}\delta\varepsilon(R,\theta_1)&=\delta\varepsilon_1(R)+\delta\varepsilon_{\text{int}}(R,\theta_1),\\ \delta\varepsilon_1(R)&=pV-\delta\sigma[1-\eta(R)]S,\\ \eta(R)&=\frac{\langle S_m(R,R_1)\rangle}{S},\\ \delta\varepsilon_{\text{int}}(R,\theta_1)&=\sigma\langle WS_m\rangle\approx\sigma W(z,\theta_1)\eta(R).\end{aligned} \tag{18}$$

The area of the menisci S_m in Eqs. (18) is determined by the nearest environment of the chosen pore. Consequently,

$$\eta(R)=\frac{1}{4\pi R^2}\int_0^\infty z(R,R_1)s_m(R,R_1)f(R_1)dR_1. \tag{19}$$

Here, $s_m(R,R_1)$ is the area of one meniscus in the throat of the chosen pore with the radius R connected to the pore of the radius R_1. Thus, to calculate the energy $\delta\varepsilon(R,\theta_1)$, it is necessary to calculate the change in the number of menisci at the depletion of the pore $W(z,\theta_1)$ and the connectivity factor $\eta(R)$.

To calculate $W(z,\theta_1)$, we note that the extrusion of the liquid from the completely filled medium first occurs through the formation of individual empty pores and clusters of empty pores at the reduction of the pressure and, at smaller θ values, the formation of the fractal percolation cluster of filled pores on the shell. At $\theta_1>\theta_c$, the function $W(\theta_1>\theta_c)$ should be defined as the average difference between the numbers of menisci after and before the depletion of the pore:

$$W(z,\theta_1>\theta_c)=\sum_{n=0}^{z-1}(1-\theta_1)^n[P(\theta_1)]^{z-n}\frac{z-2n}{z}\frac{z!}{n!(z-n)!}. \tag{20}$$

Here, $P(\theta_1)$ is the probability that the filled pore belongs to the infinite cluster of filled pores. The first and second factors correspond to the probability of the location of an empty pore near the infinite cluster of filled pores under the condition that this pore is surrounded by n empty and $z-n$ filled pores and, hence, contains n menisci. The third factor determines the difference between the relative numbers of menisci after $(z-n)$ and before (n) the filling of the pore. The combinatory factor presents the variants of the distribution of n menisci over the neighbors nearest to the given pore and corresponds to the degeneracy of the local geometric configuration state of the given pore and the filled pores in the first coordination sphere. Thus, each term in the sum in Eq. (20) describes the change in the number of menisci at a given relation between filled and empty pores. Summation in Eq. (20) includes all possible variants of the mutual arrangement of the empty and filled pores and makes it possible to take into account on average variations of fluctuations in the configurations of the pore and its environment consisting of filled and empty pores in the space of the porous disordered medium.

The sum in Eq. (20) can be calculated analytically:

$$W(\theta_1)=[\theta_1+P(\theta_1)-1][P(\theta_1)-\theta_1+1]^{z-1}-(1-\theta_1)^z. \tag{21}$$

Figure 1 shows the dependence $W(z,\theta_1)$ calculated by Eq. (21) for various numbers of the nearest neighbors z. These dependencies reflect the change in the energy of the collective interaction between the filled pore and its environment and the relation between the numbers of neighboring empty and filled pores with the variation of the degree of filling. The calculations were performed with the $P(\theta_1)$ dependence from [42]. Authors of [42] considered regular 3D lattices, whereas in this paper a disordered medium is considered. At the same time, all the analytical calculations further will perform for an arbitrary function $P(\theta_1)$. This function will enter into the expressions in the integral form. Therefore, when calculating the observed values, weak dependence should be expected on

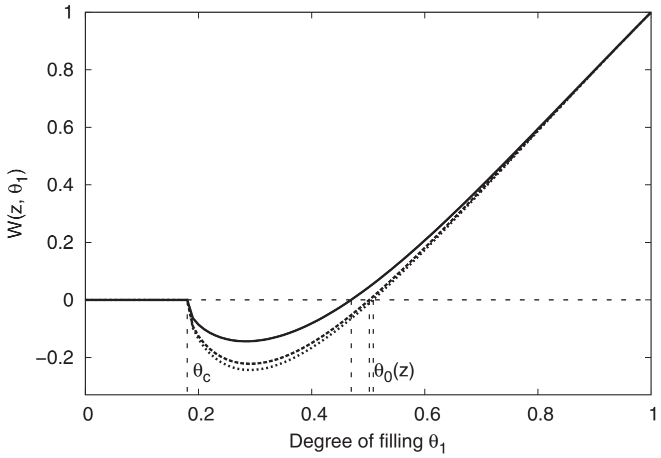

FIG. 1. Change in the number of menisci at the extrusion of the liquid from the filled pore $W(z,\theta_1)$ versus the degree of filling θ_1 at the number of the nearest neighbors $z=$ (solid line) 4, (dashed line) 6, and (dotted line) 8. The functions $W(z,\theta_1)$ changes sign at the points $\theta_0(z)$.

the concrete form of $P(\theta_1)$. According to Eq. (21) (see Fig. 1), the quantity $W(z,\theta_1)$ at $\theta_1 \to 1$ approaches 1, corresponding to the change in the number of menisci at the extrusion of the liquid from one pore in the completely filled porous medium (Fig. 1). A decrease in the degree of filling leads to a decrease in $W(\theta_1)$ owing to the reduction of the number of neighboring filled pores and to an increase in the number of menisci around the filled pore at the extrusion of the liquid. A further decrease in the degree of filling is accompanied by the reduction of the number of menisci after the extrusion of the liquid from the pore and to the change in the sign of $W(z,\theta_1)$ at $\theta_1 = \theta_0(z)$. As will be shown in the following, this behavior indicates that liquid nanoclusters in pores can become unstable and free of the liquid. As can be seen in Fig. 1, the degree of filling $\theta_0(z)$ at which the function $W(z,\theta_1)$ changes sign depends only slightly on the number of the nearest neighbors z in the range from $z = 4$ to 8 and, correspondingly, on the radius of the pore (16). For this reason, approximation (17) can be used in the following. At degrees of filling below the percolation threshold $\theta_1 < \theta_c$, the infinite cluster is absent. In this case, $W(z,\theta_1 \leqslant \theta_c) = 0$ and the liquid can be extruded only from individual clusters connected to the boundary of the porous medium. According to the known distribution function of clusters in the number of pores [36], their number is small, so that the volume of the extruded liquid remains macroscopically unchanged. In this case, $W(z,\theta_1 \leqslant \theta_c) = 0$.

To calculate the connectivity factor $\eta(R)$, a model of the porous medium is necessary. In this work, this factor was calculated in the model of randomly distributed spheres [33] with pores of various radii taking into account correlations in the spatial distribution of the pores in the medium. In this model,

$$\begin{aligned} s_m(R,R_1) &= \frac{1}{V}\int_{|R-R_1|}^{R+R_1} \frac{\pi R\big(R_1^2-(r-R)^2\big)}{r} \\ &\quad\times g_2(R,R_1,r)4\pi r^2 dr, \\ V &= 4\pi/3((R+R_1)^3-|R-R_1|^3), \end{aligned} \tag{22}$$

where $g_2(R,R_1,r)$ is given by Eq. (14).

The calculations by Eqs. (19) and (20) for the Gaussian pore radius distribution function $f(R)$ with the average radius $\bar{R}$ and small half-width $\frac{\delta R}{\bar{R}} < 1$ in this model give [41]

$$\eta = q(R_0/R)^{-\alpha}, \quad \alpha \approx 0.3 \tag{23}$$

where the parameter $q \sim 1$ depends on the porosity φ and R_0 is the minimum radius of the pores in the porous medium, which is determined by the radius distribution function and is on the order of the average radius of the pores divided by the average number of the nearest neighbors $R_0 \sim \bar{R}/\bar{z}$. It follows from Eqs. (16), (19), and (23) that the change in the energy of the liquid in the pore $\delta\varepsilon(\theta,R,p) = \delta\varepsilon_1(R,p) + \delta\varepsilon_{\rm int}(R,\theta_1)$ at the extrusion of the liquid from the spherical pore with the radius R in the partially filled porous medium has the form

$$\begin{aligned} \delta\varepsilon(\theta_1,R,p) &= p\frac{4\pi}{3}R^3 - 4\pi R^2\delta\sigma\left[1-\left(\frac{R_0}{R}\right)^{\alpha} q\right] \\ &\quad + 4\pi q R^{2-\alpha}R_0^{\alpha}\sigma[(\theta_1+P(\theta_1)-1] \\ &\quad \times [P(\theta_1)-\theta_1+1)^{z-1}-(1-\theta_1)^z]. \end{aligned} \tag{24}$$

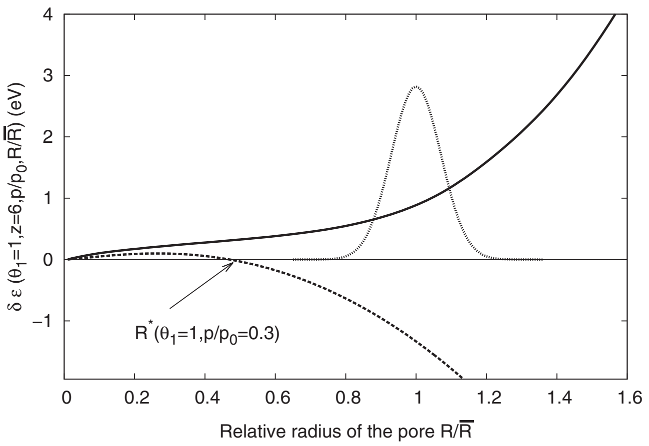

FIG. 2. Change in the relative energy of the liquid in the pore $\delta\varepsilon$ versus the relative radius of the pore $\frac{R}{\bar{R}}$, where $\bar{R}$ is the average radius of the pores, at the relative pressure $p/p_0 =$ (solid line) 1 and (dashed line) 0.3, where $p_0 = \frac{3\sigma}{\bar{R}}$, for $\frac{\sigma}{\delta\sigma} = 4$, $\theta_1 = 1$, and $z = 6$. The dotted line is the normalized Gaussian distribution function of pores with the relative half-width $\frac{\delta R}{\bar{R}} = 0.1$. The radius of the pore R^* is determined from the condition $\delta\varepsilon = 0$.

