Foams in porous media as a problem in polymer physics

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A model is proposed for gas flow through porous media in the presence of a foam. It is assumed that the foam is transported through the porous medium as a system of bubbles bound in trains. It is assumed that the length of a train (or "caravan") is governed by the local capillary pressure and is a universal function of the degree of saturation with water, the properties of the porous matrix, and the properties of the surfactant. Since the train is a macroscopic entity (its length is much greater than the pore size), it behaves like a polymer chain immersed in a "Darcy fluid." A governing relation for the gas flow is derived in the spirit of the theory of Doi–Edwards polymeric liquids. Results predicted by the theory agree with experiment. The model also reproduces certain observed effects which existing theories have failed to explain.

1. INTRODUCTION

Various aspects of the flow of foam through porous media have been discussed actively in the literature, but the fundamental question of the mechanisms for the motion of foam remains unresolved. The motion of a foam in a porous medium is usually represented as the flow of two interpenetrating phases: a liquid phase and a gaseous one. Analysis of extensive experimental information has established that the flow of a liquid in a foam flow can be described well by a generalized Darcy's law through the introduction of an ordinary relative permeability.[1–3] On the other hand, certain features of gas flow in the presence of a foam cannot be described by a generalized Darcy's law. In other words, the foam radically changes the nature of the seepage flow of gas. A series of visualizing experiments has been carried out to identify the mechanism for the flow of a gas-foam system. It has been found[3–6] as a result that the foam in a porous medium is a gas dispersed in a wetting porous surface of liquid in such a way that some of the pores are partially covered by thin films which are stabilized by the surfactant and which are called "lamellae." The radius of a lamella is on the order of the pore radius.[7] A gas in a porous medium in the presence of a foam moves as a free gas and also as a system of gas bubbles. The mobility of a gas in the presence of a foam is several orders of magnitude lower than that of a free gas.[1,2] The mobility is reduced both by a blocking of gas paths by individual lamellae of the foam and also by friction of the lamellae with the wall of the effective channel in the motion of a gas bubble. (We are restricting the present paper to the case of a foam in which the typical size of an individual bubble is comparable to the size of a pore. The lamellae in this case cover the pore channel. In the opposite case, the foam moves through a porous medium as an ordinary bulk foam, with all the distinctive features of that case.[8])

Two approaches are currently taken in modeling the flow of a gas in the presence of a foam. Along the first approach, which starts from the lamella "break-and-reform mechanism,"[9,10] the foam in a pore space is modeled by a system of "valves" which are continually opening and closing. These valves are localized in certain (dangerous) positions in the gas channels. The valve lamellae effectively block the gas paths, reducing the permeability of the gas. The process by which each valve breaks and reforms is regulated by the local pressure drop in the pores and by physical and chemical conversions in a lamella.[10]

Along the second approach it is assumed that all the gas in the porous medium is moving as an ensemble of bubbles which are bound in trains or "caravans" (the "bubble-train"[11] flow mechanism). The train of bubbles moves as some hypothetical entity averaged over a long time interval (see Sec. 2 for more details). According to this hypothesis, the resistance of the gas increases because of the friction of lamellae with the wall of the effective channel as the train moves. Although the picture of the interaction of the free surfaces of a lamella with the hydrodynamic field within menisci is complex,[11] simple estimates in Sec. 2 show that a channel containing N lamellae increases the resistance of the gas by a factor of $N\nu$, where ν is the viscosity of the film wetting the pore.

Patzek[12] and Radke *et al.*[5] have proposed a mechanical model for the motion of a foam based on the theory of two-phase seepage with certain elements of kinetics required for describing the generation and coalescence of bubbles. That approach is ordinarily referred to as the "population-balance method." This two-phase model is far from complete, since deriving the closure relations will require the statistical analysis of a large body of experimental evidence.

We restrict the present paper to rheological aspects of the flow of a foam through a porous medium. In particular, we discuss a new flow model. The crucial mechanism for the motion of the foam in this model is a sliding of mobile lamellae along an effectively smooth channel. This channel forms from trapped lamellae and the wetting liquid adjacent to the grains of the porous matrix. Inside a channel the foam flows as a system of bubbles (oscillators) bound in a train. Each part of the train stretches or contracts by virtue of the compressibility of the gas in the bubbles. The joint flow of such trains through a system of self-organizing active channels is interpreted as the motion of a foam. It is assumed that the system of active channels is altered by both the average macroscopic motion and a random walk of the bubble trains

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in the pore space. Here we should point out that in the standard approach (the second of those listed above) the lamellae move in unison only when the length of the bubble train is related in a certain way to the applied pressure gradient. Simple estimates lead to the relation[13–16] $\xi \approx (\nabla p)^{-2}$, where ξ is the length of the train. These estimates do not apply in the present context, since the gas is not identified with the bubbles. The length of a bubble train serves as an adjustable parameter of the model; i.e., it serves as a universal function of the degree of water saturation, the properties of the pore space, and the properties of the surfactant.

This paper is organized as follows. In Sec. 2.1 we construct a model for the motion of an individual bubble train through an effective channel. We then (in Sec. 2.2) derive certain relations for the flow of a gas in the presence of a foam, as in the theory of Doi–Edwards polymeric liquids. In Sec. 3 we use the example of a 1D foam flow to discuss consequences of the model. The results of this study are summarized in Sec. 4.

2. BASIC MODELS

In constructing a model we restrict the discussion to the case of a two-phase system, e.g., gas-water foams in the absence of oil. Such foams are used to control the mobility of gases in porous media.[17,18] Some other applications are discussed in Ref. 18.

The fundamental entity in the modeling is the foam-carrying gas (a "continuous-gas" foam[5]). In this case there are gas channels not covered by foam lamellae in the porous medium. The flow of gas through such channels is absolutely the same as the ordinary two-phase seepage regime. We recall that in the standard theory of two-phase seepage the entire pore space is partitioned into two interpenetrating continua.[19] The degree of saturation of each phase is determined by the local capillary pressure: a characteristic function of a porous material and of saturating gases called the "Leverett function." The curve of the flow of each phase can be described completely by introducing relative permeabilities in a generalized Darcy's law.

Since the hydrodynamic behavior of a liquid in a foam flow can be described well by a generalized Darcy's law, we will focus on a gaseous continuum. In it, part of the gas circulates freely, while another part is distributed among bubbles. The freely circulating part of the gas will be called the "free gas." In the spirit of the hypothesis of bubble trains, we assume that the bubbles are moving in the form of a system of trains through the porous medium. We need to stress that in each realization (i.e., at each instant of time) bubbles may also be moving individually. However, the hydrodynamic processes in which we are interested occur over a seepage time scale which is far longer than the time scale for the sliding of a lamella along a pore. Specifically this time scale is characteristic of the motion of a lamella at the microscopic level, since, after it is produced, a lamella cannot traverse a distance greater than a few pore radii.[20] At the seepage time scale the sliding of individual foam lamellae along the effective channel is perceived as motion of a bubble train (in a time exposure).

