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Mass Transport of Adsorbed-Phase in Stochastic Porous Medium with Fluctuating Porosity Field and Nonlinear Gas Adsorption Kinetics

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Abstract Using an upscaling approach based on small perturbation theory, the authors have previously investigated the influence of local heterogeneities in matrix porosity on Darcy flow and Fickian-type pore diffusion in the presence of linear non-equilibrium gas adsorption Fathi and Akkutlu, J. Transp. Porous Med. **80**, 281–3044 (2009). They identified non-trivial macro-transport and -kinetics effects of the heterogeneity which significantly retard gas release from the matrix and influence the ultimate gas recovery adversely. The work was a unique fundamental approach for our understanding of gas production and sequestration in unconventional reservoirs; however, it was simplified and did not consider (i) the presence of nonlinear sorption kinetics and (ii) a transport mechanism for the adsorbed phase. In this article, we incorporate the nonlinearity and surface diffusion effects of the adsorbed-phase into their formulation and apply the same upscaling approach to further study the heterogeneity effects. Gas sorption involves the so-called Langmuir kinetics, which is reduced to the well-known Langmuir isotherm in the equilibrium limit. It is found that the nonlinearity participates into both macro-transport and -kinetics, promoting primarily the surface diffusion effects. Whereas surface diffusion, although commonly ignored during modeling subsurface phenomena, brings an intricate nature to the gas release dynamics. Through macro-transport effect of the heterogeneity, it increases ultimate gas recovery and, through the macro-kinetics effect of the heterogeneity, it significantly decreases the time needed to reach the ultimate recovery. As the consequence of these effects, it is shown that the gas–matrix system practically does not reach the equilibrium adsorption limit during any stage of the matrix gas release.

Keywords Adsorption · Diffusion · Heterogeneity · Upscaling · Macro-transport · Macro-kinetics · Langmuir isotherm · Shale gas

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List of Symbols

B_0	Absolute matrix permeability (cm^2)
C	Free gas amount (mol/cc pore)
C_μ	Adsorbed gas amount (mol/cc solid)
$C_{\mu s}$	Maximum adsorbed gas amount (mol/cc solid)
D	Molecular diffusion coefficient (cm^2/s)
$\mathcal{D}$	Apparent diffusion coefficient (cm^2/s)
D_s	Surface diffusion coefficient (cm^2/s)
E	Potential energy (J)
g	Average molar density of free gas (mol/cc)
K	Partition (distribution) coefficient
k_f	Gas adsorption rate coefficient (1/s)
k_r	Gas desorption rate coefficient (1/s)
R_g	Universal gas constant (J K^{-1} mol^{-1})
t	Time coordinate(s)
T	Temperature(K)
x	Space coordinate (cm)
z	Gas compressibility factor

Greek Letters

α	Effective drift velocity (m/s)
ϕ	Porosity
Φ	Solid-to-bulk volume ratio
σ_f^2	Variance of porosity fluctuations
μ	Gas viscosity (kg/cm s)
λ	Porosity correlation length (cm)
ν	vibration frequency factor (1/s)

1 Introduction

Physical adsorption of gaseous phase fluid components in porous materials is commonly associated with separation processes (McCabe et al. 1993). In physical sciences and modern engineering fields, however, a large number of cases and applications exist where gas adsorption and its related phenomena find other important roles. In the energy sector, in particular, they are often closely related to storage of natural gases and hydrogen. In addition, adsorption is more frequently at the center of discussions involving natural gas in-place estimation and production from thermally mature coal seams and organic-rich gas shale reservoirs (Ambrose et al. 2010; Kang et al. 2010). These same natural gas resources are in parallel being considered as the places of CO_2 sequestration, in this case using adsorption as the means of trapping the greenhouse gases.