According to Eq. (24), the change in the energy $\Delta E(\theta,R,p) = \delta\varepsilon_1(R,p) + \delta\varepsilon_{\rm int}(R,\theta_1)$ in the partially filled porous body at the extrusion of the liquid from the pore is determined by the the parameters of the porous medium and liquid $\delta\sigma$, σ, z, and η and depends on the pore radius R, the degree of filling θ_1, the pressure of the liquid in the pore p, and the temperature T, in view of the temperature dependencies of the surface tension coefficients $\delta\sigma(T)$ and $\sigma(T)$.

Figures 2 and 3 show the dependence $\delta\varepsilon(\theta_1,R,p)$ on the radius of the pore at various pressures p and degrees of filling θ_1. The possibility of the extrusion of the liquid from the pore or the entrapment of the liquid in the pore with an

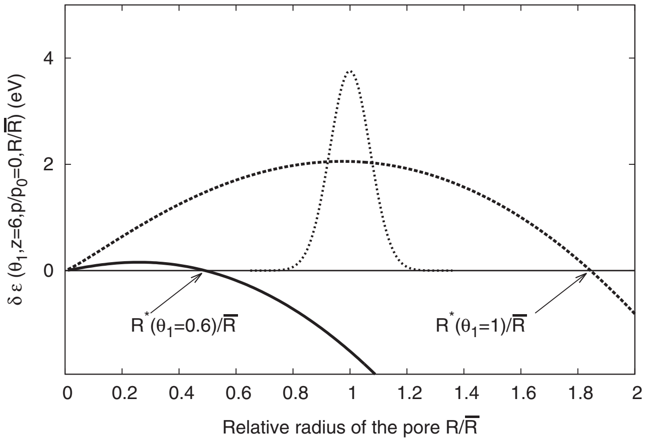

FIG. 3. Change in the energy of the liquid in the pore $\delta\varepsilon$ for $\frac{\sigma}{\delta\sigma} = 4$ and the degree of filling $\theta_1 =$ (dashed line) 1 and (solid line) 0.6 versus the relative radius of the pore $\frac{R}{\bar{R}}$, where $\bar{R}$ is the average radius of the pores at the pressure $p = 0$ and $z = 6$. The dotted line is the normalized Gaussian pore size distribution function with the relative half-width $\frac{\delta R}{\bar{R}} = 0.1$. The equality $\delta\varepsilon = 0$ occurs for $\theta = 0.6$ at $R^*/R = 0.52$ and for $\theta = 1$ at $R^*/R = 1.82$.

increase in its radius is determined by competition between the energetic favorability of extrusion owing to the change in the surface energy of the pore {term $-\delta\sigma[1-\eta(R)]S$ in Eqs. (16) and (24)}, the energetic unfavorability of extrusion because of the presence of the pressure of the liquid [term pV in Eqs. (16) and (24)], and the change in the energy owing to the change in the number of menisci at the extrusion [term $\sigma W \eta S$ in Eqs. (16) and (24)]. Competition between these components of the energy results in the change of the sign of $\delta\varepsilon$ at

$$R^*(z,\theta_1) = q^{\frac{1}{\alpha}} R_0 \left(1 + \frac{\sigma}{\delta\sigma} W(z,\theta_1)\right)^{\frac{1}{\alpha}}. \tag{25}$$

It follows from Eqs. (19), (24), and (25) (see Fig. 3) that the energetic favorability of the entrapment of the liquid from the pore is determined by the sign of the function $W(z,\theta_1)$: if $W(z,\theta_1) < 0$, the extrusion of the liquid from the pore of any size is energetically favorable. At $W(z,\theta_1) > 0$, the entrapment of the liquid in the pore with the radius $R_0 < R < R^*(z,\theta_1)$ becomes energetically favorable, whereas extrusion is energetically favorable for pores with the radius $R > R^*(z,\theta_1)$. Thus, there is an energy barrier that should be overcome for the extrusion of the liquid from the pore [Figs. 2 (dashed line) and 3]. The height and existence of such a barrier depend on the radius of the pore and the degree of filling θ_1 (Figs. 2 and 3). According to Fig. 2 and Eqs. (16) and (23), the change in the energy of the system per pore at the extrusion of the liquid from it at the pressure of the liquid $p/p_0 = 1$ is positive $\delta\varepsilon(\theta, R \to \infty, p) \sim pR^3 > 0$ because the work pV spent on an increase in the volume of the system V dominates. As a result, the extrusion of the liquid from pores of any radius becomes energetically unfavorable. As the pressure decreases, the extrusion or entrapment of the liquid is determined by the competition between the change in the surface energy of the pore and the change in the energy because of the change in the number of menisci at extrusion. For this reason, the extrusion of the liquid from pores with the radius $R_0 < R < R^*(z,\theta_1,p)$ is unfavorable, $\delta\varepsilon(\theta_1,p) > 0$ [Fig. 2 (dashed line)], whereas the extrusion of the liquid from pores with the radius $R > R^*(z,\theta_1,p)$ is favorable, $\delta\varepsilon(\theta_1,p) < 0$ [Fig. 2 (solid line)]. In the case of zero pressure in the liquid $p = 0$ (Fig. 3) and dependence $\eta(R)$ given by Eq. (23), the change in the energy at the extrusion of the liquid from the pore is positive (i.e., entrapment is energetically favorable) at $R_0 < R < R^*(z,\theta_1)$. In this case, the dependence of the energy $\delta\varepsilon(\theta_1,p)$ in Fig. 3 (dashed line) corresponds to complete entrapment because all of the pores in the porous medium satisfy this condition. At $R > R^*(z,\theta_1)$ and negative $\delta\varepsilon(\theta_1,p)$ value, the extrusion of the liquid from the pore is energetically favorable. The solid line in Fig. 3 corresponds to complete extrusion because all of the pores in the porous medium satisfy the condition $R > R^*(z,\theta_1)$.

The energy barrier is maximal (Fig. 3) at the radius of the pore $R = R_{\max}(z,\theta_1) < R^*(z,\theta_1)$. It follows from Eq. (24) that the highest barrier at $p = 0$ is $\delta\varepsilon[z,\theta_1, R = R_{\max}(z,\theta_1)] = \delta\varepsilon_{\max}(z,\theta_1)$ and the corresponding $R_{\max}(z,\theta_1)$ value at various degrees of filling can be calculated from Eq. (24). The result has the form

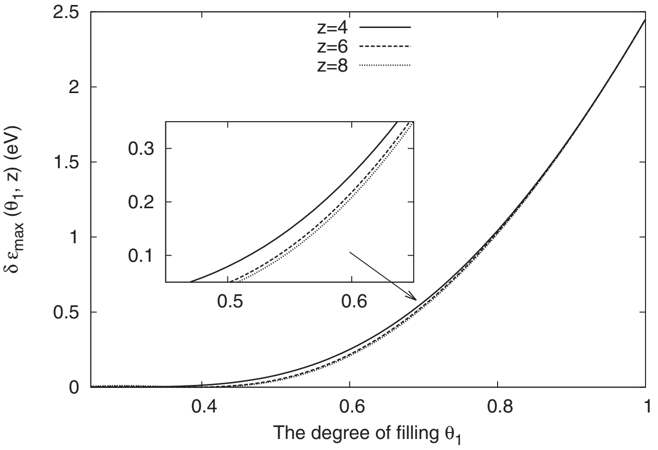

FIG. 4. Barrier height $\delta\varepsilon_{\max}(z,\theta_1)$ eV versus the degree of filling θ_1 at various numbers of the nearest neighbors z at room temperature for $\sigma = 72\ \mathrm{mJ/m^2}$, $\delta\sigma = 22\ \mathrm{mJ/m^2}$, $\bar{R} = 3.6$ nm, $\delta R = 0.4$ nm, and $\varphi = 0.5$.

$$\delta\varepsilon_{\max}(z,\theta_1) = 4\pi R_0^2 \delta\sigma \left(1 - \frac{\alpha}{2}\right)^{\frac{2}{\alpha}-1} q^{\frac{2}{\alpha}} \left[1 + \frac{\sigma}{\delta\sigma} W(z,\theta_1)\right]^{\frac{2}{\alpha}},$$
$$R_{\max}(z,\theta_1) = \left(1 - \frac{\alpha}{2}\right)^{\frac{2-\alpha}{2\alpha}} q^{\frac{1}{\alpha}} \left[1 + \frac{\sigma}{\delta\sigma} W(z,\theta_1)\right]^{\frac{1}{\alpha}}$$
$$= \left(1 - \frac{\alpha}{2}\right)^{\frac{2-\alpha}{2\alpha}} R^*(z,\theta_1). \tag{26}$$

At $R_0 \sim 0.5$ nm, $\delta\sigma \sim 25$ mN/m, $\frac{\sigma}{\delta\sigma} = 3$, and $z = 6$, estimates give $4\pi R_0^2 \delta\sigma \sim 0.01$ eV and $\delta\varepsilon_{\max}(z,\theta_1 = 1) \sim 2.3$ eV.

Figure 4 shows the dependence of the barrier height $\delta\varepsilon_{\max}(z,\theta_1)$ on the degree of filling θ_1 at various numbers of the nearest neighbors. It can be seen in the figure that the barrier height that should be overcome for the extrusion of the liquid from the pore depends only slightly on the number of the nearest neighbors, decreases with θ_1, and is ~2.3 eV at complete filling $\theta_1 = 1$ and decreases to 0.01 eV with a decrease in the degree of filling θ_1 to $\theta_1 \approx 0.35$.