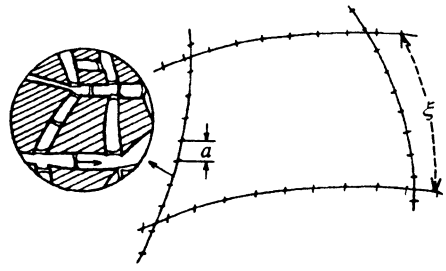

FIG. 1. Partitioning of the pore space into a system of active channels and blocks along which the free gas moves. The distance between neighboring effective lamellae is much greater than the size of a pore, so each link of a bubble train contains a multitude of elementary bubbles (the grains of the pore matrix are hatched in the inset).

A bubble train cannot move in just any arbitrary way, since the pore space imposes an effective sliding channel on it. This region of the pore space is controlled by the mechanisms for the creation and disappearance of foam lamellae and also by the presence of other bubble trains and the flow of free gas. For a macroscopic description of the hydrodynamic picture of the flow, the detailed structure of the network of active channels is unimportant. It can be characterized by the single parameter ξ, the typical mesh size.[16] This parameter is on the order of the length of an individual bubble train.

In accordance with the discussion above, we partition the overall pore space (the gaseous continuum) into a system of active channels and a system of porous blocks filled with free gas. We can then assume that each bubble train is moving independently in an average hydrodynamic field, which incorporates collective effects. Along this approach, the bubble-train model plays the role played by the Routh model in polymer physics[21] (Fig. 1).

2.1. Bubble train in an active channel

We turn now to a construction of a model of a bubble chain. We assume that the train consists of N lamellae whose centers of mass are at the coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$. The lamellae are connected by links of length a (this is the "wagon length"). We also assume that the interval between lamellae is much smaller than ξ. Generally speaking, the pressure within each bubble differs from the pressure of the gas surrounding the train. As has been shown[1)] experimentally,[23] this picture of the foam flow is fairly realistic, and it incorporates the possible deformation of the individual bubbles in a chain.

We denote by p_g the initial gas pressure in an individual bubble. We wish to derive an equation of motion of the bubble train after a pressure perturbation. Under the influence of the perturbation, the ith bubble is deformed, and its length becomes $a_i = a + \rho_i$. Using the equation of state of the gas, we have

$$p_i a_i = p_{i-1} a_{i-1} = \ldots = p_g a. \tag{1}$$

For two neighboring bubbles we thus have

$$p_{i-2}(a + \rho_{i-1} - \rho_{i-2}) = p_{i-1}(a + \rho_i - \rho_{i-1}). \tag{2}$$

Going over from a discrete variable to a continuous variable $s=ai$ in (2), we find

$$-\frac{\partial p}{\partial s}-p\,\frac{\partial^2\rho}{\partial s^2}-\frac{\partial p}{\partial s}\frac{\partial\rho}{\partial s}=0,$$

or

$$\frac{\partial p}{\partial s}=-p\,\frac{\partial^2\rho}{\partial s^2}\left(1+\frac{\partial\rho}{\partial s}\right)^{-1}. \tag{3}$$

Using Newton's law with a friction constant γ, we can write the equation of motion of the foam lamellae as

$$\gamma\,\frac{\partial\rho_i}{\partial t}=-A(p_i-p_{i-1}), \tag{4}$$

where A is the cross-sectional area of the channel. Taking the continuum limit in (4), we find

$$\gamma\,\frac{\partial\rho}{\partial t}=aAp\,\frac{\partial^2\rho}{\partial s^2}\left(1+\frac{\partial\rho}{\partial s}\right)^{-1}. \tag{5}$$

Also using the equation of state of the gas in differential form,

$$p=p_g\left(1+\frac{\partial\rho}{\partial s}\right)^{-1}, \tag{6}$$

we can rewrite Eq. (5) as

$$\gamma\,\frac{\partial\rho}{\partial t}=aAp_g\,\frac{\partial^2\rho}{\partial s^2}\left(1+\frac{\partial\rho}{\partial s}\right)^{-2}. \tag{7}$$

The structural irregularity of the pore space renders the motion of a lamella along a pore channel stochastic. Prieditis and Flumenfelth[13] and, a bit later, Rossen[14] showed that a lamella moves through a capillary within a regular structure by jumping from one stable position to another. Such a motion can be described as a random walk in pressure space. In this context, it is more convenient to introduce a stochastic force in the main equation. This force will model the pulsating component of the capillary forces, which tend to pull a lamella into a contracting throat of a pore channel and to expel it from a diverging throat. Since the stochastic force is of a microscopic nature, it is δ-correlated in time and space:

$$\langle F(s,t)F(s',t')\rangle=B\,\delta(s-s')\,\delta(t-t'),\quad \langle F\rangle=0.$$

The main equation describing the motion of the bubble train thus becomes

$$\gamma\,\frac{\partial\rho}{\partial t}=aAp_g\,\frac{\partial^2\rho}{\partial s^2}\left(1+\frac{\partial\rho}{\partial s}\right)^{-2}+F. \tag{8}$$

To demonstrate the collective properties of the motion of the lamellae in the train, we use a linear version of Eq. (8); i.e., we consider the case of small pressure perturbations. In this limit the average displacement of a lamella (the average is taken over realizations of the stochastic force) is described by a diffusion equation:

$$\gamma\,\frac{\partial\langle\rho\rangle}{\partial t}=aAp_g\,\frac{\partial^2\langle\rho\rangle}{\partial s^2}. \tag{9}$$

There is an instructive example demonstrating the transition of a bubble train from a state of rest into motion. We assume that the gas pressure at the right end of the train abruptly increases by an amount Δp. The pressure elsewhere in the active channel is constant, equal to its initial value. The boundary conditions and the initial condition of the problem are thus

$$\left.\frac{\partial\langle\rho\rangle}{\partial s}\right|_{s=0}=0,\quad \left.\frac{\partial\langle\rho\rangle}{\partial s}\right|_{s=\xi}=-\frac{\Delta p}{p_g},$$

$$\langle\rho\rangle|_{t=0}=0. \tag{10}$$

We solve (9), (10) by the standard methods, writing the solution in the form

$$\langle\rho\rangle=-\frac{\Delta p}{p_g}\left[\frac{aAp_gt}{\gamma\xi}+\frac{3s^2-\xi^2}{6\xi}+\frac{2\xi}{\pi^2}\right.$$

$$\left.\times\sum_{k=1}^{\infty}(-1)^{k+1}\,\frac{\exp(-\lambda_kt)}{k^2}\cos\frac{k\pi s}{\xi}\right], \tag{11}$$

where

$$\lambda_k=\frac{k^2}{T_r},\quad T_r=\frac{\xi^2\gamma}{\pi^2nRT},\quad k=1,2,3\ldots.$$

Here R is the universal gas constant, n is the number of moles of gas in a bubble, and T is the temperature. The pressure distribution along the train tends toward a linear distribution as time elapses:

$$p=\Delta p\left[\frac{s}{\xi}-\frac{2}{\pi}\sum_{k=1}^{\infty}(-1)^{k+1}\,\frac{\exp(-\lambda_kt)}{k}\sin\frac{k\pi s}{\xi}\right]. \tag{12}$$

The average velocity of the train remains constant, equal to

$$u=\frac{1}{\xi}\int_0^{\xi}\frac{\partial\langle\rho\rangle}{\partial t}\,ds=-\frac{\Delta pa}{\gamma\xi}A. \tag{13}$$