Separation, storage and entrapment are the consequences of certain gas molecules (with a certain molecular weight, geometry, or polarity) being transferred to and held more strongly on the porous surfaces than others. Hence, these processes involve intricate mass transfer phenomena in porous media in addition to—often nonlinear—adsorption kinetics. Due to short lengths of the characteristic pore size and low permeability, mass transport mechanisms of the adsorbed and free gas could be considered mainly diffusive in these porous materials.

A vast literature exists on transport of free gas in porous media. It is well-recognized that the free gas transport is due to viscous —Darcian—flow and molecular diffusion and that the overall movement of the gas could be significantly retarded in the presence of adsorption. If large enough voids are available, diffusive transport of free gas could take place in pores and throats due to random movement and collisions of molecules from high- to low-concentration regions, i.e., bulk (or pore) diffusion. With the decreasing pore sizes, however, and depending on the pore pressure and temperature, molecular streaming (or Knudsen diffusion) could develop as an additional transport mechanism indicating the dominant effect of collisions between the gas and pore wall molecules. Surface and solid (or interstitial) diffusion, on the other hand, are often associated with mass transport of the sorbed (adsorbed and dissolved, respectively) phase. The latter transport mechanisms have been the subjects of research for several decades, see Tiselius (1934, 1935) for the earliest discussion. Carman and Raal (1951), Ash et al. (1963), Aylmore and Barrer (1966), Do and Wang (1998), and Siemons et al. (2007) independently performed experiments using different gases to investigate the magnitude of gas transport mechanisms in microporous materials such as carbon and coal. They found that the sorption rate in porous media cannot be accounted for only by free gas diffusion and there must be an additional transport of the adsorbed-phase. In several experiments, although a slow mechanism of transport, surface diffusion is quantified as the dominant one, in some cases with a significantly larger contribution than viscous gas flow.

A simple approach to describe surface diffusion of the adsorbed-phase is to consider a net adsorbed-phase mass flux as molecules hopping from one adsorption site to another adjacent site due to thermal motion of the molecules under the influence of pore walls. Accordingly, the adsorbed-phase transport is an activated diffusion that could be described as Fickian where the flux is proportional to the adsorbed-phase concentration gradient with a diffusivity in Arrhenius form: $D_s = \nu \exp(-E/RT)$. Hence, only the activated adsorbed molecules with a desorption energy beyond the activation energy threshold could participate in the transport process. This may be an appropriate approach to model the adsorbed-phase transport in geological formations such as coal and shale, since the local reservoir conditions are typically below the capillary condensation threshold. When loading exceeds monolayer adsorption limit, one needs to consider a hydrodynamic model such as the one earlier proposed by Gilliland et al. (1958).

Solid diffusion represents the movement of small gas molecules inside the macromolecular openings of the solid phase that make up the matrix. As a transport mechanism, it has been proposed to consider transient solid dissolution of the gases. It may be distinguished from the surface diffusion by investigating changes in the rate of mass transport due to changes in gas type. Solid diffusion rate decreases (while surface diffusion increases) as molecular size of the gas becomes larger and heavier (Do 1998). Depending on the porous material, these diffusive transport mechanisms could act individually or simultaneously (Sevenster 1959; Thimons and Kissell 1973).

In this article, using a continuum approach, we consider the adsorbed-phase transport in the presence of free gas in heterogeneous porous materials and show that the adsorbed-phase transport could be significantly enhanced by local fluctuations in porosity. The enhancement is beyond the levels that can be explained using the adsorbed-phase concentration gradient arguments. Hence, the work brings new insight to previous experimental observations on how a slow transport process such as surface diffusion can dominate the overall gas mass transfer across porous materials.

In our formulation, the adsorbed-phase behavior is due to a mass balance equation that includes non-linear adsorption kinetics. We consider that surface diffusion is the only mechanism of transporting the adsorbed phase and that its mass flux is proportional to the gradient of the adsorbed-phase concentration. The assumption of having monolayer gas adsorption is held and the amount of gas as condensate and at a dissolved state is assumed to be negligible in the solid. In addition, for clarity during the analysis, we consider the effects of bulk and Knudsen diffusion combined in one effective pore diffusion which accounts for the overall free gas transport.