According to Eqs. (25) and (26), $R^*(z,\theta_1)$ and $\delta\varepsilon_{\max}(z,\theta_1)$ depend on the temperature due to the temperature dependencies of the surface tension coefficients $\sigma(T)$ and $\delta\sigma(T)$. Figure 5 shows the dependencies of the energy change given by Eq. (24) on the radius of the pore at various temperatures. It can be seen in Fig. 5 that the change in the temperature from 279 to 293 K qualitatively changes the the behavior of the system. At 279 K, all of the pores in the porous medium are in the region $\delta\varepsilon(R) > 0$ [Fig. 5 (solid line)] and, consequently, the extrusion of the liquid is unfavorable from all pores of the porous medium. At $T = 293$ K, $\delta\varepsilon(R) < 0$ for all pores in the porous medium. In this case, the quantity $\delta\varepsilon(R)$ at $R_0 < R < R^*(T = 293\,\mathrm{K})$ is smaller than $\delta\varepsilon(R)$ at $R_0 < R < R^*(T = 279\,\mathrm{K})$.

IV. DYNAMICS OF THE DISPERSION TRANSITION: THE VOLUME OF THE DISPERSED LIQUID

We now discuss the dynamics of the formation of the dispersed state of the liquid in the nanoporous medium.

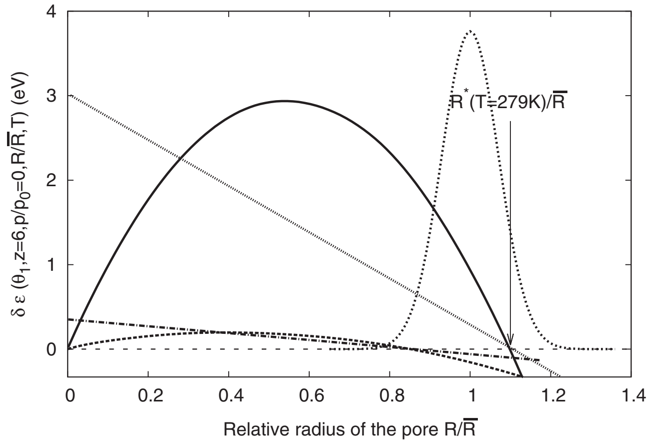

FIG. 5. Radius dependence of the change in the energy given by Eqs. (24) and (40) for $\theta_1 = 1$ at temperatures $T =$ (solid line) 279 and (dashed line) 293 K for $\sigma(T = 279\,\mathrm{K}) = 72\ \mathrm{mJ/m^2}$, $\delta\sigma(T = 279\,\mathrm{K}) = 22\ \mathrm{mJ/m^2}$, and $R_0 = 0.6$ nm. The line of closely spaced dots and dashed-dotted line are the calculations by approximate formula (40) for the temperatures $T =$ (closely spaced dots) 279 and (dashed-dotted line) 293 K. The line of widely spaced dots is the pore radius distribution function $f(R)$ with $\delta R/\bar{R} = 0.1$. The temperature dependence $\sigma(T)$ for water was taken from [43] and the temperature dependence $\delta\sigma(T)$ was taken from [19].

According to Eq. (1), the extrusion barrier determines the time of the extrusion of the liquid from the pore in the porous medium. In the isothermal case under consideration, the isothermal work δA that should be spent on the extrusion of the liquid from the pore is equal to the change in the energy of the pore $\delta\varepsilon(\theta,R,p,z)$. The time of the extrusion of the liquid from the pore of the radius R can be represented in the form

$$w^{-1} \sim \tau_1(R) = \tau_0 \exp[\delta\varepsilon(R,\theta_1,p,z)/T]. \tag{27}$$

Here, τ_0 is the preexponential factor taking into account the extrusion dynamics of the liquid from the porous medium. The time τ_0 can be estimated as follows. Let the liquid flow from the pore of the radius R through a channel of filled pores with the same radius. In this case $\tau_0 = \frac{4\pi R^3}{Q(R)}$ and using the known expression for the liquid flow rate in the channel with the radius R: $Q(R) = \frac{\pi}{8\eta_0}\frac{\Delta p}{L}R^4$ [23] (L is the characteristic size of the granule of the porous body), we get at the following expressions for the times τ_0 and $\tau_1(R)$:

$$\tau_0 = \frac{4\eta_0 L}{3R(p_g - p)}, \quad \tau_1(R) = \tau_0 \exp[\delta\varepsilon(R,\theta_1,p,z)/T]. \tag{28}$$

Here, p_g is the pressure at which the porous medium is filled with the liquid and η_0 is the viscosity coefficient. We consider the case $p = 0$ corresponding to the extrusion of the liquid from the porous medium at the complete removal of the pressure. For the parameters $p = 0$, $L \sim 1\ \mu$m, $\bar{R} \sim 3$ nm, and $p_g \sim 100$ atm, we obtain $\tau_0 \sim 10^{-8}$ s for water. According to Eqs. (28), the time of the extrusion of the liquid from the pore of the radius R is given by the expression

$$\tau_1(R) = \frac{4\eta L}{3Rp_g} \exp[\delta\varepsilon(R,\theta_1,p = 0,z)/T]. \tag{29}$$

It follows from Eqs. (24) and (29) that the time of the extrusion of the liquid from the pore in the case under consideration is determined by the sign of $\delta\varepsilon(\theta_1,R,p = 0,z)$ and, according to Eq. (24) [see Fig. 6(a)], strongly depends on the radius of the pore. As can be seen in Fig. 6(a), the quantity $\delta\varepsilon(R,\theta_1 = 1, p = 0, z = 6, T = 279\,\mathrm{K})$ for pores with the radius $R > 1.1\bar{R}$ in the porous medium is negative, indicating the extrusion of the liquid from such pores in the time $\tau_1 \sim \tau_0$. In this case, the characteristic time of the extrusion of the liquid from the pore for $L = 1\ \mu$m, $\eta_0 = 0.01$ g/(cm s) [43] is estimated as $\tau_1 \sim 10^{-8}$ s. At $R < 1.1\bar{R}$, the barrier height $\delta\varepsilon(R < 1.1\bar{R}, \theta_1 = 1, p = 0, z = 6, T = 279\,\mathrm{K})$ is positive; as a result, the time of extrusion from pores of this size is exponentially large $\tau_1 \gg \tau_0$. For the barrier height $\delta\varepsilon(R < 1.1\bar{R},\theta_1 = 1, p = 0, z = 6) \sim 2$ eV and temperature $T = 279$ K, the time of the extrusion from pores with the radius $R < 1.1\bar{R}$ is estimated as $\tau_1 > 10^5$ s, which corresponds to the entrapment of the liquid in these pores at the observation time $\sim 10^3$ s. The characteristic time of extrusion is $\tau_1 \sim 10^2$ s for pores with the radius $1.1\bar{R} < R < 1.12\bar{R}$ and is $\tau_1 \sim \tau_0 \sim 10^{-8}$ s for pores with the radius $1.12\bar{R} < R < 1.13\bar{R}$. Therefore, the liquid is extruded from pores with different sizes in different times and the number of pores involved in extrusion depends on the observation time. In particular, this should be manifested in the dependence of the amount of the liquid trapped in the porous medium on the observation time.

In order to analyze the entrapment of the liquid in the porous medium, we find the time dependence of the amount of the trapped liquid. The time of the extrusion of the liquid is determined by the time $\tau(R_1,R_2 \ldots R_N,\vec{r}_1 \ldots \vec{r}_N)$ of the extrusion of the liquid from all filled pores with the radii $R_1,R_2 \ldots R_N$ located in the porous medium at the points $\vec{r}_1 \ldots \vec{r}_N$, respectively, where N is the number of the pores in the porous medium. In the disordered porous medium with randomly distributed pores with various sizes, the time $\tau(R_1,R_2 \ldots R_N,\vec{r}_1 \ldots \vec{r}_N)$ is a random function of the radii of filled pores and their spatial configurations.

The distribution function of the times of the extrusion of the liquid from pores $F(t)$ determines the fraction of pores $dN(t)$ from which the liquid is extruded in the time dt: $dN(t) = F(t)dt$. For the nonrandom time of the extrusion of the liquid τ, this function is $F(t) = \delta(t - \tau)$, where $\delta(t)$ is the Dirac delta function. In the case of the random time of the extrusion of the liquid $\tau(R_1,R_2 \ldots R_N,\vec{r}_1 \ldots \vec{r}_N)$, the distribution function is obtained by averaging over all configurations of pores with the radii $R_1,R_2 \ldots R_N$ located in the porous medium at the points $\vec{r}_1 \ldots \vec{r}_N$, respectively:

$$\begin{aligned} F(t) = \int & dR_1 d\vec{r}_1 \ldots dR_N d\vec{r}_N \delta \\ & \times [t - \tau(R_1,R_2 \ldots R_N,\vec{r}_1 \ldots \vec{r}_N)] \\ & \times F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2 \ldots \vec{r}_N,R_N). \end{aligned} \tag{30}$$

