Corrections

APPLIED MATHEMATICS

The authors note that on page 20310, left column, second full paragraph, line 2, “ρ = ρ0(1 − α(p − p0))” should instead appear as “ρ = ρ0(1 + α(p − p0))”.

On page 20310, right column, Eq. 7, “δρ = χ(δρ)_{m+1}”, should instead appear as “δρ = χ(δρ)_{m+1}, χ = A_n^m”.

The constant factor ρ0 should be omitted from the right side of Eq. 7. The authors thank Wenchao Liu and his colleagues for noticing this error.

These errors do not affect the further content of the article.

www.pnas.org/cgi/doi/10.1073/pnas.1302983110

BIOPHYSICS AND COMPUTATIONAL BIOLOGY

The authors note that on page E2515, left column, Equation 1, “P_{inc}(i, N) = 4^N \sum_{n=0}^{N/2} \left( 0.25 + B \sin \left( 2\pi \left( \frac{x}{2} + \frac{1}{2} \delta_{GC} \right) \right) \right)” should instead appear as “P_{inc}(i, N) = 4^N \sum_{n=0}^{N/2} \left( 0.25 + B \cos \left( 2\pi \left( \frac{x}{2} + \frac{1}{2} \delta_{GC} \right) \right) \right)”.

On page E2520, left column, Equation 2, “P(Y_i | Y_{i+1}) = P_0 + B \sin \left( 2\pi \left( \frac{x}{2} + \frac{1}{2} \delta_{GC} \right) \right)” should instead appear as “P(Y_i | Y_{i+1}) = P_0 + B \cos \left( 2\pi \left( \frac{x}{2} + \frac{1}{2} \delta_{GC} \right) \right)”.

On page E2520, left column, third full paragraph, lines 2–4, “The dinucleotides AC, AG, and AT follow \frac{1}{2}(1 − P(A|A)), GA, GG, and GT follow \frac{1}{2}(1 − P(C|G)), and TC and TG follow \frac{1}{2}(1 − P(T|T)), because P(A|A) = P(T|T)” should instead appear as “The dinucleotides AC, AG, and AT follow \frac{1}{2}(1 − P(A|A)), GA, GG, and GT follow \frac{1}{2}(1 − P(C|G)), and TC and TG follow \frac{1}{2}(1 − 2P(T|T)), because P(A|A) = P(T|T)”.

These errors do not affect the conclusion of the article.

www.pnas.org/cgi/doi/10.1073/pnas.1301591110

CELL BIOLOGY

The authors note that, in the affiliations, the text, “Laboratories for Morphogenetic Signaling, Cell Asymmetry, and Developmental Dynamics, RIKEN Center for Developmental Biology, Kobe 650-0047, Japan” should instead appear as “Laboratory for Morphogenetic Signaling, RIKEN Center for Developmental Biology, Kobe 650-0047, Japan; Laboratory for Cell Asymmetry, RIKEN Center for Developmental Biology, Kobe 650-0047, Japan; Laboratory for Developmental Dynamics, RIKEN Quantitative Biology Center, Kobe 650-0047, Japan; Laboratory for Developmental Dynamics, RIKEN Quantitative Biology Center, Kobe 650-0047, Japan.” The corrected author and affiliation lines appear below. The online version has been corrected.

www.pnas.org/cgi/doi/10.1073/pnas.1303361110
CHEMISTRY


The authors note that Fig. 1 appeared incorrectly. The scanning tunneling microscopy image shown in the left inset has been replaced. The corrected figure and its legend appear below. This error does not affect the conclusions of the article.