Natural or synthetic porous materials involving adsorption-related phenomena are often characterized by a network of relatively small pores. The common characteristics are large internal surface area, providing enough adsorption sites to store significant amounts of fluid, and very low matrix porosity and permeability. In some of these studies, the porous materials have adjustable characteristics that could be a symmetry in pore sizes and homogeneity in porosity, while in the others (such as natural gas resources and for CO_2 sequestration) the porous material is fairly large and heterogeneous in its petrophysical qualities. Particularly in the latter case, the porous material shows complexity in pore structure and material content. In this study, we consider such case in which the porosity of the material is considered heterogeneous with spatially-correlated random fluctuations. Complexity in structure and material content of the porous material is due to a random porosity field that holds the assumption of first and second-order stationarity.

The effect of locally fluctuating porosity field on the free and the adsorbed gas is analyzed using small perturbations theory, a proven approach widely used in various other disciplines where analysis of flow and multi-physics is necessary. A similar approach has been considered by the same authors recently to investigate the effects of fluctuations in porosity and material content on the free gas phase transport in heterogeneous porous media (Fathi and Akkutlu 2009). This recent work was inspired by Forster (1977), Gelhar (1993), and L'Heureux (2004).

2 Local Governing Equations Describing Gas Behavior in Homogeneous Matrix

2.1 Kinetics of Gas Sorption in Porous Media

In this study, we introduce surface diffusion as the mechanism of transport for the adsorbed phase under isothermal conditions. Previously, linear approaches for the adsorption kinetics of fluids in porous media have been used by several authors, see for example, Brusseau et al. (1991), Hu et al. (1995), Alvarado et al. (1998), and Fathi and Akkutlu (2009), assuming that the adsorption rate is independent of the adsorbed gas concentration. However, when single-component sorption rates are considered, it is more realistic to consider that adsorption follows the so-called Langmuir kinetics. Koss et al. (1986) showed that the gas behavior in carbons may not be diffusion-limited, therefore it can be accurately modeled using rate expressions. The nonlinear sorption kinetics behavior of gas has previously been studied by several authors, see, for example, Srinivasan et al. (1995) and Schlebaum et al. (1999). These studies have shown that the nonlinearity can influence diffusive processes. In essence, the nonlinearity could also be considered as the concentration-dependency of the diffusion coefficients (Farooq and Ruthven 1991). In this study, we introduce the nonlinear sorption kinetics as the rate of interchange between the adsorbed-phase and free gas using the following mass balance:

$$\frac{\partial C_\mu}{\partial t} = k_f (C_{\mu s} - C_\mu) C - k_r C_\mu \tag{1}$$

C is the molar density of the free gas in moles per unit pore volume, whereas C_μ the molar density of the adsorbed-phase in moles per unit solid volume. k_f and k_r are the adsorption and desorption rate coefficients, respectively. $C_{\mu s}$ is maximum monolayer gas adsorption of the matrix solid surface. If thermodynamic equilibrium is reached, Eq. 1 simplifies to the well-known Langmuir equation:

$$C_{\mu} = \frac{C_{\mu s} K C}{1 + KC} \tag{2}$$

Here, $K = k_f / k_r$ is often referred to as the equilibrium partition (or, distribution) coefficient.