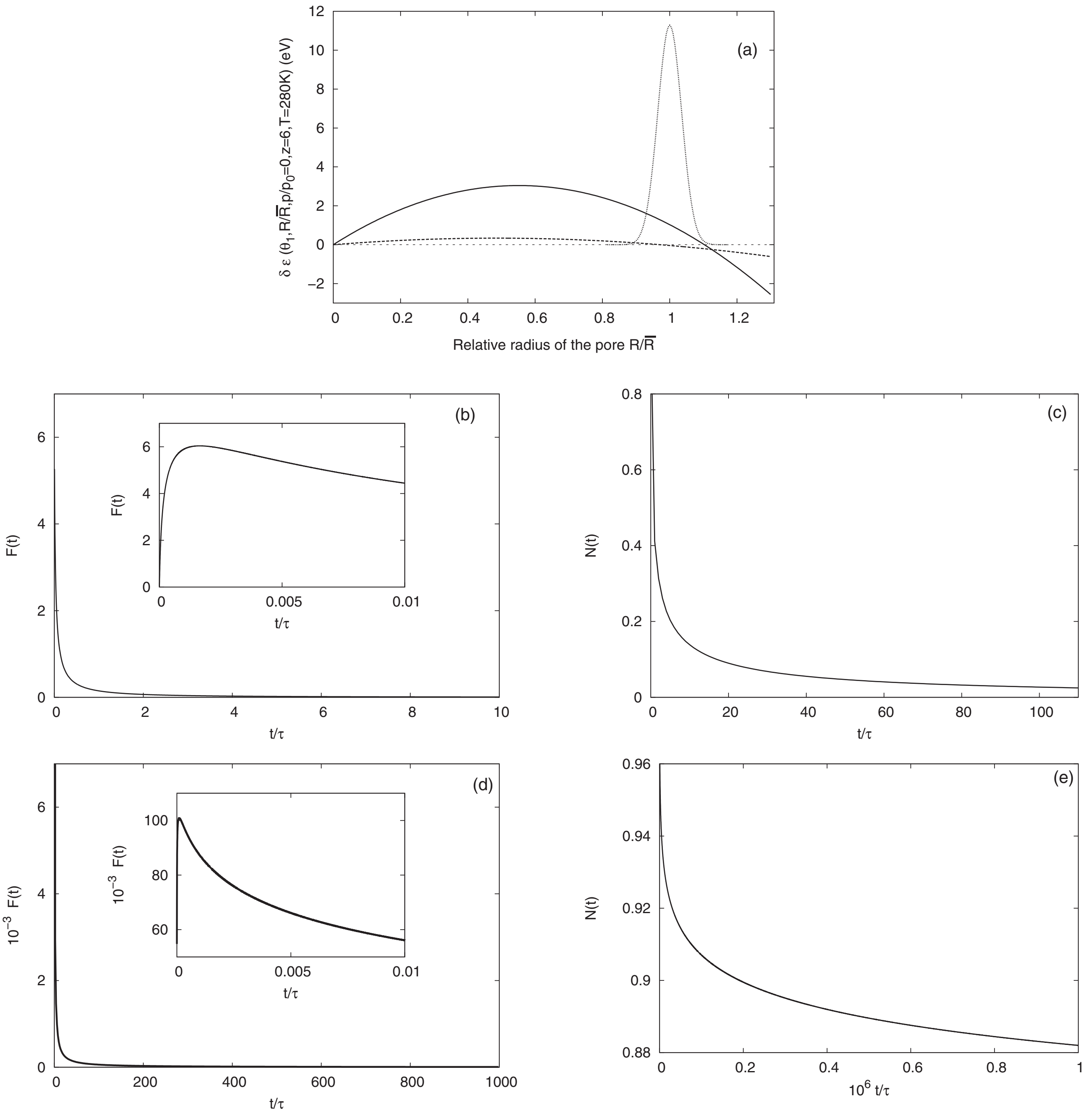

FIG. 6. Change in the energy (a) of the pore $\delta\varepsilon$ versus the relative radius of the pore $\frac{R}{\bar{R}}$ at the degrees of filling $\theta_1 =$ (solid line) 0.85 and (dashed line) 1 and the corresponding (b), (d) distribution functions $F(t)$ and (c), (e) the number $N_1(t)$ of pores in which the liquid is trapped versus the relative time t/τ for $z = 6$ and for (dotted line) the Gaussian functions $f(R)$ with $\bar{R} = 3$ nm, the half-width $\frac{\delta R}{\bar{R}} = 0.1$, and $T = 279$ K for $\sigma = 75$ mJ/m^2, $\delta\sigma = 22$ mJ/m^2, $L = 1$ μm, and $p_g = 100$ atm.

Here, $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ is the multiparticle distribution function of empty and filled pores in the porous medium with the degree of filling θ [see Eq. (8)]. Below, it is suggested that $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ is normalized to unity:

$$\int F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)dR_1\ldots dR_N dr_1\ldots dr_N = 1. \tag{31}$$

According to Eq. (30), the function $F(t)$ is also normalized to unity, $\int_0^\infty d\tau\, F(\tau) = 1$, and the integral of $F(t)$,

$$\int_0^t d\tau\, F(\tau) = N(t), \tag{32}$$

is the fraction of pores $N(t)$ from which the liquid is extruded in the time interval from zero to t.

In the framework of the above mean-field approach, we assume that the distribution function $F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N)$ is the product of the single-particle distribution functions of filled pores, and the time $\tau(R_1,R_2\ldots R_N,\vec{r}_1\ldots\vec{r}_N)$ is the sum of the times $\tau_1(R_i,\vec{r}_i)$ of extrusion from the pore of the radius R_1 located at the point $\vec{r}_1$:

$$\begin{aligned} F_\theta(\vec{r}_1,R_1,\vec{r}_2,R_2\ldots\vec{r}_N,R_N) &= \prod_{i}^{N} f(\vec{r}_i,R_i),\\ \tau(R_1,R_2\ldots R_N,\vec{r}_1\ldots\vec{r}_N) &= \sum_{i=1}^{N} \tau(R_i,\vec{r}_i). \end{aligned} \tag{33}$$

Here, $f(\vec{r}_1,R_1)$ is the normalized single-particle distribution function of filled pores in the porous medium with the degree of filling θ. For the homogeneous medium at $p=0$, the quantity $\tau(R_1,R_2\ldots R_N,\vec{r}_1\ldots\vec{r}_N)$ is independent of the coordinates of the pores $\vec{r}_1\ldots\vec{r}_N$ and is determined by the sum of the times given by Eq. (29):

$$\begin{aligned} \tau(R_1,R_2\ldots R_N) &= \sum_{i=1}^{N}\tau_1(R_i)\\ &= \sum_{i=1}^{N}\frac{4\eta L}{3R_i p_g}\exp[\delta\varepsilon(R_i,\theta_1,p=0,z)/T]. \end{aligned} \tag{34}$$

The approximation specified by Eqs. (33) and (34) implies that the extrusion channel is single for all pores and the configurations of the pore and its environment are independent for each pore. They correspond to an upper estimate for the time of extrusion $\tau(R_1,R_2\ldots R_N,\vec{r}_1\ldots\vec{r}_N)$.

Since the pores with various radii exist in the porous medium with the probability determined by the pore size distribution function, it follows from Eq. (29) that the barrier height $\delta\varepsilon(R,\theta_1,p=0,z)$, preexponential factor $\tau_0=\frac{4\eta L}{3Rp_g}$, and the time of extrusion $\tau(R)$ are random functions.

Using Eqs. (33), we calculate the distribution function $F(t)$ over the times of extrusion of the liquid from the porous medium. Using the representation of the $\delta(t)$ function in the form of the Fourier integral, we write $F(t)$ given by Eq. (30) with $\tau(R_1,R_2\ldots R_N)$ from Eq. (34) in the form

$$\begin{aligned} F(t) &= \int_{-\infty}^{\infty} dk\, e^{ikt} e^{-ik\sum_{i=1}^{N}\tau_1(R_i)} \prod_{i=1}^{N} f_1(R_i)dR_1\ldots dR_N\\ &= \int_{-\infty}^{\infty} dk\, e^{ikt}\prod_{i=1}^{N}\int dR_i\, f_1(R_i)e^{-ik\tau_1(R_i)}\\ &= \int_{-\infty}^{\infty} dk\, e^{ikt} Z^N(k),\\ Z(k) &= \int dR\, f_1(R)e^{-ik\tau_1(R)}. \end{aligned} \tag{35}$$

Here, $f_1(R_1)=\int d\vec{r}\, f(\vec{r},R)$ is the normalized size distribution function of filled pores in the porous medium with the degree of filling θ. Integral (35) is zero for all values $k\neq 0$ because the integrand in Eq. (35) is a rapidly oscillating function at $\tau_1(R)\geqslant\tau_0$ for all k values except for $k\to 0$. Hence, it follows from Eqs. (35) and (29) that the region where $k\tau_1(R)\ll 1$ is significant in the integral determining the function $Z(k)$. In this case, the function $Z^N(k)$ can be represented in the form

$$\begin{aligned} Z^N(k) &= \int dRf_1(R)[1-ik\tau_1(R)]^N\\ &\approx \int dRf_1(R)[1-ikN\tau_1(R)]\\ &\approx \int dRf_1(R)e^{-ikN\tau_1(R)}. \end{aligned} \tag{36}$$

Relation (36) is obtained with the normalization condition for the function $f_1(R_1)$: $\int dRf_1(R)=1$.