Expressions (11)–(13) are evidence of the collective nature of the motion of the foam lamellae. The pressure drop causes the foam lamellae to move nonuniformly; i.e., the bubbles in the train become deformed in such a way that the pressure gradient tends toward a constant value along the chain. The time scale of the restructuring, T_r, depends on the friction constant of an individual lamella, on the initial pressure, and—the most important point—on the length of a train. Let us estimate the friction constant. We recall that a lamella consists of a plane film and menisci. We assume that the characteristic longitudinal and transverse dimensions of the menisci are comparable in magnitude. Modeling a lamella by a rigid disk, and ignoring end effects, we then find the lamella resistance force:

$$F_r\approx\nu\cdot2\pi r\,\frac{\partial\rho}{\partial t}.$$

Consequently, the friction constant is given in order of magnitude by $\gamma\approx2\pi\nu r$, where r is the pore radius. End effects lead to a more complicated dependence of the friction constant on the pore radius and to a dependence of this constant on the lamella velocity.[11] Nevertheless, this estimate is cor-

rect in order of magnitude, and it allows us to distinguish the collective "elastic" effect from other interactions within a train. It also leads to the conclusion that the relaxation rate of the pressure gradient in pore space is governed by the relaxation rate of the pressure gradient along the bubble trains. Let us clarify the latter assertion. We consider a pore channel of length ξ filled with a free gas. In a first approximation, the pore channel can be represented as a system of wide pores each of volume V, connected by narrow capillaries of length l and radius r. We assume that the gas in the capillaries is flowing in accordance with the Poiseuille law. We write a balance equation for the gas flow rate in the ith pore:

$$q_i=\alpha(p_i-2p_{i-1}+p_{i-2}).$$

In the continuum limit, this equation reduces to a differential equation with a diffusion coefficient

$$D_g=l^2\alpha=\pi lr^4p_g/8\nu_gV.$$

Here ν_g is the viscosity of the gas. Assuming $l\approx r$, and repeating the calculations for a determination of the relaxation time for the preceding problem, we find

$$T_g=\frac{\xi^2}{D_g}\approx\frac{8\pi\xi^2r\nu_g}{nRT}.$$

The ratio T_r/T_g is thus on the order of the ratio of viscosities ν/ν_g. Using this estimate, we conclude that the pressure in a gas block relaxes to its steady-state distribution essentially instantaneously after the application of the pressure gradient, while the pressure relaxation in the active channels takes place over a time on the order of $T_r\gg T_g$.

2.2. Motion of a bubble train in an average field

Our basic purpose in this subsection of the paper is to derive governing relations for gas flow in the presence of a foam, allowing for the particular features of the motion of lamellae at the microscopic level. Since the original problem is quite complex, we introduce some simplifying assumptions.

Assumption 1. As we have already stated, we are restricting the discussion to the simple case in which the number of lamellae in a train is constant. We will call this the "saturation limit" and distinguish it from the "flow regime," in which growth and division processes play a governing role.

Assumption 2. We consider exclusively slow flows, for which the seepage time scale is longer than the relaxation time T_r. In such flows the pressure distribution in the blocks at any instant can be regarded as a steady-state distribution. Actually, this assumption is not particularly restrictive. There is a fairly substantial class of flows which arise in problems of chemical technology, e.g., in oil and gas recovery, which satisfy these conditions.

Let us use these assumptions to derive governing relations for gas flow in the presence of a foam. These equations can be written down immediately provided that we know how the effective force acting at a given point in the porous medium can be calculated from the bubble-train model. This problem is conceptually close to the problem of calculating effective stresses in the physics of the elasticity of rubber. In the case of the flow of bubble trains, the elastic force acting along a chain plays the role of entropic intramolecular forces. To calculate the contribution of elastic forces to the effective force we can thus use the familiar formula[24]

$$\mathbf{F}_f=cA\int_0^{\xi}\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle\cdot\nabla p(s,t)ds. \tag{14}$$

Here we have used the continuum version of the bubble-train model, so $\mathbf{u}(s,t)$ is a unit vector directed along the sth link of the train, A is the cross-sectional area of the active channel, and c is the concentration of trains in the flow. The angle brackets mean an average over the orientation of the links.

To pursue the calculations we rewrite Eq. (14) in the form

$$\mathbf{F}_f=-cA\int_0^{\xi}S(s,t)\cdot\nabla p(s,t)ds,$$
$$S(s,t)=\langle\mathbf{u}(s,t)\mathbf{u}(s,t)-\tfrac{1}{3}I\rangle,\quad I_{ij}=\delta_{ij}. \tag{15}$$

Here we have introduced the isotropic tensor δ_{ij} in the definition of the pressure [see expression (36) below]. This formula is our starting point for deriving the governing relations.

We can demonstrate the derivation of the equations by making use of a gedanken experiment proposed by Doi and Edwards.[25] We assume that at time $t=0$ a sample containing a foam undergoes a sudden uniform deformation and is then maintained at a constant deformation. Since the carrier phase has no rigidity, the system must go into a new equilibrium state similar to its initial state. The problem thus reduces to a description of how the relaxation occurs.

In this context, a "sudden deformation" of the sample is to be understood as the sudden introduction of the sample into a flow with a constant velocity gradient, i.e., the imaginary organization of a "tensile" or "shear" flow (Fig. 2).

The motion of the foam after the deformation can be broken up somewhat arbitrarily into stages. In the first stage the system of active channels is deformed because of the flow of the carrier gas. To describe this motion we introduce.

Assumption 3. In the first stage of the motion, the lamellae are carried freely by the gas. In other words, each point of the active channel is subjected to an affine deformation.

This is the strongest of the assumptions introduced here, and it requires some comments. The active channels, which in turn consist partly of foam lamellae, change configuration as a result of the velocity gradient. This effect is at odds with the picture of these channels as rigid tubes. Direct observations confirm this picture of the self-organization of an active channel:[22] the nonuniform pressure gradient causes some of the lamellae forming an active channel to break up, while others jump to new stable positions in pore channels. In addition, some of the lamellae reappear. As a result, the active channel takes on a new configuration. The hypothesis of an affine deformation is equivalent to a coarsening of our original picture of the self-organization of the effective tube. It conforms to the spirit of the bubble-train hypothesis. We recall that the length scale of a train is much longer than the

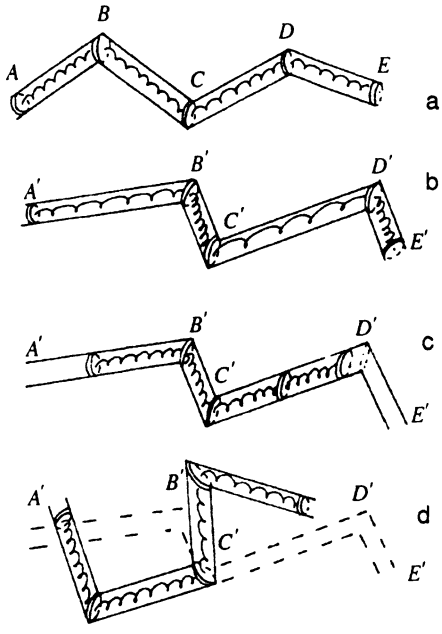

FIG. 2. Schematic diagram of the relaxation process. The trains represent a compressible gas in an effective bubble. a) Bubble train in the original state (points A,B,C,D,E); b) immediately after deformation (points A',B',C',D',E'), the bubbles are either stretched or compressed; c) after the first relaxation process, the lamellae are displaced in such a manner that the pressure gradient is balanced; e) after the second relaxation process, the bubble train "creeps out" of the deformed channel through reptations.

size of the pores. We can easily verify this point by estimating the effective length of a link. Using the approximate formula[16] $a \approx r^2 p_g/\sigma$ for this estimate, and assuming $p_g=3$ bar, $\sigma=30$ dyn/cm, and $r=10^{-3}$ cm (Ref. 17), we find $a \approx 10^2 r$. We thus see that the microscopic level in this problem corresponds to a length scale much larger than the pore size. In this approach, the bubble train is modeled in the deformation stage by an infinitely thin soap filament in a Darcy fluid (i.e., a fluid with characteristics averaged over the pore space).