2.2 Conservation of Gas Mass in Porous Media

Both bulk diffusion and viscous flow are considered for the free gas transport in the matrix. Consequently, local equations describing gas transport become:

$$\phi \frac{\partial C}{\partial t} + (1-\phi) \frac{\partial C_{\mu}}{\partial t} = \frac{\partial}{\partial x}\left(\phi\, D \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial x}\left(\phi C \frac{B_0}{\mu} \frac{\partial p}{\partial x}\right) + \frac{\partial}{\partial x}\left[(1-\phi)\, D_s \frac{\partial C_{\mu}}{\partial x}\right] \tag{3}$$

$$\frac{\partial C_{\mu}}{\partial t} = k_r \left[K (C_{\mu s} - C_{\mu}) C - C_{\mu}\right] \tag{4}$$

Here, x–t are the space–time coordinates, ϕ the interconnected porosity, $D(\phi)$ the tortuosity-corrected coefficient of molecular diffusion, B_0 the absolute permeability of the porous medium, p the pore pressure, and μ the dynamic gas viscosity. Note that the formulation contains a diffusive transport term which is Fickian in nature. This roughly corresponds to bulk (pore) diffusion as the mechanism of transport. The existence of other mechanisms (e.g., Knudsen diffusion) will not be considered in this work. The pressure is obtained converting the molar density of the gas using lower order virial equation of state $p \cong R_g T C + R_g T X C^2$ with the parameter X representing the second virial coefficient. Previous sensitivity analysis on ultimate gas recovery and concentration profiles (Fathi and Akkutlu 2009) showed that the ideal gas assumption is safe in our case, so $p \cong R_g T C$ is used to convert the gas molar density to pore pressure.

According to this new formulation the resistance controlling adsorption dynamics is only due to adsorbed-phase diffusion, i.e., surface diffusion, with the adsorbed-phase diffusivity D_s. This indicates that, although the adsorbed gas molecules are always under the restrictive influence of the solid walls, the concentration gradient $\partial C_{\mu} / \partial x$ may be high such that significant surface fluxes are possible in the matrix (Yi et al. 2008, 2009). Next Eqs. 3–4 are re-organized and written in the following form:

$$\frac{\partial C}{\partial t} + \Phi \frac{\partial C_{\mu}}{\partial t} = \alpha_1 \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} + \beta \alpha' \frac{\partial C}{\partial x} + \beta C \frac{\partial^2 C}{\partial x^2} + \alpha_2 \frac{\partial C_{\mu}}{\partial x} + \Phi D_s \frac{\partial^2 C_{\mu}}{\partial x^2} \tag{5}$$

$$\frac{\partial C_{\mu}}{\partial t} = k_r \left[K (C_{\mu s} - C_{\mu}) C - C_{\mu}\right] \tag{6}$$

Here, we introduce $\alpha_1 = \dfrac{\partial(\phi D)}{\phi \partial x}$ as an effective drift velocity, reflecting changes in free gas concentration due to a non-constant diffusivity with a gradient and $\alpha_2 = \dfrac{\partial[(1-\phi) D_s]}{\phi \partial x}$ as an effective drift velocity of adsorbed phase due to non-constant surface diffusion coefficient with a gradient. In addition, we define $\alpha' = \dfrac{\partial(\phi C)}{\phi \partial x}$, $\beta = B_0 R_g T / \mu$ as the gas mobility, and $\Phi = (1-\phi)/\phi$ as the solid-to-bulk volume ratio.

3 Gas Behavior in Heterogeneous Matrix

Consider a porous medium where medium heterogeneity is defined by a time-independent, spatially fluctuating porosity field. The porous medium still maintains an average porosity and absolute permeability. Application of the random porosity field, instead of random permeability, is more appropriate because the transport is mainly diffusive. Next the classical perturbation theory was employed where porosity ϕ is defined in terms of its mean $\bar{\phi}$ and its small fluctuation $\tilde{\phi}$ such that $\phi = \bar{\phi} + \tilde{\phi}$. The latter is assumed to be Gaussian random number of zero average around the mean porosity. Further, the assumption of first- and second-order stationarity, i.e., mean and variance of porosity kept constant, is held with a well-defined spatial covariance function. The dependent variables, transport and rate coefficients will be affected by the random porosity field; therefore, they should also be considered as random variables. We thus have