In view of Eqs. (35) and (36), the distribution function $F(t)$ for the time of the extrusion of the liquid from the porous medium has the form

$$\begin{aligned} F(t) &= \int_0^{\infty}\delta(t-\tau_N(R))f_1(R)dR,\\ \tau_N(R) &= N\tau_1(R)=\tau\exp[\Delta E(R,\theta_1,p,z)/T],\\ \tau &= N\tau_0. \end{aligned} \tag{37}$$

Here, $\tau_0(R)$ is determined by Eq. (28), $\delta(t)$ is the Dirac delta function, and $f_1(R)$ is the normalized pore size distribution function. The quantity $\tau=N\tau_0$ has the meaning of the time of the hydrodynamic barrierless extrusion of the liquid from all N pores of the porous medium. For $p=0$, $L\sim 1\ \mu$m, $\bar{R}\sim 3$ nm, and $p_g\sim 100$ atm, the hydrodynamic time of the extrusion of the liquid from all $N\sim(\frac{L}{\bar{R}})^3$ pores of the porous medium is estimated $\tau\sim 0.2$ s. This estimate correlates with the time of extrusion $\tau\approx 10^{-1}$ s in the experiments on intrusion-extrusion dynamics at almost zero excess pressure [22]. Calculating integral (37), we obtain the distribution function $F(t)$ in the form

$$F(t)=f(R(t))\frac{dR(t)}{dt}. \tag{38}$$

Here, $R(t)$ is the solution of the equation

$$\tau(R(t))=t. \tag{39}$$

Equation (39) for $\tau(R)$ that is determined by Eqs. (24) and (37) can not be solved analytically. For this reason, we consider the case $p=0$ and assume that

$$\delta\varepsilon(R,\theta_1,p=0,z)\approx\frac{\delta\varepsilon_{\max}(z,\theta_1)}{R^*(z,\theta_1)}[R^*(z,\theta_1)-R]. \tag{40}$$

Here, $\delta\varepsilon_{\max}(z,\theta_1)$ and $R^*(z,\theta_1)$ are given by Eqs. (26) and (25), respectively. Approximation (40) correctly determines the quantity $R^*(z,\theta_1)$ and provides the qualitatively correct sign and height of the barrier $\delta\varepsilon(R,\theta_1,p=0,z)<0$ at $R>R^*(z,\theta_1)$ and $\delta\varepsilon(R,\theta_1,p=0,z)>0$ at $R_{\max}<R<R^*(z,\theta_1)$ (Fig. 5). At $R<R_{\max}$, the behavior of $\delta\varepsilon(R,\theta_1,p=0,z)$ specified by Eq. (40) differs from the behavior of $\delta\varepsilon(R,\theta_1,p=0,z)$ given by exact expression (24). However, it can be seen in Fig. 5 that the number of pores with the radius $R<R_{\max}$ is much smaller than the number of pores with the radius $R>R_{\max}$; consequently, Eq. (40) can be used for a qualitative description throughout the entire range of the radii of pores. According to Fig. 5 (closely spaced dots and dashed-dotted line), approximate expression (40) ensures the qualitatively correct description of the behavior of $\delta\varepsilon(\theta_1,R,z)$ at $p = 0$ for the pore size distribution presented in the figure.

Using Eq. (40), we can obtain the following analytical expression for the distribution function $F(t)$ for the time of the extrusion of the liquid from pores:

$$\begin{aligned} F(t) &= \frac{T R^*(z,\theta_1) W_L(r) f\left(\frac{R^*(z,\theta_1)W_L(r)T}{\delta\varepsilon_{\max}(z,\theta_1)}\right)}{\delta\varepsilon_{\max}(z,\theta_1) t[1 + W_L(r)]}, \\ r &= \frac{\delta\varepsilon_{\max}(z,\theta_1)}{T}\frac{\bar{\tau}_0}{t}\frac{\bar{R}}{R^*(z,\theta_1)}\exp\left(\frac{\delta\varepsilon_{\max}(z,\theta_1)}{T}\right). \end{aligned} \tag{41}$$

Here, $W_L(r)$ is the Lambert function [44]; T is the temperature; $\bar{\tau}_0 = N\frac{4\eta L}{3\bar{R}p_g}$, $\delta\varepsilon_{\max}(z,\theta_1)$ and $R^*(z,\theta_1)$ are specified by Eqs. (26), (28), and (27), respectively; and N is the number of pores in the porous medium. In the limit $r \to 0$, $W_L(r) \approx r$; therefore, it follows from Eq. (41) that $F(t) \sim \frac{N\tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})}{t^2}\bar{R} f(R = R_0)$ at $t > N\tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})$. Since $W_L(r) \approx \ln(r)$ in the limit $r \to \infty$, the behavior of $F(t)$ at $t \to 0$ is determined by the variation rate of the pore distribution function $f(R)$ at $R \to \infty$. In particular, in the case of the Gaussian distribution function $f(R)$, the function $N\tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})F(t)$ approaches zero at $t \to 0$. Thus, the distribution function $F(t)$ has a maximum at times $t \sim N\tau_0$. The behavior of the distribution function $F(t)$ at $z = 6$ is shown in Figs. 6(b) and 6(d) at various degrees of filling $\theta_1 = 0.85, 1$, respectively, for $\sigma/\delta\sigma = 4$ and the Gaussian function $f(R)$ with the half-width $\frac{\delta R}{R} = 0.1$. The energy $\delta\varepsilon_{\max}(z,\theta_1)R^*(z,\theta_1)$ was calculated by Eqs. (26)–(28) for $T = 279$ K. In the cases under consideration, $\delta\varepsilon_{\max}(z,\theta_1)$ and $R^*(z,\theta_1)$ are estimated as $\delta\varepsilon_{\max} \sim 0.1$ eV and $R^* \sim 0.9\bar{R}$ at $z = 6, \theta_1 = 0.85$ and as $\delta\varepsilon_{\max} \sim 3$ eV and $R^* \sim 1.1\bar{R}$ at $z = 6$, $\theta_1 = 1$.

According to the definition of the distribution function $F(t)$ for the time of extrusion and Eq. (37), the fraction of pores $N_1(t)$ from which the liquid is not extruded in the time interval from zero to t is given by the expression

$$N_1(t) = 1 - \int_0^t d\tau\, F(\tau). \tag{42}$$

It follows from Eqs. (41) and (42) that the fraction $N_1(t)$ at $t > \tau \exp(\frac{\delta\varepsilon_{\max}}{T})$ decreases with increasing time t:

$$\begin{aligned} N_1(t) &\sim \frac{\tau \exp\left(\frac{\delta\varepsilon_{\max}}{T}\right)}{t}\bar{R} f(R = R_0), \\ t &> \tau \exp\left(\frac{\delta\varepsilon_{\max}}{T}\right). \end{aligned} \tag{43}$$

It can be seen in Figs. 6(b) and 6(d) that the distribution function $F(t)$ for the time of extrusion at $\theta_1 = 0.85$ decreases at times $t/\tau \sim 1$ and this function $F(t)$ at $\theta_1 = 1$ decreases at much longer times $t/\tau \sim 10^3$. According to Figs. 6(c) and 6(e), the fraction $N_1(t)$ of pores from which the liquid is not extruded at $\theta_1 = 0.85$ decreases at times $t/\tau \sim 100$, whereas $N_1(t)$ at $\theta_1 = 1$ decreases at much longer times $t/\tau \sim 10^6$. Therefore, at $\theta_1 = 0.85$ and $T = 279$ K, the nonwetting liquid is extruded from the porous medium with granules of the size $L = 1$ μm and pores of the size $\bar{R} = 3$ nm at $\sigma = 75$ mN/m and $\delta\sigma = 22$ mN/m in the time $t \sim 10$ s, whereas the time of the extrusion of the liquid from the same porous medium at $\theta_1 = 1$ is $t \geqslant 10^5$ s, which corresponds to the experimentally observed entrapment of the liquid.

Thus, there is the critical degree of filling $\theta_{\rm cr}$ at which the nonwetting liquid can be trapped in the porous medium for the time of the experiment $t_{\rm ex} < \tau \exp(\frac{\delta\varepsilon_{\max}}{T})$ at excess pressure $p = 0$. The equation for the determination of $\theta_{\rm cr}$ can be obtained from Eq. (43). First, we note that Eq. (43) contains factors having various physical meanings. In particular, $N_1(t) \sim \frac{\tau \exp(\frac{\delta\varepsilon_{\max}}{T})}{t}\bar{R} f(R = R_0)$ and $\bar{R} f(R = R_0)$ determine the minimum number of pores from which extrusion is possible, whereas $\tau \exp(\frac{\delta\varepsilon_{\max}}{T})$ determines the time of extrusion from such pores. The liquid remains in the porous medium for the time $t < \tau \exp(\frac{\delta\varepsilon_{\max}}{T})$, if $\exp(\frac{\delta\varepsilon_{\max}}{T})\bar{R} f(R = R_0) = \exp(\frac{\delta\varepsilon_{\rm eff}}{T}) \gg 1, \delta\varepsilon_{\rm eff} = \delta\varepsilon_{\max} + T\ln[\bar{R} f(R = R_0)]$ and is completely extruded in the time $t \sim \tau \exp(\frac{\delta\varepsilon_{\max}}{T})$ if $\exp(\frac{\delta\varepsilon_{\rm eff}}{T}) \leqslant 1$. Here, the quantity $\delta\varepsilon_{\rm eff}$ has the meaning of the effective entrapment barrier. Consequently, the critical degree of filling $\theta_{\rm cr}$ is determined from the condition of the disappearance of the effective entrapment barrier $\delta\varepsilon_{\rm eff}(z,\theta_c) \sim T$. It follows from Eq. (24) that the equation for the determination of $\theta_{\rm cr}$ has the form

$$W(z,\theta_{\rm cr}) = \frac{\delta\sigma}{\sigma}\left[\left(\frac{T}{\Delta E_0}(1 + \mu)\right)^{\frac{\alpha}{2}} - 1\right], \tag{44}$$

where $\Delta E_0 = 4\pi R_0^2 \delta\sigma (1 - \frac{\alpha}{2})^{\frac{2}{\alpha}-1} q^{\frac{2}{\alpha}}$ and $\mu = -\ln[\bar{R} f(R_0)]$. The parameter μ is determined by the pore size distribution. Estimates show that $\mu \geqslant 1$ for narrow Gaussian pore size distributions with $\delta R/R < 0.3$.