As a result of the deformation, some parts of the train are stretched out, and others compressed. For slow flows we can assume that the ends of the trains are maintained at a constant pressure gradient immediately after the deformation. Each train thus relaxes after the deformation to a state in which the pressure gradient is constant along the train. We will call this train deformation process the "first relaxation process." During this first relaxation process, we might note, there can be no change in the conformation of an active channel.

After the first relaxation process has ended, the bubble train moves in serpentine manner without any change in length. At each instant, the ends of the train change spatial positions because of a displacement of the "point of birth" of foam lamellae at the tail of the train and of the "point of death" of the lamellae at the head of the train. After the first relaxation process has ended, the train thus "creeps" out of the deformed tube and creates a new active channel through a random walk of a head bubble. We will call this "liberation" process the "second relaxation process." A corresponding problem for a polymer chain was studied by de Gennes[26] and Doi and Edwards.[25] Over a short time interval Δt, the lamellae move along the channel in such a way that a link of the train with the coordinate s occupies that point of the tube which at the time t was the position of the link with the coordinate $s+\Delta s$:

$$\mathbf{u}(s,t+\Delta t)=\mathbf{u}(s+\Delta s,t). \tag{16}$$

Here Δs is the random distance traversed by the bubble train over the time Δt. This motion—the creep of a chain along a tube—is called "reptation."[26] Calculating the diffusion coefficient, defined as

$$D_f=\frac{\langle \Delta s^2 \rangle}{2\Delta t}$$

is an important problem for this approach. The diffusion coefficient depends on the properties of the pore space, the degree of water saturation, the concentration of trains, etc. For rough estimates, on the other hand, it is sufficient to consider only two types of forces which control the motion of the train at the microscopic level: viscous and capillary forces. A random motion of a train along an active channel is possible if these forces are balanced: $\nu U \approx \sigma$, where U is a characteristic velocity of a lamella, and σ is the surface-tension coefficient. We thus find a time scale for the diffusive motion of a lamella:

$$\tau_r \approx \frac{a}{U} \approx \frac{a\nu}{\sigma}.$$

The diffusion coefficient is thus given in order of magnitude by

$$D_f \approx \frac{a^2}{\tau_r} = \frac{a\sigma}{\nu}.$$

The complete set of parameters on which the diffusion coefficient depends thus reduces to a single parameter: the effective length of a bubble in a train.

We turn now to the basic calculations. We consider the change in the effective force over a short time interval τ''. This change is determined by three components:

$$\Delta \mathbf{F}_f = \Delta_d \mathbf{F}_f + \Delta_g \mathbf{F}_f + \Delta_r \mathbf{F}_f, \tag{17}$$

$$\Delta_d \mathbf{F}_f = cA\nabla P(t)\cdot\int_0^\xi \delta S(s,t)ds, \quad \Delta_r \mathbf{F}_f = cA\nabla P(t) \times \int_0^\xi \Delta S(s,t)ds,$$

$$\Delta_g \mathbf{F}_f = cA\int_0^\xi \delta\nabla p(s,t)\cdot S(s,t)ds.$$

Here $\nabla P(t)$ is the pressure gradient in a block at the time t, δS is the change in the tensor S due to the macroscopic deformation, ΔS is the change in the tensor S due to reptations, and $\delta\nabla p(s,t)$ is the change in the pressure gradient along a train due to the first relaxation process. Equation (17) is none other than the first term of a series expansion of the

effective elastic force in τ'. We are assuming that before the deformation was applied, the foam was moving along with the gas under a pressure gradient $\nabla P(t)$.

We will first calculate the first term in (17). Over the time interval τ the active channels undergo changes in configuration because of the macroscopic deformation. If E is the tensor describing the macroscopic deformation, then the point with Cartesian coordinate $\mathbf{R}$ goes into the point $\mathbf{R}'=E\cdot\mathbf{R}$. Making use of the affine nature of the deformation, we find an equation which relates the tangent vectors before and after the deformation:

$$\mathbf{u}'=\frac{E\cdot\mathbf{u}}{|E\cdot\mathbf{u}|}.$$

Substituting this equation and the expression[21]

$$E_{ij}(t+\tau')=\delta_{ij}+\nabla_i v_j\tau' \tag{18}$$

into Eq. (15), we find

$$\begin{aligned}\mathbf{F}_f(t+\tau')-\mathbf{F}_f(t)&=\Big\{\nabla\mathbf{v}\cdot\mathbf{F}_f+\mathbf{F}_f\cdot(\nabla\mathbf{v})^{\dagger}+\frac{2}{3}\varphi D\cdot\nabla P(t)\\&\quad-2cA\nabla P(t)\times\int_0^{\xi}\langle\mathbf{u}(s)\mathbf{u}(s)\mathbf{u}(s)\mathbf{u}(s)\rangle:D\,ds\Big\}\tau'.\end{aligned} \tag{19}$$

Here $\mathbf{v}$ is the velocity of the free gas, $D_{ij}=(\nabla_i v_j+\nabla_j v_i)/2$, and φ is the number of bubble trains per unit volume in the flow. To calculate the third term in (19) we make use of the results of Doi and Edwards[25] (a brief derivation of this equation is offered in Appendix I):

$$\begin{aligned}\mathbf{F}_f(t+\tau')-\mathbf{F}_f(t)=\Big\{&\nabla\mathbf{v}\cdot\mathbf{F}_f+\mathbf{F}_f\cdot(\nabla\mathbf{v})^{\dagger}+\frac{2}{3}\varphi D\cdot\nabla P(t)\\&-2cA\nabla P(t)\int\int_{-\infty}^{t}\mu(t-t')\\&\times\frac{E\cdot\mathbf{u}_0E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|^2}\frac{\mathbf{u}_0E\cdot D\cdot E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|^2}d^2\mathbf{u}_0dt'\Big\}\tau,\end{aligned} \tag{20}$$

where

$$\mu(t)=\xi\sum_i\frac{8}{\pi^2i^2\tau_i}\exp(-t/\tau_i),\quad \tau_i=\frac{\xi^2}{\pi^2i^2D_f},$$

$$i=1,3,5\ldots\ . \tag{21}$$

Equations (20) and (21) describe the change in the effective force immediately after the macroscopic deformation. We wish to calculate the change in the effective force during the first relaxation process. We recall that during this first relaxation process there is a redistribution of lamellae in the train in such a manner that the applied pressure gradient is balanced by the elasticity of the gas in the bubbles. In this stage of the relaxation, the conformation of the active channels remains essentially the same. To calculate the longitudinal pressure gradient in a channel we use the linear version of the bubble model. Introducing $g(s,t')=\langle\nabla p(s,t')\cdot\mathbf{u}(s,t)\rangle$ for the longitudinal pressure gradient, we find from (9)

$$\gamma\frac{\partial g}{\partial t'}=aAp_g\frac{\partial^2 g}{\partial s^2}. \tag{22}$$