![Corrected STM image of gold nanoparticles](image_url)

**Fig. 1.** STM image of gold nanoparticles coated with a 2:1 ratio of OT/MPA showing ordered phase separation in their ligand shell. (Scale bar, 25 nm.) (Insets) Close up of nanoparticles showing the encircling, ribbon-like domains (Left) and a corresponding simplified schematic diagram in which the red pillars represent MPA, and the yellow represent OT (Right). (Scale bar, 5 nm.)

www.pnas.org/cgi/doi/10.1073/pnas.1303732110
A mathematical model of fluid and gas flow in nanoporous media

Paulo J. M. Monteiro,a,b Chris H. Rycroft,c,d and Grigory Isaakovich Barenblatt,e,f

*Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720-1710; Departments of *Materials and *Mathematics, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; *Department of Mathematics, University of California, Berkeley, CA 94720-3840; and *Institute of Oceanology, Russian Academy of Sciences, Moscow 119997, Russia

Contributed by Grigory Isaakovich Barenblatt, November 2, 2012 (sent for review October 24, 2012)

The mathematical modeling of the flow in nanoporous rocks (e.g., shales) becomes an important new branch of subterranean fluid mechanics. The classic approach that was successfully used in the construction of the technology to develop oil and gas deposits in the United States, Canada, and the Union of Soviet Socialist Republics becomes insufficient for deposits in shales. In the present article a mathematical model of the flow in nanoporous rocks is proposed. The model assumes the rock consists of two components: (i) a matrix, which is more or less an ordinary porous or fissurized-porous medium, and (ii) specific organic inclusions composed of kerogen. These inclusions may have substantial porosity but, due to the nanoscale of pores, tubes, and channels, have extremely low permeability on the order of a nanodarcy (\(\sim 10^{-21}\) m²) or less. These inclusions contain the majority of fluid: oil and gas. Our model is based on the hypothesis that the permeability of the inclusions substantially depends on the pressure gradient. At the beginning of the development of the deposit, boundary layers are formed at the boundaries of the low-permeable inclusions, where the permeability is strongly increased and intensive flow from inclusions to the matrix occurs. The resulting formulae for the production rate of the deposit are presented in explicit form. The formulae demonstrate that the production rate of deposits decays with time following a power law whose exponent lies between −1/2 and −1. Processing of experimental data obtained from various oil and gas deposits in shales demonstrated an instructive agreement with the prediction of the model.

The US Energy Information Administration estimates that American shale gas resources comprise over 20 trillion cubic meters, which is approximately one-third of the total natural gas reserve (1). China, Canada, Saudi Arabia, Germany, and Australia, among other countries, are also developing strong programs to study and explore the extraction of shale gas, which has led to a massive effort to study the mineralogy of shales. The challenges facing the mathematical modeling of gas flow in shales are insightfully discussed in the work of Silin and Kneafsey (2), who also provided contributions on the multiscale characterization of the structure of shales, ranging from the nanoscale up to the scale of a deposit. Improvements in the mathematical modeling of the flow of fluids and gas in nanoporous geometrías can create a new branch of subterranean fluid mechanics.

Shales are fine-grained sedimentary rocks containing high-volume fractions of clay minerals and organic matter, including kerogen, which is resistant to hydrochloric and hydrofluoric acids (3). Although there is agreement on the importance of kerogen in the generation of gas in shales, no mathematical model has explicitly incorporated them in the formulation. Therefore, large-scale development of oil and gas deposits in shales, which started in the past several decades, requires a principally new mathematical model of the flow of oil and gas in these rocks. Loucks et al. (4) reported that most of the nanopores in the Barnett shale exist in the discrete grains of the organic matter; additional nanopores were observed in the bedding plane-parallel wisps of organic-rich matter and in association with extremely fine-grained matrix material. A 30–40% porosity in kerogen has been reported for Barnett shale (2). For the Fayetteville shale at a depth of 700 m, the porosity in kerogen was 40–50%, with nanopores in the range of 10–50 nm (5). The nanoscale size of pores and channels in shales leads to extremely low permeability on the order of a nanodarcy (\(\sim 10^{-21}\) m²). This excludes the practical application of classic models of subterranean fluid dynamics, which were always the basis of the technology to develop oil and gas deposits.