According to Eq. (44), the quantity $\theta_{\rm cr}$ depends on the pore size distribution and temperature because of the temperature dependence of the surface tension coefficients $\sigma(T)$, $\delta\sigma(T)$, and the temperature dependence of the second factor in Eq. (44). Figure 7 shows the temperature dependence of $\theta_{\rm cr}$ calculated from Eq. (44). The surface tension coefficient $\sigma(T)$ and its temperature dependence were taken from [39,43]. At $T = 293$ K, the surface tension coefficient of water is 72 mJ/m^2 [39,43]. The quantity $\delta\sigma$ and its temperature dependence were

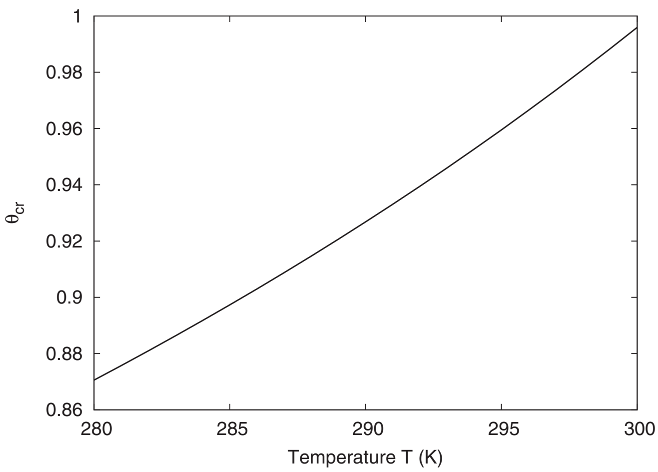

FIG. 7. Temperature dependence of $\theta_{\rm cr}$ calculated by Eq. (44) at $z = 6$ with a surface tension coefficient of 72 mJ/m^2 at $T = 293$ K [43], $\delta\sigma = 22$ mJ/m^{2}at $T = 293$ K, for the Gaussian function $f(R)$ with the half-width $\frac{\delta R}{R} = 0.1$ and $R_0 = 1$ nm.

determined from the temperature dependence of the pressure of extrusion using the method described in [19]. At $T = 293$ K, $\delta\sigma = 22$ mJ/m^2. The calculations were performed for the Gaussian function $f(R)$ with the half-width $\frac{\delta R}{R} = 0.1$ at $R_0 \sim 1$ nm. As can be seen in Fig. 7, the critical degree of filling is $\theta_{\text{cr}} \sim 0.87$ at $T = 279$ K and increases to $\theta_{\text{cr}} = 0.99$ at $T = 300$ K.

Thus, it follows from Eq. (43) that, when the degree of filling is $\theta > \theta_{\text{cr}}$ and the observation time is shorter than the fluctuation decay time of the state of the system, i.e., $t_{\text{ex}} < \tau \exp(\frac{\delta\varepsilon_{\max}}{T})$, the state of the nonwetting liquid in the disordered nanoporous medium is a metastable state with the characteristic decay time determined by the degree of filling θ_1 and the temperature of the medium. In particular, at complete filling $\theta_1 = 1$ and $T = 279$ K, the lifetime of the metastable state is $t \geqslant 10^5$ s (dispersed liquid), whereas the lifetime of the metastable state at $\theta_1 = 0.86$ and $T = 279$ K is $t \sim 10$ s.

The fraction of the volume V of the nonwetting liquid in the porous medium in the long-lived (the lifetime longer than the time of the experiment) metastable state can be calculated by analogy with Eqs. (37)–(42):

$$V(t) = \theta_1 - \int_0^t d\tau\, F_v(\tau), \tag{45}$$

$$F_v(t) = \frac{4\pi}{3} \int_0^\infty \delta(t - \tau_N(R)) R^3 f(R) dR. \tag{46}$$

Here, the pore size distribution function $f(R)$ is normalized to the degree of filling θ_1 of the porous medium:

$$\int_0^\infty dR\, R^3 f(R) = \theta_1 \tag{47}$$

and $\tau_N(R)$ is determined by Eq. (37). It follows from Eqs. (46) and (47) that

$$V(t) = \theta_1 - \int_0^\infty \Theta(t - \tau_N(R)) R^3 f(R) dR, \tag{48}$$

where $\Theta(x)$ is the Heaviside step function.

Using the property $\Theta(-x) = 1 - \Theta(x)$ of the Heaviside step function and normalization condition (48), we obtain the fraction of the volume of the liquid in the form

$$V(t) = \int_0^\infty \Theta(\tau_N(R) - t) R^3 f(R) dR. \tag{49}$$

According to Eq. (49), the fraction of the volume of the trapped liquid $V(t)$ is determined by the contribution from the pores for which the time of extrusion exceeds the observation time t_{ex}. Therefore, entrapment occurs in the pores for which $t_{\text{ex}} < \tau_N(R)$. It follows from Eqs. (24) and (29) and Fig. 4 that the condition $\tau_N(R) > t_{\text{ex}}$ for the observation times $\tau \exp(\frac{\delta\varepsilon_{\max}}{T}) > t_{\text{ex}} > \tau \sim 0.1$ s under the reliable condition $t_{\text{ex}} < 10^6$ s is equivalent to the condition of the positiveness of the argument of the exponential in $\tau_1(R)$ in Eqs. (28).

Thus, $\Theta(\tau(R) - t) \approx \Theta(\delta\varepsilon(R,\theta_1,p,z))$ in this case and the volume ΔV of the trapped liquid is obtained from Eq. (49) as

$$\Delta V(\theta_1) = \int_0^\infty w(R) R^3 f(R) dR, \tag{50}$$

where

$$w(R) = \Theta(\delta\varepsilon(R,\theta_1,p,z)). \tag{51}$$

The quantity $w(R)$ has the physical meaning of the probability of the entrapment of the liquid in the pore [2]. It follows from Eq. (50) that, if $\delta\varepsilon(R,\theta_1,p,z) > 0$, the probability is $w = 1$ and the liquid nanocluster in the pore is stable, whereas if $\delta\varepsilon(R,\theta_1,p,z) < 0$, $w = 0$ and the liquid is extruded from the pore. At the degree of filling $\theta > \theta_c$, the liquid can be trapped in the pores whose radius is smaller than the critical radius R^* given by Eq. (25).

Expressions (50) and (51) make it possible to simplify the calculations of the volume of the liquid remaining in the porous medium. Since the pore size distribution is narrow, we set $W(z,\theta_1) \approx W(\bar{z},\theta)$, where $\bar{z}$ is the average number of the nearest neighbors in the model of randomly distributed spheres, which depends only on the porosity φ: $\bar{z} = -8\ln(1-\varphi)$ [33]. In this case, from Eq. (25) we obtain

$$R^*(\theta_1,T) = R_0\left(1 + \frac{\sigma}{\delta\sigma} W_1(\bar{z},\theta_1)\right)^{\frac{1}{\alpha}}. \tag{52}$$

According to Eq. (52), $R^*(\theta_1,T)$ depends on the porosity φ and temperature owing to the temperature dependencies of the surface tension coefficients σ and $\delta\sigma$. The volume $\Delta V(\theta_1)$ [Eq. (50)] of the liquid remaining in the porous medium for “the energy reason” is determined by the integral of the distribution function $f(R)$:

$$\Delta V(\theta_1) = \int_0^{R^*(\theta_1,T)} R^3 f(R) dR. \tag{53}$$

We now calculate the volume of the liquid trapped owing to the geometry of the space of pores. We assume that the pore size distribution is narrow, i.e., $\Delta R/R < 1$. The probability $W_v(\theta_1)$ that the pore belongs to the geometric cluster of filled pores that is not connected to the infinite cluster of such pores per pore at the degree of filling $\theta < 1$ is determined by the product of the probability $\theta_1 - P(\theta_1)$ that the pore does not belong to the infinite cluster of filled pores and the probability $1 - \theta_1$ that the surrounding pores are empty. This condition guarantees the absence of paths for the extrusion of the liquid. If the number of the nearest neighbors in the porous medium is z, this probability is determined by the following expression taking into account possible geometric configurations of clusters of n filled pores:

$$\begin{aligned} W_v(\theta_1) &= \sum_{n=1}^{z} [\theta_1 - P(\theta_1)]^n (1-\theta_1)^{z-n} \frac{z!}{zn!(z-n)!} \\ &= \frac{(1-\theta_1)^z - [1 - P(\theta_1)]^z}{z}. \end{aligned} \tag{54}$$

Sum (54) includes all possible configurations of the mutual arrangement of filled and empty neighboring pores. According to Eq. (54), in the limit $\theta_1 \to 0$, $P(\theta_1) \to 0$ and $W_v(\theta_1) \to 0$. This corresponds to the absence of clusters of filled pores in which the liquid can be trapped at $\theta_1 \to 0$. Since $P(\theta_1) \to \theta_1$ at $\theta_1 \to 1$, then $W_v(\theta_1) \to 0$ at $\theta_1 \to 1$. This corresponds to extrusion from any pore in the infinite cluster. Thus, the probability of the break of the infinite cluster as a function of the degree of filling approaches zero at small ($\theta_1 \to 0$) and large ($\theta_1 \to 1$) degrees of filling and is maximal near the percolation threshold $\theta_1 \geqslant \theta_c$. At $\theta_1 \geqslant \theta_c$, the character of a decrease in $W_v(\theta_1)$ is determined by the difference between the total degree of filling θ_1 and the fraction $P(\theta_1)$ of the filled pores belonging to the infinite cluster. The total volume of the liquid trapped in the clusters formed owing to the break of the infinite cluster of filled pores is determined by the fraction of pores $\Delta N_1(\theta_1)$ located in the clusters from which the liquid is not extruded because of the absence of possible paths for extrusion $\Delta N_1 = \int_0^{\theta_1} d\theta\, W_v(\theta)$. Consequently, $\Delta N_1(\theta_1)$ is independent of the temperature. Since the probability $W_v(\theta_1)$ is maximal at the degree of filling near the percolation threshold, $\Delta N_1(\theta_1)$ above the percolation threshold in θ_1 tends to the constant $\Delta N_\infty = \int_0^1 d\theta\, W_v(\theta)$, which is determined by the dependence $P(\theta_1)$ and by the number of the nearest neighbors z. The character of the tendency of $\Delta N_1(\theta_1)$ to $\Delta N_\infty(\theta_1)$ is determined by the integral of the difference between the total degree of filling θ_1 and the number of filled pores belonging to the infinite cluster $P(\theta_1)$. The calculations show that the quantity $\Delta N_1(\theta_1)$ for known $P(\theta_1)$ dependencies [42] rapidly approaches the constant $\Delta N_\infty(\theta_1)$ and can be treated as constant already at $\theta_1 \sim (1.1 \div 1.2)\theta_c$.