At the ends of the train the pressure gradient is related directly to the pressure gradient in a block, so we write the boundary conditions as

$$\begin{aligned}g(0,t')&=\nabla P(t)\cdot\mathbf{u}(0,t)=g_0,\\g(\xi,t')&=\nabla P(t)\cdot\mathbf{u}(\xi,t)=g_\xi.\end{aligned} \tag{23}$$

Immediately after the deformation, the distribution of the pressure gradient along the channel becomes an initial condition of the problem:

$$g(s,t')=w(s,t),\quad t'=t. \tag{24}$$

We can write a solution of problem (22)–(24) in the form

$$\begin{aligned}g(s,t')=g_0+g_\xi-g_0\frac{s}{\xi}+\sum_i w_i\sin\left(\frac{\pi is}{\xi}\right)\\\times\exp(-\lambda_i(t'-t)),\quad i=1,3,5\ldots,\end{aligned} \tag{25}$$

where

$$w_i=\frac{2}{\xi}\int_0^{\xi}\left[w(s)-g_0-g_\xi+g_0\frac{s}{\xi}\right]\sin\left(\frac{\pi is}{\xi}\right)ds.$$

Substituting these expressions into (15), we find the effective force in the first relaxation stage:

$$\begin{aligned}\mathbf{F}_f=cA\int_0^{\xi}\left\langle\left(g_0+g_\xi-g_0\frac{s}{\xi}\right)\mathbf{u}(s,t)-\frac{1}{3}I\cdot\nabla P(t)\right\rangle ds\\+cA\sum_i\int_0^{\xi}\langle w_i\mathbf{u}(s,t)\rangle\sin\left(\frac{\pi is}{\xi}\right)\exp[-\lambda_i(t'\\-t)]ds.\end{aligned} \tag{26}$$

Since the directions of the end bubbles of a train are random, uncorrelated with the directions of interior links, the first term on the right side of Eq. (26) drops out:

$$\begin{aligned}&\int_0^{\xi}\left\langle\left(g_0+g_\xi-g_0\frac{s}{\xi}\right)\mathbf{u}(s,t)-\frac{1}{3}I\cdot\nabla P(t)\right\rangle ds\\&=\nabla P(t)\cdot\int_0^{\xi}\Big[\langle\mathbf{u}(0,t)\mathbf{u}(s,t)\rangle+\langle\mathbf{u}(\xi,t)\mathbf{u}(s,t)\rangle\\&-\langle\mathbf{u}(0,t)\mathbf{u}(s,t)\rangle\left(\frac{s}{\xi}-\frac{1}{3}I\right)\Big]ds=\nabla P(t)\cdot\int_0^{\xi}\Big[\delta(s)\\&\times\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle+\delta(s-\xi)\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle-\delta(s)\\&\times\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle\left(\frac{s}{\xi}-\frac{1}{3}I\right)\Big]ds=\frac{1}{3}\nabla P(t)\\&\times I\left(\frac{1}{2}+\frac{1}{2}-1\right)=0.\end{aligned}$$

The final expression is

$$\mathbf{F}_f(t,t')=cA\sum_i \int_0^{\xi}\langle w_i\mathbf{u}(s,t)\rangle\sin\left(\frac{\pi is}{\xi}\right)$$
$$\times\exp(-\lambda_i(t'-t))ds. \quad (27)$$

Taking the limit $t'-t=\tau'\to 0$, we find the increment in the effective force caused by the first relaxation process:

$$\Delta_g\mathbf{F}_f=-\left\{cA\right.$$
$$\left.\times\sum_i \lambda_i\int_0^{\xi}\langle w_i(s,t)\mathbf{u}(s,t)\rangle\sin\left(\frac{\pi is}{\xi}\right)ds\right\}\tau'. \quad (28)$$

To simplify (28) we use the method proposed by Yarin.[27] Introducing a spectral decomposition of the force,

$$\mathbf{F}_f(t,t)=\sum_i \mathbf{F}_{fi}(t,t),$$

and comparing Eqs. (28) and (27), we find

$$\Delta_g\mathbf{F}_{fi}=-\lambda_i[\mathbf{F}_{fi}(t,t)]\tau'. \quad (29)$$

After the deformation, each mode in the expansion of the effective force thus relaxes to its equilibrium value over a time scale $1/\lambda_i$. To simplify the governing equation we use the single relaxation time T_r. This approximation has proved successful in problems in polymer physics. Restricting the discussion to processes which play out over a time much longer than T_r, we thus find an equation describing the first relaxation process:

$$\Delta_g\mathbf{F}_f=-\frac{1}{T_r}\mathbf{F}_f\tau'. \quad (30)$$

After the first relaxation process has ended, a constant pressure gradient is set up along the train. This gradient is approximately equal to the pressure gradient in a block. On the other hand, the conformation state of the train is far from equilibrium, because the train is in a state with a reduced configurational entropy. The train tends to escape from its original channel, "creeping" out of it. Using (16) and the definition of the tensor $S(s,t)$, we write the condition for reptation motion:

$$S(s,t+\Delta t)=\langle S(s+\Delta s,t)\rangle,$$

where the angle brackets mean an average over realizations of Δs. Expanding the right side of this equation in powers of Δs, we find

$$S(s,t+\Delta t)=\left\langle S(s,t)+\Delta s\,\frac{\partial}{\partial s}S(s,t)\right.$$
$$\left.+\frac{1}{2}(\Delta s)^2\frac{\partial^2}{\partial s^2}S(s,t)+\ldots\right\rangle$$
$$=S(s,t)+\langle\Delta s\rangle\frac{\partial}{\partial s}S(s,t)$$
$$+\frac{1}{2}\langle(\Delta s)^2\rangle\frac{\partial^2}{\partial s^2}S(s,t)+\ldots. \quad (31)$$

The factor in the second term referring to the small time interval $\langle\Delta s/\Delta t\rangle$ is none other than the average velocity of a lamella, which is directly proportional to the vectors $\mathbf{u}(0,t)$ and $\mathbf{u}(\xi,t)$ [see (25)]. Since the end links of the train are in random directions, the second term on the right side of this equation drops out after division by Δt. Equation (31) thus reduces to an equation which was first derived for the problem of a polymer chain by Doi and Edwards:[25]

$$\frac{\partial S}{\partial t}=D_f\frac{\partial^2 S}{\partial s^2}. \quad (32)$$

By virtue of the random orientation of the end links of the train, the boundary conditions of the problem become

$$S(0,t')=0,\quad S(\xi,t')=0. \quad (33)$$

An initial condition is imposed by the structure of the active channel after the deformation:

$$S(s,t')=S_0(s,t),\quad t'=t. \quad (34)$$

Problem (32)–(34) is analogous to problem (22)–(24), so by comparing $\Delta_r\mathbf{F}_f$ with (28) we find

$$\Delta_r\mathbf{F}_f=-\frac{1}{\vartheta}\mathbf{F}_f\tau'. \quad (35)$$

Here $\vartheta=\xi^2/\pi^2D_f$ is the time scale of the reptation motion of the bubble train. A corresponding expression was derived by Yarin[27] for the increment in the stress tensor due to reptation motion of polymer chains in melts.