In the present report, such a model is presented based on the assumption of a specific nanostructural transformation of rocks under the action of a large pressure gradient. The basic concepts of the model are presented, and a simple example of the flow in a nanostructural filter is considered in detail. The mathematical equations and their solutions are presented and discussed. After that, more sophisticated models of oil and gas flow in the development of deposits in nanoporous rocks are given. The basic result following from the mathematical model, power law decay of production with time, is confirmed by comparison with the data obtained from shale deposits.

Basic Model of the Unsteady Flow in Nanoporous Rock

The equation of mass conservation in a permeable medium is taken in its usual form as

\[ \phi \partial_t \rho + \nabla \cdot \mathbf{j} = 0. \]  \[ \text{(1)} \]

Here, \(\rho\) is the fluid density; \(\phi\) is the porosity, which can be substantial (i.e., 0.3–0.4); \(\mathbf{j}\) is the flux density; and \(t\) is time. Eq. 1 is complemented by the expression for the flux

\[ \mathbf{j} = \frac{k \rho}{\mu} \nabla p. \]  \[ \text{(2)} \]

where \(p\) is the pressure and \(\mu\) is the dynamic fluid viscosity. We assume that the viscosity and porosity are constant. We emphasize that Eq. 2 is not yet the Darcy law, but the introduction of a new rock characteristic, the permeability \(k\). Eq. 2 becomes the ordinary or a generalized Darcy law only when the permeability is defined explicitly as a material property of the rock. For nanoporous rocks, this is not the case, as we will discuss later.

From Eqs. 1 and 2, the relation

\[ \phi \partial_t \rho = \nabla \cdot \left( \frac{k \rho}{\mu} \nabla p \right) \]  \[ \text{(3)} \]

is obtained. At the beginning of the development of the deposit, the pressure in the matrix decreases rather rapidly; however, due to the extremely low permeability of the inclusions, there appears to be a sharp pressure difference at the inclusion boundaries (Fig. 1). The pressure gradients at close vicinity to
the fluid compressibility coefficient and \( p_0 \) and \( \rho_0 \) are the values of pressure and density, respectively, in the pristine state: \( \alpha(p - p_0) \ll 1 \). The second case is that of isothermic gas flow, where the relation \( p = C_\rho \) can be assumed for a given constant \( C \). In these cases, Eq. 6 becomes closed and takes the form

\[
\partial_\rho = \frac{\rho _0 }{\alpha \mu_\phi},
\]

for the case of weakly compressible fluid and

\[
\partial_\rho = \kappa_\mu \left( \rho_0 (\rho_0 p_{m+1}) \right), \quad \kappa = \frac{A \rho_0} {\mu \phi}
\]

for isothermic gas flow. In the special case of \( m = 0 \), when the equation becomes the classic Darcy law, Eq. 7 takes the form of the equation of piezoconductivity (7, 8), coinciding with the classic equation of diffusion and thermoconductivity. In the case of \( m = 0 \), Eq. 8 takes the form of the classic Boussinesq–Leibenson equation of isothermic gas flow (7, 8) in a porous medium of constant permeability.

**Illustrative Example: Flow of Weakly Compressible Fluid in a Nanoporous Filter**

The problem statement is clearly seen in Fig. 2. The mathematical problem consists of solving Eq. 7 under the boundary conditions

\[
p(0, t) = P + p_0, \quad p(-l, t) = p_0
\]

and the initial condition

\[
p(x, 0) = p_0.
\]

The system of Eqs. 7, 9, and 10 is invariant with respect to the transformation group \( p' = p + \text{const.} \); therefore, we can assume further that \( p_0 = 0 \). We can pass to dimensionless variables

\[
P = \frac{p}{p_0}, \quad \rho = \frac{\rho - \rho_0}{\rho_0 - \rho_0}, \quad \alpha = \frac{\alpha_0}{\alpha_0 - \rho_0}, \quad \mu = \frac{\mu_0}{\mu_0 - \rho_0}, \quad \Lambda = \frac{\Lambda_0}{\Lambda_0 - \rho_0}, \quad \phi = \frac{\phi_0}{\phi_0 - \rho_0}
\]