Finally, the total volume of the liquid trapped in the porous body is given by the expression

$$\Delta V(\theta_1,T) = \int_0^{R^*(\theta_1,T)} R^3 f(R) dR + \int_0^{\infty} \Delta N_1(\theta_1) f(R) R^3 dR. \tag{55}$$

It can be seen from Eqs. (51), (54), and (55) that the volume of the liquid trapped in the porous medium is determined by the terms with different dependencies on the degree of filling and temperature. In particular, according to Eq. (51), the relative volume of the liquid trapped in the porous medium for "the energy reason" [the first term in Eq. (55)] can vary from zero to unity under the variation of the degree of filling, whereas the second term in Eq. (55) depends on the temperature and approaches a constant above the percolation threshold, i.e., when $\theta_1 > \theta_c$ and $P(\theta_1) > 0$.

V. DISCUSSION OF THE RESULTS

The calculations were performed with Eqs. (44), (52), (54), and (55). Figures 8 and 9 show the dependencies of the fraction of the nonwetting liquid trapped in the porous body on the degree of filling calculated by Eq. (55) for the temperatures $T = 279$ and 286 K, respectively. Figure 10 shows the temperature dependence of the fraction of the nonwetting liquid trapped in the porous body at the degree of filling $\theta_1 = 1$. The parameters of the porous medium and liquid (φ, $\bar{R}$, $\delta R/R$, $\delta\sigma$, σ) used in the calculations were taken to be equal to the experimentally found values in independent experiments [17]. The surface tension coefficient of water and its temperature dependence were taken from [39,43]. The surface tension coefficient of water at $T = 293$ K is 72.9 mJ/m^2 [39,43]. The quantity $\delta\sigma$ and its temperature dependence were determined from the temperature dependence of the extrusion pressure using the method described in [40]. At $T = 293$ K, $\delta\sigma = 22$ mJ/m^2. It can be seen in the figure that the dispersion is of critical character depending on the degree of filling with the inclusion of the porosity φ, the average size of pores $\bar{R}$, the half-width of the pore size distribution, and the surface tension coefficient of the liquid at the liquid-gas, liquid-frame, and frame-gas interfaces.

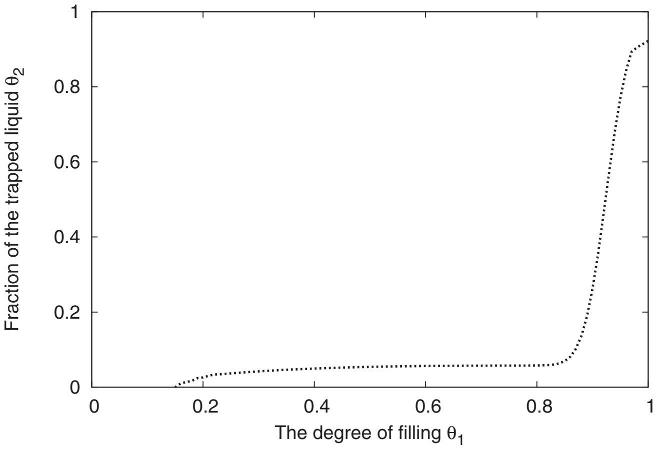

FIG. 8. Fraction θ_2 of the volume of the liquid trapped in the porous medium after the first intrusion versus the fraction of the filled volume of pores in the first intrusion-extrusion cycle θ_1 for a temperature of 279 K.

Figure 11 shows the dependencies of the volume fraction θ_2 of the trapped liquid on the fraction of the filled volume θ_1 for two temperatures 293 and 323 K as calculated by the integration of Eq. (54) with the subsequent multiplication of the resulting relation by the average volume of filled pores. As can be seen in Fig. 10, the quantity $\theta_2(\theta_1 = 1{,}0)$ varies by more than an order of magnitude from 0.05 to 0.90 with an increase in the temperature in a narrow interval from 279 to 293 K.

The dependence of the volume of the trapped liquid (mercury) on the size of granules of the porous medium was experimentally revealed in [15], where it was found that entrapment occurs in large granules of the porous medium and decreases after the fragmentation of granules. According to the theory developed above, this behavior can be explained by a nonlinear dependence of the time of extrusion on the

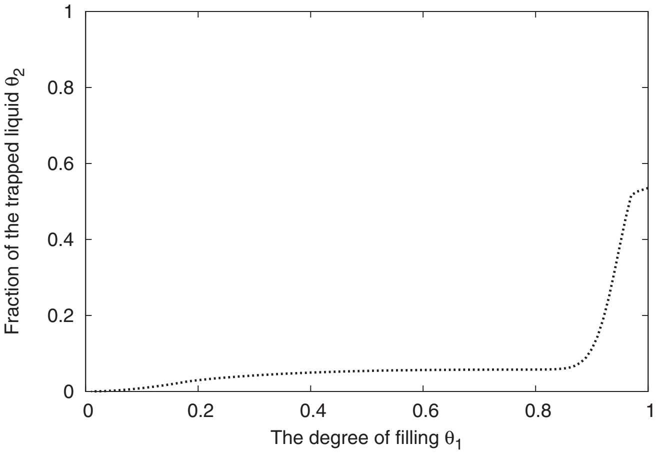

FIG. 9. Fraction θ_2 of the volume of the liquid trapped in the porous medium after the first intrusion versus the fraction of the volume of filled pores in the first intrusion-extrusion cycle θ_1 for a temperature of 286 K.

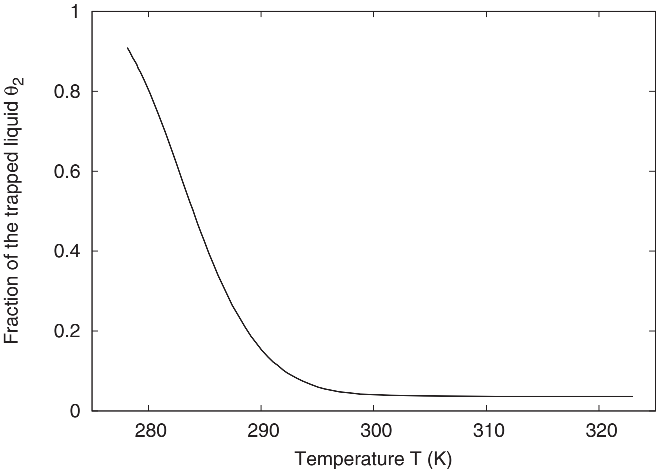

FIG. 10. Temperature dependence of the fraction θ_2 of the volume of the trapped liquid at the complete filling of the porous body ($\theta_1 = 1$) in the first intrusion-extrusion cycle.

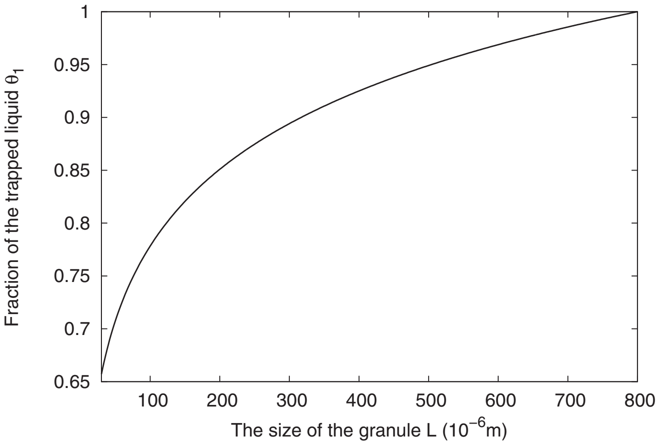

FIG. 12. Fraction of the liquid trapped in the porous body θ_1 versus the size of the granule as calculated by Eqs. (29), (30), and (36) with the Gaussian function $f(R)$ with the half-width $\frac{\delta R}{\bar{R}} = 0.1$ for $T = 300$ K at $\sigma = 402$ mJ/m^2, $\delta\sigma = 100$ mJ/m^2, $\bar{R} = 3$ nm, and $p_g = 1000$ atm.

size of granules L. According to Eqs. (28) and (37), the time of the extrusion of the liquid increases with the size of granules. The character of the dependence of the amount of the trapped liquid can be determined from Eqs. (29), (37), and (42). Figure 12 shows the dependence of the fraction of the liquid trapped in the porous body on the size of granules as calculated with Eqs. (29), (37), and (42) for $z = 6$, the degree of filling $\theta_1 = 1$, and the Gaussian function $f(R)$ with the half-width $\frac{\delta R}{\bar{R}} = 0.1$, $\sigma = 402$ mJ/m^2, $\delta\sigma = 100$ mJ/m^2, $\bar{R} = 7$ nm, and $p_g = 1000$ atm.

As can be seen in Fig. 12, as the size of the granule decreases from 800 to 30 μm, the fraction of the trapped liquid decreases in the observation time by 30%. The volume of the trapped liquid for 30-μm granules is halved when the observation time increases from 30 to 300 s. This is in agreement with the experimental data reported in [15] and estimates obtained in [20].