To close the model we consider some conservation laws. The condition expressing the equality of the viscous forces, the pressure gradient, and the internal forces in this case plays the role of a governing relation for the gas flow in the absence of the foam:

$$\frac{\mathbf{v}}{k}=-\nabla P-\mathbf{F}_f, \quad (36)$$

where k is a seepage coefficient. Taking the limit $\tau'\to 0$ in (17), and using (20), (30), and (35), we find an equation for the internal force:

$$\frac{d\mathbf{F}_f}{dt}=\nabla\mathbf{v}\cdot\mathbf{F}_f+\mathbf{F}_f\cdot(\nabla\mathbf{v})^{\dagger}+\tfrac{2}{3}\varphi D\cdot\nabla P(t)-\frac{1}{\tau_r}\mathbf{F}_f$$
$$-2cA\nabla P(t)\cdot\int\int_{-\infty}^{t}\mu(t-t')\,\frac{E\cdot\mathbf{u}_0E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|^2}$$
$$\times\frac{\mathbf{u}_0\cdot E\cdot D\cdot E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|^2}\,d^2u_0dt'. \quad (37)$$

Here[21]

$$\frac{dE(t,t')}{dt'}=-E(t,t')\cdot\nabla\mathbf{v}(t'),\quad E(t,t)=I, \quad (38)$$

and $1/\tau_r=1/T_r+1/\vartheta$. System (36)–(38) describes the flow of a gas in the presence of a foam in a porous medium at a constant degree of water saturation. For an incompressible porous medium and for slow flows, we can ignore the compressibility of the gas in the blocks and use the balance equation in the form

$$\nabla \cdot \mathbf{v}=0. \tag{39}$$

3. FLOW OF FOAM IN A POROUS TUBE

We assume that the foam is injected into a sample of length H at a constant degree of water saturation. To describe the flow of the foam in this case we can use the system of equations which we have derived. We introduce dimensionless variables and dimensionless functions:

$$p=\frac{P}{p_0}, \quad L=\frac{F}{f}, \quad v\to\frac{v}{v_0}, \quad t\to\frac{t}{\tau_r}, \quad x\to\frac{x}{H},$$

where $p_0=H^2/\tau_r k$ is the scale value of the pressure, f is the scale value of the effective internal force, and $v_0=H/\tau_r$ is the velocity scale. In terms of these variables, the system of equations becomes

$$\frac{\partial v}{\partial x}=0, \tag{40}$$

$$\frac{\partial L}{\partial t}+v\,\frac{\partial L}{\partial x}=-L, \tag{41}$$

$$v=-\frac{\partial p}{\partial x}-bL. \tag{42}$$

The parameter $b=fk\tau_r/H$ serves as a measure of the ratio of the internal forces which arise in the motion of the bubble trains to the viscous forces, incorporating the resistance of the effective medium in the gas flow. In the limit $b\to\infty$ the internal forces outweigh the viscous forces; in the opposite case, the flow obeys the ordinary Darcy's law for a gas without a foam.

Let us look at a possible experimental situation. In the case of a given pressure drop, the boundary conditions and initial conditions become

$$\begin{aligned} &p=P_0(t), \quad L=1, \quad x=0,\\ &p=0, \quad x=1,\\ &p=0, \quad L=0, \quad t=0. \end{aligned} \tag{43}$$

For convenience in solving system (40)–(43), we introduce a new independent time variable:

$$\frac{d\tau}{dt}=v(t), \quad \tau(0)=0. \tag{44}$$

The solution of transport equation (41) in terms of the new variables then becomes

$$L=\theta(\tau-x)\exp\left(-\int_{\tau-x}^{\tau}\frac{d\beta}{V(\beta)}\right), \quad V(\tau)=v(\tau), \tag{45}$$

where $\theta(x)$ is the unit step function.

Using Eq. (45), we examine two foam flow regimes of practical interest (detailed calculations are presented in Appendix II). The first displacement regime corresponds to propagation of foam through a sample, while the second describes a relaxation of the system to a steady state. The first stage of the flow is described by the equation

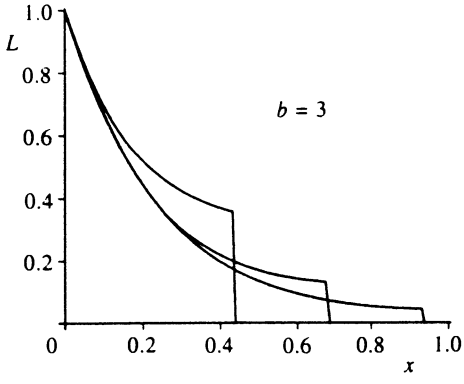

FIG. 3. Distribution of the effective internal force along a tube at various times. The foam is propagating with a moving front.

$$v(\tau)=P_0(\tau)-b\int_0^{\tau}\exp\left(-\int_{\tau-x}^{\tau}\frac{d\beta}{V(\beta)}\right)dx, \quad \tau<1 \tag{46}$$

while the second is described by an equation with finite integration limits:

$$\tau\geqslant 1, \quad v(\tau)=P_0(\tau)-b\int_0^{1}\exp\left(-\int_{\tau-x}^{\tau}\frac{d\beta}{V(\beta)}\right)dx. \tag{47}$$

Let us consider a flow at a constant pressure drop. Figure 3 demonstrates the characteristic features of the conditions under which the tube becomes filled with foam. After an increase in the pressure drop at the ends of the tube, a constant pressure gradient is set up instantaneously along the tube [as follows from Eq. (42)]. On the other hand, the gas seepage rate along the tube cannot reach a steady-state value instantaneously. As long as the film front is moving along the tube, the pressure distributions behind and ahead of the front are different. While the pressure gradient ahead of the front is uniform, the distributions of the effective internal force and of the pressure gradient behind the front are nonuniform. Figure 3 shows distributions of the internal force characterizing the effect of the foam at various times. After the breakthrough at the time t^*, the foam relaxes to a steady-state flow regime. The breakthrough time is found from the transcendental equation

$$1=P_0\left\{\frac{t^*}{1+b}+\frac{b}{1+b}\cdot\frac{1-\exp(-(1+b)t^*)}{1+b}\right\}. \tag{48}$$

Figure 4 demonstrates the quality of a foam as a function of the parameter b. With increasing b, the breakthrough time increases; i.e., the quality of the foam improves. We will come back to this fact later on in a discussion of experiments which have been carried out.