Two special cases will be considered. The first is a weakly compressible fluid (e.g., oil), when \( \rho = \rho_0 (1 - \alpha (p - p_0)) \). Here, \( \alpha \) is

---

**Fig. 1.** Schematic shows a small region within a shale, consisting of (I) a porous, fissurized matrix that has a permeability sufficient to be treated by classic subterranean fluid mechanics and (II) a kerogen inclusion with very low permeability. During exploitation, a boundary layer of flow forms in the kerogen, as shown by the textured brown strip, with fluid moving out of the inclusion, as indicated by the red arrows. The formation of the boundary layer can be analyzed in terms of the coordinate \( x \) that is normal to the interface between the matrix and the inclusions.

**Fig. 2.** (Upper) Schematic of a nanoporous filter of width \( l \) in a fluid with pressure \( P + p_0 \) in the region \( x > 0 \) and \( p_0 \) in the region \( x < -l \). It is assumed that \( P > 0 \), which causes fluid to flow in the negative direction, as shown by the blue arrows. Under the influence of a large pressure gradient, the structure of the filter is deformed and a boundary layer of finite width forms, as shown by the textured blue and gray region. (Lower) Corresponding pressure profile is shown by the solid purple line. The dashed purple lines show the pressure profile at later times as the boundary layer widens to stretch across the width of the filter until it reaches \( x = -l \). After this, the stabilization process begins, as shown by the dotted purple lines, and a constant pressure gradient across the filter is achieved eventually.
\[ F(\xi, \tau) = \frac{P}{p} \xi = \frac{x}{[\chi(t-t_0)p_m]^{1/m+1}} \]

\[ \tau = \frac{(t-t_0)p_m}{p_n^{m+2}} \]

and consider at first the asymptotics for \( \tau \ll 1 \) assuming its complete similarity, such that

\[ p = Pf(\xi), \quad f(\xi) = F(\xi, 0). \]

Substituting Eq. (12) for Eq. (7), we obtain for \( f(\xi) \) the ordinary differential equation

\[ \frac{\xi}{m+2} df + \frac{d}{d\xi} \left[ \left( \frac{df}{d\xi} \right)^{m+1} \right] = 0 \]

with the boundary conditions

\[ f(0) = 1, \quad f(-\infty) = 0. \]

The results of calculations are presented in Fig. 3. The numerical calculations revealed an instructive property of the solution: It has compact support. This means that it is different from 0 not for all \( \xi < 0 \) but only for \( -\xi_0 < \xi \leq 0 \), where \( \xi_0 \) is a positive constant. Consequently, the “tongue” of filtering fluid reaches the back end of the filter \( x = -l \) not instantaneously but at the moment

\[ t_f = t_0 + \frac{pm+2}{\chi^{m+2}n^2} \]

It is possible to determine an analytical formula for \( \xi_0 \). By writing \( v = df/d\xi \), Eq. (13) can be written as

\[ \frac{\xi^v}{m+2} + (m+1)v^2 \frac{dv}{d\xi} = 0. \]

Integration of this equation using the condition \( v = 0 \) at \( \xi = -\xi_0 \) gives

\[ v^m = \frac{m(\xi_0^m - \xi^m)}{2(m+1)(m+2)}. \]