The entrapment of the nonwetting liquid can be attributed to the formation of a potential barrier owing to fluctuations, which lead to the appearance of various spatially inhomogeneous geometric configurations of the liquid cluster in the pore and its environment in the disordered nanoporous medium. Such inhomogeneity can appear according to the model of randomly distributed overlapping spheres at $R = \text{const}$ [33,38] in the case of the spatial inhomogeneity of the porosity. According to Eqs. (24) and (27), the number of the nearest neighbor pores and, as a result, variations of the potential barrier and the probability of extrusion of the liquid from the pore, are inhomogeneous in this case. Another reason can be the dependence of the connectivity parameter η of the pores [see Eq. (23)] on the radius of the pore in the porous medium with pores of various sizes. Then, for example, a large pore can be surrounded by smaller pores or by a smaller number of neighboring pores. As a result, spatial variations of geometric configurations of the pore and its environment appear. An additional reason for variations of the local configuration of the pore and its environment consisting of filled and empty pores is the formation of a percolation cluster of filled pores in the process of filling. Thus, the entrapment of the nonwetting liquid can be attributed to the formation of the potential barrier because of fluctuations in the number of menisci in the mouths of throats connecting neighboring filled and empty pores, which are due to fluctuations in the sizes of pores in the porous medium that are determined by the pore size distribution function $f(R)$ and by variation of the local configuration of the pore and its environment consisting of filled and empty pores on the shell of the percolation cluster.

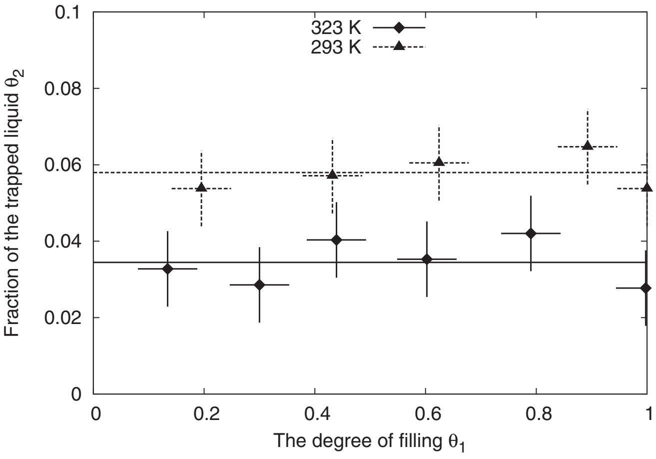

FIG. 11. Fraction of the volume of the trapped liquid versus the fraction of the filled volume for two temperatures.

It follows from Eq. (26) that fluctuations in the number of the nearest neighbors are insignificant (Fig. 8). Owing to fluctuations in the sizes of pores in the porous medium that are determined by the pore size distribution function $f(R)$, the liquid is extruded from pores with different sizes in different times and the number of pores involved in extrusion depends on the observation time. In particular, this is manifested in the power-law dependence of the amount of the liquid trapped in the porous medium on the observation time. Similar effects are well known in the kinetics of disordered systems [45].

Because of variations of the local configuration of the pore and its environment consisting of filled and empty pores on the shell of the percolation cluster, the energy of the filling and depletion of the pore and, consequently, the pressure of the intrusion (extrusion) of the liquid into (from) the porous medium depend on the degree of filling [19]. This makes it possible to explain the experimentally observed decrease in the intrusion pressure in the second intrusion-extrusion cycle [16]. Indeed, as was shown in [19], the intrusion pressure decreases with an increase in the degree of filling; therefore, the intrusion pressure in the second cycle decreases under the condition of the partial entrapment of the liquid in the porous medium in the first intrusion cycle.

Fluctuations in the local configurations of pores are responsible for the existence of the critical degree of filling θ_{cr} at which the nonwetting liquid can be trapped in the porous medium at zero excess pressure $p = 0$ for the observation time $t_{\mathrm{ex}} < \tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})$. It follows from Eq. (43) that, when the degree of filling is above the critical value $\theta > \theta_{\mathrm{cr}}$, and the extrusion observation time is shorter than the fluctuation decay time of the state of the system $t_{\mathrm{ex}} < \tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})$, a metastable state of the nonwetting liquid appears in the form of an ensemble of liquid nanoclusters in pores, i.e., a dispersed liquid. At times $t_{\mathrm{ex}} > \tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})$, the metastable state decays with the characteristic decay time determined by the degree of filling θ_1 and the temperature of the medium. In particular, the lifetime of the metastable state at complete filling $\theta_1 = 1$ and temperature $T = 279$ K is $t \geqslant 10^5$ s (dispersed liquid), whereas the lifetime of the metastable state at $\theta_1 = 0.86$ and $T = 279$ K is $t \sim 10$ s. The amount of the liquid trapped in the porous medium at these times satisfies the law $N(t) \sim \tau_N/t$, which corresponds to the nonergodic behavior of the system under consideration. Thus, all phenomena under study are due to the structure of the disordered porous medium.

The time of extrusion from pores with the radius $R < 1.1\bar{R}$ at the barrier height $\delta\varepsilon(R < 1.05\bar{R}, \theta_1 = 1, p = 0, z = 6) \sim 2$ eV for the temperature $T = 279$ K is estimated as $\tau_1 > 10^5$ s, which corresponds to the entrapment of the liquid in these pores. The characteristic time of extrusion is $\tau_1 \sim 10^2$ s for pores with the radius $1.12\bar{R} > R > 1.1\bar{R}$ and is $\tau_1 \sim \tau_0 \sim 10^{-8}$ s for pores with the radius $1.13\bar{R} > R > 1.12\bar{R}$. According to these estimates, the liquid is extruded from pores with different sizes in different times and the number of pores involved in extrusion depends on the observation time. This is the case, e.g., if the polydisperse medium includes configurations of pores where large pores are surrounded by small pores. Thus, the system under consideration is nonequilibrium and nonergodic, because the relaxation time is so long that it can not reach the equilibrium state in the observation time and the physical properties of the system depend on the kinetics of the proceeding processes.

According to Eqs. (24), (27), and (37), the change in the energy $\delta\varepsilon(\theta, R, p = 0)$ of the liquid in the spherical pore of the radius R given in Eqs. (27) in the partially filled porous medium when the liquid is extruded from the pore can be represented in the form

$$\delta\varepsilon(\theta_1, R, p = 0) = \frac{1}{z}\sum_{n=0}^{z-1} \delta\varepsilon_n,$$

where

$$\delta\varepsilon_n = -4\pi R^2 \delta\sigma\left[1 - q\left(\frac{R_0}{R}\right)^{\alpha}\right] + 4\pi q R^{2-\alpha} R_0^{\alpha} \sigma (1 - \theta_1)^n \times [P(\theta_1)]^{z-n} \frac{z - 2n}{z} \frac{z!}{n!(z - n)!}. \qquad (56)$$

Here, the second term is positive at $n < z/2$ and is negative at $n > z/2$. For this reason, the quantity $\delta\varepsilon_n$ at a given degree of filling θ_1 can be both positive and negative, depending on the number n. The negativeness of $\delta\varepsilon_n$ means the energy favorability of the extrusion of the liquid from pores in the state n in the porous medium. The positiveness of $\delta\varepsilon_n$ means the energy unfavorability of the extrusion of the liquid from pores in this state. Thus, it follows from Eq. (56) that there are local maxima and minima of the energy necessary for the extrusion of the liquid from the state with the number n. Consequently, the system under consideration is characterized by the spectrum of the relaxation times of various configurations of clusters of empty and filled pores. The relaxation of the system is the process of its successive transition through the local energy maxima. The state with the number n is not single. According to Eq. (56), the number of configurations corresponding to this state is determined by the combinatorial factor in Eq. (56) and is $N_n = \frac{z!}{n!(z-n)!}$. If the energies $\delta\varepsilon_n$ and $\delta\varepsilon_{n'}$ corresponding to different values $n \neq n'$ are close or equal to each other, configurations of pores appear with close energies extrusion of the liquid from which it is energetically unfavorable. The number of such configurations is $M \sim 2(\frac{\log_2(\sum_{n=1}^{z/2} \frac{z!}{n!(z-n)!})}{z})^N \sim 2^{\beta(z)N}$, where $\beta(z) \sim 0.8$ at $4 < z < 8$. These configurations constitute the metastable state of the nonwetting liquid in the form of the ensemble of liquid nanoclusters in pores, i.e., the dispersed liquid. At the times $t_{\mathrm{ex}} > \tau_0 \exp(\frac{\delta\varepsilon_{\max}}{T})$, the metastable state decays with the characteristic decay time determined by the degree of filling θ_1 and the temperature of the medium. In the case considered in this work, at complete filling $\theta_1 \sim 1$, $\delta\varepsilon_{\max} \sim 2.3$ eV; correspondingly, the decay time of the metastable state at $T \sim 300$ K is $\tau \exp(\frac{\delta\varepsilon_{\max}}{T}) \sim 10^{49}$ s.

Systems that are nonergodic during a macroscopic but finite time interval are quasinonergodic [26,46]. The relaxation time for truly nonergodic systems near the transition point diverges [47]. In the system under consideration, the relaxation time of the states formed in the process of extrusion is infinite in the case of the decomposition of the infinite cluster of filled pores with the formation of a finite filled liquid cluster where paths for extrusion are absent. The probability of this process is given by Eq. (54). Since the metastable state of the liquid in the porous medium at $\theta_1 \sim 1$ decays in the time $t \sim 10^{49}$ s, the quasinonergodic behavior of the system under study is physically undistinguishable from the nonergodic behavior.

To summarize, the system under study undergoes the dispersion transition and is nonequilibrium and nonergodic because the relaxation time is so long that it can not reach the equilibrium state in the observation time. The physical properties of this system depend on the kinetics of the proceeding processes. The nonergodic behavior of the system is due to the formation of the local energy minima corresponding to various configurations of pores from which the liquid can not be extruded.

ACKNOWLEDGMENTS

We are grateful to L. A. Maksimov for discussion of the results. This work was supported by the Ministry of Education and Science of the Russian Federation (Projects No. 2.6310.2011 and No. 2.5466.2011, program for support of research in higher education institutions for 2013 and 2014 2015 planning period, and the federal program Human Capital for Science and Education in Innovative Russia for 2009-2013).

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