Figure 5 illustrates the primary effect of the foam on the seepage flow of gas: As time elapses, we observe a lowering of the rate of the seepage flow of gas. This effect was observed in the experiments of Refs. 1, 17 and 18 and was labeled a "gas-blocking state."[17–18] This seepage regime is characterized by a significant lowering of the gas flow rate at

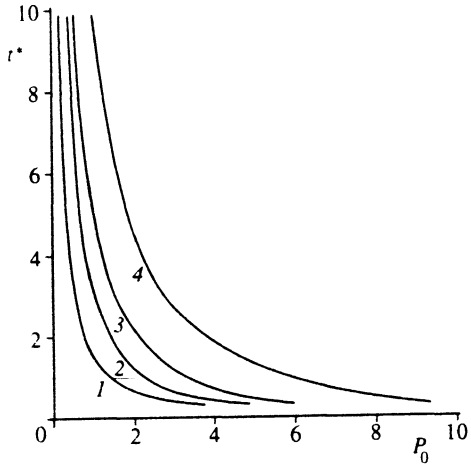

FIG. 4. Breakthrough time as a function of the pressure drop. *1*—$b=1$; *2*—$b=3$; *3*—$b=5$; *4*—$b=20$.

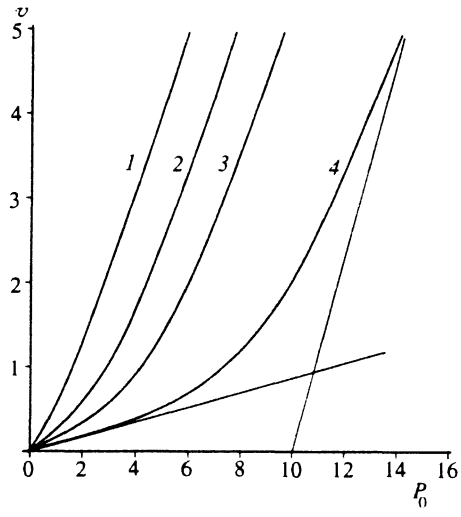

FIG. 6. Typical diagram of the seepage rate versus the pressure drop, which is similar to the experimental curves. *1*—$b=1$; *2*—$b=3$; *3*—$b=5$; *4*—$b=10$.

constant water saturation. It was pointed out in Refs. 17 and 18 that the gas-blocking state cannot be reproduced in the existing models.

Another effect of the foam is seen in a nonlinear dependence of the gas flow rate on the applied pressure drop in the steady state (Fig. 6). In the model proposed here, this regime is described by the system of transcendental equations

$$L=\exp\left(-\frac{x}{v}\right), \tag{49}$$

$$p_0=v+bv\left(1-\exp\left(-\frac{1}{v}\right)\right). \tag{50}$$

It follows from Eq. (49) that internal forces have an appreciable effect on the gas flow only in a layer of thickness v adjacent to the entrance cross section of the tube. It is worthwhile to look at two limiting cases: the regime of slow gas flow and the high-velocity seepage regime. In the first limit, Eq. (50) reduces to

$$P_0=(1+b)v, \quad v\to 0.$$

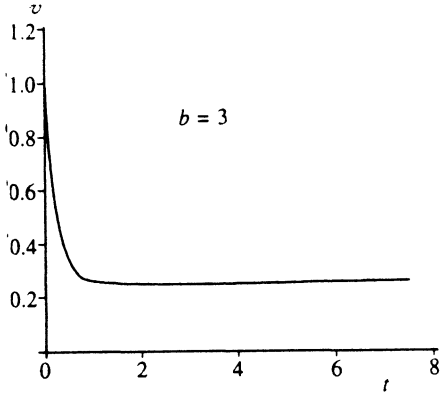

FIG. 5. The "gas-blocking" flow regime.

In this case the effect of the internal forces propagates over the entire sample and reduces to a renormalization of the permeability. In the opposite limit, Eq. (50) becomes

$$P_0=v+b, \quad v\to\infty. \tag{51}$$

Here the effect of the foam reduces to the onset of a critical pressure gradient in the seepage law. In other words, the foam exhibits the characteristic features of a pseudoplastic. Combining the asymptotic results found, we can approximate the nonlinear seepage law by a piecewise-linear law. The point at which the straight lines intersect (Fig. 6) has the coordinates

$$\tilde{v}=1, \quad \tilde{p}=1+b(1-e^{-1})\approx 1+b.$$

Various versions of the piecewise-linear approximation have been proposed and discussed in the literature in connection with the description of the flow of foams through porous media (see the reviews[5,18]). In that approximation of the seepage law, the quality of the foam is governed by the slopes of the straight lines and by the point at which they intersect. A simplified version of this approximation—the "pseudoplastic" model, in which the foam quality is characterized by a critical pressure gradient—is often used. In that model the foam quality is characterized by the parameter b, which is the critical pressure gradient in asymptotic limit (51). As the critical pressure gradient (or the parameter b) increases, the effectiveness of the foam increases. We recall that an increase in the parameter b also leads to an increase in the foam breakthrough time. These conclusions agree qualitatively with the experiments of Refs. 17 and 18. In addition, it was suggested in those papers that the breakthrough time be used as a test of the foam quality. Summarizing, we can conclude that the model reproduces the basic features of the flow of a foam through a porous medium. The flow which we have been discussing is governed by the parameters τ_r and b. These parameters can be extracted from experimental data. Let us take a more detailed look at a

version of the experimental data represented in the form of a seepage law with a limiting gradient. In this case, we know the values of the critical pressure drop P_0, the effective permeability K, and the foam breakthrough time T^*. Using Eq. (51), we can relate the initial parameters to the model parameters:

$$P_0 \frac{\tau_r k}{H^2} = b, \quad K = k\nu_g, \quad T^* = t^*\left(b, P_0 \frac{\tau_r k}{H^2}\right)\tau_r. \quad (52)$$

The system of equations (52) is closed, so the parameters b, τ_r, and k can be found in each individual experiment and then plotted as a function of the degree of water saturation, the pressure drop, and the properties of the surfactant. Unfortunately, most of the experimental papers have reported results on only the steady-state seepage regime, or the effort has been focused on analyzing the propagation of the foam front. As a result, it is difficult at this point to identify the input parameters of the model. Nevertheless, we can work from the existing data to find some rough estimates of the effective length of a bubble train and thereby test the internal consistency of the model. We first estimate the relaxation time τ_r, assuming $\sigma = 30$ dyn/cm, $r = 10^{-3}$ cm, and $p_g = 3$ bar (Ref. 17). We use the approximate expression[16] $a \approx r^2 p_g/\sigma$ for the length of a link. Substituting these values into the expression $1/\tau_r = 1/T_r + 1/\vartheta$, we find

$$\frac{\vartheta}{T_r} = \frac{\xi^2 \nu \pi^2 nRT}{\pi^2 a\sigma 2\pi\nu r\xi^2} = \frac{nRT}{2\pi a\sigma r} = \frac{rp_g}{2\sigma} \approx 10^2 \gg 1.$$