Because \( f = 0 \) at \( \xi = -\xi_0 \) and \( f = 1 \) at \( \xi = 0 \), it follows that

\[ 1 = \int_{-\xi_0}^{0} \left( \frac{df}{d\xi} \right) d\xi \]

\[ = \left( \frac{m}{2(m+1)(m+2)} \right)^{1/m} \int_{0}^{\xi_0} (\xi_0^m - \xi^m)^{1/m} d\xi. \]
By making the substitution $\xi^2 = \xi_0^2 q$, the integral can be simplified to give

$$1 = \left( \frac{m}{2(m+1)(m+2)} \right)^{1/m} \int_0^1 \xi_0^{2/m} (1-q)^{1/m} \xi_0 \frac{d\xi}{\sqrt{q}}$$

$$= \left( \frac{m_{m+2}^m}{2(m+1)(m+2)} \right)^{1/m} \frac{1}{\sqrt{q} \Gamma \left( \frac{1}{2} \left( 1 + \frac{1}{m} \right) \right)}$$

where $B$ is the Euler $\beta$-function; therefore,

$$\xi_0 = \left( \frac{2(m+1)(m+2)}{m} \right)^{1/m} \frac{1}{\beta \left( \frac{1}{2} \left( 1 + \frac{1}{m} \right) \right)}$$

After $t = t_1$, the stabilization of the filtering begins; this is not a self-similar process. It was computed numerically for some typical values of $m$, and it was demonstrated that the pressure gradient becomes constant inside the filter with 1% accuracy at $\tau = 0.308, 0.157, 0.101$ for the cases of $m = 0.5, 1.5, 2.5$, respectively. As can be seen from Eq. 15, the time of stabilization of the filtration in the nanoporous filter grows significantly with its thickness.

**Oil and Gas Flow in Shales**

According to our basic model, we assume that starting from the moment $t = t_0$ of the beginning of the development of the deposit, the inclusions in the rocks are enveloped by the boundary layers of elevated permeability (Fig. 1) through which the fluid is flowing out of the inclusions.

The boundary layers are thin; thus, the flow in these layers can be assumed to be 1D as we explained previously. The pressure $p_0$ in the matrix is varying slowly; thus, we come to Eqs. 7 and 8, respectively, for the oil and gas flows. The boundary conditions are

$$p(0, t) = p_0, \quad p(\infty, t) = P.$$  [21]

Taking the condition at $x = \infty$ is justified by the same argument as the general boundary layer arguments for viscous flows. Therefore, the pressure distribution across the boundary layer in weakly compressible oil flow is described by the same self-similar solution as in the case of the filter, such that

$$p = Pf(\xi), \quad \xi = \frac{x}{\sqrt[2]{(t-t_0)P_0}}^{1/(m+2)},$$

where $f(\xi)$ satisfies the same equation (Eq. 13), but with different boundary conditions

$$f(0) = \frac{P_0}{P} = \sigma, \quad f(\infty) = 1.$$  [23]

In Fig. 4, results of the numerical computation of the function $f$ and its derivative $df/d\xi$ for the case $\sigma = 0.9$ are shown. As we see, in this case, the function $f$ also has compact support, which can also be proved analytically.

The obtained solution gives the possibility of evaluating the most interesting quantity: the production rate per unit of area, the instantaneous flow from the inclusions to the matrix. We obtain

$$Q = Sj_n = S\rho_0 u_n = \frac{S\rho_0}{\mu} \left( \frac{df(0)}{d\xi} \right)^{m+1} \frac{P^{m+1}}{\sqrt[2]{(t-t_0)P_0}^{(m+1)/(m+2)}}$$

$$= \frac{S\rho_0 P^{(m+1)\sqrt[2]{(t-t_0)P_0}}}{f(0)^{m+1} \sqrt[2]{(t-t_0)P_0}^{(m+1)/(m+2)}}.$$  [24]

Here, $S$ is the specific surface of the inclusion: the surface of the inclusions per unit of volume of the rock.