We thus have $\tau_r \approx \vartheta$. We also assume that the condition $b \to \infty$ holds experimentally; then from the first equation of system (52) and from Eq. (48) we find

$$t^* \approx \frac{b}{P_0} = 1.$$

Using the experimental values of the breakthrough time, $T^* \approx 10^4$ s (Ref. 17) and of the viscosity, $\nu \approx 10$ cP (Ref. 11), we find an estimate of the length of a train: $\xi \approx 10^3$ cm. The corresponding volume occupied by the bubble train, $V_\xi \approx 10^{-3}$ cm^3, is much greater than the pore volume $V_p \approx 10^{-9}$ cm^3. We now go back to the first equation of system (52), and we use the estimates $\nu_g \approx 10^{-2}$ cP, $K \approx 10^{-9}$ cm^2, $\nabla P \approx 1$ bar, and $H = 100$ cm (Ref. 17). We verify that the condition $b \approx 10 \gg 1$ holds. The bubble train can thus indeed be treated as a macroscopic entity in a Darcy fluid. We also note that in the case $b \approx 1$ the scaling law $\xi \approx |\nabla P|^{-1/2}$ holds. This law can be found by assuming

$$f \approx \varphi |\nabla P|. \quad (53)$$

Using the definition of the parameter b, we then have $\xi \approx B|\nabla P|^{-1/2}$, where $B = \pi(a\sigma/k\nu\varphi)^{-1/2}$. Estimate (53) is exact when the order parameter satisfies $S \approx 1$. This situation is extremely likely near the entrance cross section of the tube, where the active channels tend to stretch out along the flow.

The model proposed here simplifies substantially when the time scale of the seepage flow is much shorter than the relaxation time τ_r. In this limit, we can ignore the last term in Eq. (37) and write the governing relation as a "modified Maxwell's law":

$$\frac{d\mathbf{F}_f}{dt} = \nabla \mathbf{v} \cdot \mathbf{F}_f + \mathbf{F}_f \cdot (\nabla \mathbf{v})^\dagger + \tfrac{2}{3}\varphi D \cdot \nabla P(t) - \frac{1}{\tau_r}\mathbf{F}_f.$$

4. CONCLUSION

1. The flow of a foam through a porous medium is modeled as the motion of a "bubble train" in a "Darcy fluid." Moving along with freely circulating gas, the trains undergo changes in state because of changes in their intrinsic internal energy and also because of topological transformations. We have derived a rheological governing equation for a gas flow in the presence of a foam. This equation is similar in structure to the equation for a viscoelastic liquid.

2. The model reproduces the "gas-blocking state," in which the degree of water saturation remains constant because of capillary forces, while the gas moves for a long time interval at reduced mobility. An increase in resistance is caused by bubble trains moving in the gas flow.

3. The familiar piecewise-linear approximation of the gas seepage law in the presence of a foam can be explained on the basis of a model of two asymptotic seepage regimes. The first case corresponds to a slow flow of gas through a "matrix" formed by the bubble trains. In this limit the pressure drop is so small that it is incapable of displacing foam from the sample. After a critical pressure drop is exceeded, a high-velocity seepage regime sets in. In this regime the gas moves as if there were no foam at all.

4. The effectiveness of foam as a blocking agent can be identified with microscopic characteristics of the foam on the basis of experiments on frontal displacement. The solution proposed here for the 1D problem makes it possible to identify the parameters of the model if the breakthrough time, the inclinations of links in the piecewise-linear seepage law, and the link intersection point are all known.

This study was initiated by V. M. Entov. He and V. I. Zemskikh also furnished us with some literature sources which were difficult to obtain. We wish to thank them. One of us (K. G. K.) is deeply indebted to A. V. Bazilevskiĭ and A. N. Rozhkov for experimental results which solidly supported the basic hypotheses in the initial stage of this study. In addition, this author wishes to thank J. E. Hanssen and A. Solheim for stimulating discussions and for warm hospitality in Trondheim and Stavanger (Norway). We also wish to thank I. I. Bogdanov for critical comments offered upon a reading of this manuscript.

APPENDIX I

The average value of any quantity $\psi(\mathbf{u})$ is given by

$$\langle \psi(\mathbf{u}) \rangle = \int f(\mathbf{u})\psi(\mathbf{u})d\mathbf{u}, \quad d\mathbf{u} = \frac{\sin\theta}{4\pi} d\varphi d\theta. \quad (AI.1)$$

The distribution function $f(\mathbf{u})$ can be represented as a path integral. Before we go on to the basic calculations, we would like to offer a few comments, following the original ideas of Doi and Edwards.[25] Each link of the channel has its own birth time, i.e., a time at which the part of the train occupying the given link begins its diffusive motion. We denote by t' the birth time of a segment which at time t contains the train link under consideration. We denote by the

vector $\mathbf{u}'$ the direction of the segment at the creation time. The vector $\mathbf{u}'$ is obviously distributed uniformly with respect to direction. After the birth time, the direction of a segment changes along with the macroscopic deformation of the medium, becoming

$$\mathbf{u}'(t,t')=\frac{E\cdot\mathbf{u}}{|E\cdot\mathbf{u}|},$$

at the time t. For each $\mathbf{u}'$ the distribution with respect to directions is thus given by

$$\beta(\mathbf{u})=\langle\delta(\mathbf{u}-\mathbf{u}')\rangle=\int\delta\left(\mathbf{u}-\frac{E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|}\right)d\mathbf{u}_0.$$

To find the distribution function of interest, we need to average this expression over the birth time t'. To do this we need to know the probability that the given segment was created in the time interval between t' and $t'+dt'$. This probability is given by

$$P(t-t')=\sum_i\frac{4}{\pi i\tau_i}\sin\left(\frac{\pi i s}{\xi}\right)\exp(-(t-t')/\tau_i),$$

$$\tau_i=\frac{\xi^2}{\pi^2 i^2 D_f},\quad i=1,3,5\ldots. \tag{AI.2}$$

Hence

$$f(\mathbf{u})=\int_{-\infty}^{t}P(t,t')dt'\int\delta\left(\mathbf{u}-\frac{E\cdot\mathbf{u}_0}{|E\cdot\mathbf{u}_0|}\right)d\mathbf{u}_0. \tag{AI.3}$$

Substituting (AI.2) and (AI.3) into (AI.1), and replacing $\psi(\mathbf{u})$ by the tensor $\mathbf{u}(s)\mathbf{u}(s)\mathbf{u}(s)\mathbf{u}(s)$, we obtain Eq. (20).

APPENDIX II

To solve Eqs. (40)–(43), it is convenient to integrate Eq. (42) over the length of a tube:

$$P_0(t)=v(t)+b\int_0^1 L\,dx. \tag{AII.1}$$

Substituting the solution of transport equation (45) into (AII.1), we find expressions (46) and (47). For a numerical realization, however, it is more convenient to rewrite (AII.1) in differential form,

$$\frac{dv}{dt}=\frac{dP_0}{dt}-b\int_0^1\frac{\partial L}{\partial t}\,dx=\frac{dP_0}{dt}-b\int_0^1\left(-v\,\frac{\partial L}{\partial x}-L\right)dx.$$

Using Eq. (44), we find

$$\frac{dv}{dt}=\frac{dP_0}{dt}+bv(L(1,t)-1)+P_0(t)-v(t)=\frac{dP_0}{dt}$$
$$+P_0(t)+v(t)(bL(1,t)-(b+1)), \tag{AII.2}$$

where

$$L(1,\tau)=\theta(\tau-1)\exp\left(-\int_{\tau-1}^{\tau}\frac{d\beta}{V(\beta)}\right).$$

Numerical results were found through a solution of the equation.

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