A similar consideration is appropriate for the gas flow. In this case, the basic equation for the pressure in the boundary layer is Eq. 8 and the boundary conditions are

$$p(0, t) = p_0, \quad p(\infty, t) = P.$$  [25]

The solution to Eq. 8 with the boundary conditions in Eq. 25 is also self-similar, although the independent variable is different, given by

$$p = Pf(\xi), \quad \xi = \frac{x}{\sqrt[2]{(t-t_0)P_0}^{1/(m+2)}}.$$  [26]

where the function $f$ in this case satisfies a different differential equation:

$$\frac{\xi}{m+2} \frac{df}{d\xi} + \frac{d}{d\xi} \left( \frac{df}{d\xi} \right)^{m+1} = 0.$$  [27]

The boundary conditions remain the same as in Eq. 23. The boundary value problem of Eqs. 23 and 27 was solved numerically, and the results are presented in Fig. 5A. An interesting observation followed from these calculations (Fig. 5B), which
was also proved analytically, that for the cases when $\sigma$ is close to 1 (usual practice for the development of gas deposits), there exists a certain universality (independence of the parameter $m$) of the rescaled permeability at the boundary between the matrix and inclusions. The formula for the production rate for gas deposits is given by

$$Q = \frac{SA_0}{\mu} \left( \frac{m + 1}{m + 2} \right) \left( \frac{d}{d\xi} \right)^m \frac{df(0)}{d\xi} .$$  \[28\]

### Comparison with the Data of Development of Oil and Gas Deposits in Shales

The basic result obtained for the exploitation of oil and gas deposits in shales is that the production rate $Q$ decays following the power law $Q \sim (t − t_0)^{−(m+1)/(m+2)}$, where $m$ is a positive parameter in the theory. Therefore, the predicted rate of decay is always faster than $t^{−1/2}$ but slower than $t^{−1}$. A large amount of production data has been accumulated, which makes it possible to check this result. The first dataset considered is from the Eagle Ford shale formation, which, on average, contains 20% quartz, 50% calcite, 20% clay, and 10% kerogen (9). The effective porosity of the reservoir ranged from 3 to 10%, and the permeability ranged from 3 to 400 mD (3 × 10⁻²¹ m² to 4 × 10⁻¹⁹ m²). The decay in gas and oil production is indicated in Fig. 6A, and the regression shows a good fit to a power law with exponents of approximately −0.68, corresponding to $m \approx 1.1$. It has been suggested that Austin chalk and Eagle Ford shale form a single hydrocarbon system, including the evidence that Austin chalk has the same kerogen type as one of the kerogen types in Eagle Ford shale. Therefore, for completeness, the oil production decay for Austin chalk is also included in Fig. 6A, and the results confirm that the exponent for Austin chalk is similar to the one found for Eagle Ford shale. Fig. 6B validates the quality of the decay power law for the gas production from the Barnett, Texas Panhandle, and Haynesville deposits (10). The three decay rates are $t^{−0.55}$, $t^{−0.65}$, and $t^{−0.70}$, which are all within the bounds predicted by the model, and the corresponding values of $m$ are 0.23, 0.73, and 1.3. The large variation in $m$ may reflect the fact that, unlike the Eagle Ford shale–Austin chalk data, these deposits are in separate locations, and may therefore have substantially different geology.

In the present article, a mathematical model was presented of the oil and gas flows in shales, with the rocks consisting of a porous or fissurized matrix having more or less normal porosity and permeability and the inclusions (composed of kerogen) having normal porosity but extremely low permeability due to the nanoscale length size of pores, tubes, and channels. At the boundary layers of the inclusions, under the action of a strong pressure gradient, a sharp increase in the permeability occurs, which leads to substantial flow of oil and gas. Petroleum scientists and engineers should find technological methods to improve the efficiency of the boundary layer further to increase the gas and oil production.

**Acknowledgments.** We thank Dmitriy B. Silin and Simon Strazhgorodskiy for their invaluable help. This publication was based on the work supported, in part, by Award KUS-I1-004021, made by King Abdullah University of Science and Technology. G.I.B. and C.H.R. were partially supported by the Director, Office of Science, Computational and Technology Research, US Department of Energy under Contract DE-AC02–05CH11231.

---

2. Silin D, Kneafsey TJ (2011) Gas shale: From nanometer-scale observations to well modeling (Society of Petroleum Engineers, Richardson, Texas), paper no. 149489.