$$\begin{array}{lll} \alpha_1 = \bar{\alpha}_1 + \tilde{\alpha}_1 & \alpha_2 = \bar{\alpha}_2 + \tilde{\alpha}_2 & \alpha' = \bar{\alpha}' + \tilde{\alpha}' \\ C = \bar{C} + \tilde{C} & C_\mu = \bar{C}_\mu + \tilde{C}_\mu & D = \bar{D} + \tilde{D} \\ D_s = \bar{D}_s + \tilde{D}_s & \Phi = \bar{\Phi} + \tilde{\Phi} & K = \bar{K} + \tilde{K} \end{array}$$

where a bar and a tilde over a quantity denote its average value and its fluctuations about the mean, respectively. Note that all the random variables are dependent and cross-correlated using cross correlations defined in Appendix B, Table 2. This means the porosity fluctuations have the potential to generate variations in gas adsorption and desorption rates. This is not only a reasonable but also an important consideration since porous media are often mixtures of various materials exhibiting an intricate pore-network. Variations in the material properties add to structurally complex nature of a porous medium, influencing gas retention (adsorption) capacity. Substituting these expressions into the governing equations (5–6) and taking the expectations of the equations, the mean equations for the free and adsorbed gas are obtained as follows:

$$\frac{\partial \bar{C}}{\partial t} + \bar{\Phi} \frac{\partial \bar{C}_\mu}{\partial t} - \bar{D} \frac{\partial^2 \bar{C}}{\partial x^2} - \bar{\Phi} \bar{D}_s \frac{\partial^2 \bar{C}_\mu}{\partial x^2} = \bar{R} \tag{7}$$

$$\frac{\partial \bar{C}_\mu}{\partial t} = k_r \left[\bar{K} \bar{C} (C_{\mu s} - \bar{C}_\mu) - \bar{C}_\mu + (C_{\mu s} - \bar{C}_\mu) \overline{\tilde{K} \tilde{C}} - \bar{C} \overline{\tilde{K} \tilde{C}_\mu} - \bar{K} \overline{\tilde{C}_\mu \tilde{C}} \right] \tag{8}$$

where we introduce $\bar{R}$ as

$$\begin{aligned} \bar{R} = {} & \bar{\alpha}_1 \frac{\partial \bar{C}}{\partial x} + \beta \bar{\alpha}' \frac{\partial \bar{C}}{\partial x} + \bar{\alpha}_2 \frac{\partial \bar{C}_\mu}{\partial x} + \beta \bar{C} \frac{\partial^2 \bar{C}}{\partial x^2} \\ & + \sum_{m=1,2} \overline{\frac{\xi_m \partial^m \tilde{C}}{\partial x^m}} + \beta \overline{\frac{\tilde{\alpha}' \partial \tilde{C}}{\partial x}} - \overline{\frac{\tilde{\Phi} \partial \tilde{C}_\mu}{\partial t}} + \overline{\tilde{\alpha}_2 \frac{\partial \tilde{C}_\mu}{\partial x}} + \bar{D}_s \overline{\tilde{\Phi} \frac{\partial^2 \tilde{C}_\mu}{\partial x^2}} + \bar{\Phi} \overline{\tilde{D}_s \frac{\partial^2 \tilde{C}_\mu}{\partial x^2}} \end{aligned} \tag{9}$$

Here, for simplicity we defined $\xi_1 = \tilde{\alpha}_1$ and $\xi_2 = \tilde{D}$ in Eq. 9. First, second and third terms on the right hand side of the equation are corrections to the drift velocities; the fourth term is related to viscous transport, and the remaining terms indicate non-trivial cross-correlations due to the fluctuating matrix porosity. Importantly, a series of auto- and cross-correlations appear in the formulation, such as cross-correlations among the partition coefficient, free gas and adsorbed-phase in Eq. 8, indicating the impact of local porosity fluctuations on the adsorption kinetics and gas transport. Subtracting the obtained mean equations (7–8) from the original ones (i.e., Eqs. 5 and 6 after inserting the definition of perturbed quantities), the mean-removed equations are derived:

$$\begin{aligned}
&\frac{\partial \tilde{C}}{\partial t} + \bar{\Phi}\frac{\partial \tilde{C}_\mu}{\partial t} - \bar{\alpha}_1\frac{\partial \tilde{C}}{\partial x} - \bar{D}\frac{\partial^2 \tilde{C}}{\partial x^2} - \beta\bar{\alpha}'\frac{\partial \tilde{C}}{\partial x} - \beta\bar{C}\frac{\partial^2 \tilde{C}}{\partial x^2} \\
&\quad -\beta\tilde{C}\frac{\partial^2 \bar{C}}{\partial x^2} - \bar{\alpha}_2\frac{\partial \tilde{C}_\mu}{\partial x} - \bar{\Phi}\bar{D}_s\frac{\partial^2 \tilde{C}_\mu}{\partial x^2} = \tilde{R} \qquad (10)
\end{aligned}$$

$$\frac{\partial \tilde{C}_\mu}{\partial t} + k_r\tilde{C}_\mu + k_r\bar{K}\bar{C}\tilde{C}_\mu = k_r\bar{K}\left(C_{\mu s} - \bar{C}_\mu\right)\tilde{C} + k_r M \qquad (11)$$

where $\tilde{R}$ and M are defined as follows:

$$\begin{aligned}
\tilde{R} = &-\tilde{\Phi}\frac{\partial \bar{C}_\mu}{\partial t} - \tilde{\Phi}\frac{\partial \tilde{C}_\mu}{\partial t} + \frac{\overline{\tilde{\Phi}\partial \tilde{C}_\mu}}{\partial t} + \tilde{\alpha}_1\frac{\partial \bar{C}}{\partial x} + \tilde{\alpha}_1\frac{\partial \tilde{C}}{\partial x} - \frac{\overline{\tilde{\alpha}_1\partial \tilde{C}}}{\partial x} + \tilde{D}\frac{\partial^2 \bar{C}}{\partial x^2} + \tilde{D}\frac{\partial^2 \tilde{C}}{\partial x^2} \\
&- \frac{\overline{\tilde{D}\partial^2 \tilde{C}}}{\partial x^2} + \beta\tilde{\alpha}'\frac{\partial \bar{C}}{\partial x} + \beta\tilde{\alpha}'\frac{\partial \tilde{C}}{\partial x} - \beta\frac{\overline{\tilde{\alpha}'\partial \tilde{C}}}{\partial x} + \beta\tilde{C}\frac{\partial^2 \tilde{C}}{\partial x^2} - \beta\frac{\overline{\tilde{C}\partial^2 \tilde{C}}}{\partial x^2} + \tilde{\alpha}_2\frac{\partial \tilde{C}_\mu}{\partial x} \\
&+ \tilde{\alpha}_2\frac{\partial \bar{C}_\mu}{\partial x} - \frac{\overline{\tilde{\alpha}_2\partial \tilde{C}_\mu}}{\partial x} + \bar{\Phi}\tilde{D}_s\frac{\partial^2 \tilde{C}_\mu}{\partial^2 x} + \bar{\Phi}\tilde{D}_s\frac{\partial^2 \bar{C}_\mu}{\partial^2 x} + \tilde{\Phi}\bar{D}_s\frac{\partial^2 \bar{C}_\mu}{\partial^2 x} + \tilde{\Phi}\tilde{D}_s\frac{\partial^2 \bar{C}_\mu}{\partial^2 x} \\
&- \overline{\tilde{\Phi}\tilde{D}_s}\frac{\partial^2 \bar{C}_\mu}{\partial^2 x} - \bar{\Phi}\frac{\overline{\tilde{D}_s\partial^2 \tilde{C}_\mu}}{\partial^2 x} + \tilde{\Phi}\bar{D}_s\frac{\partial^2 \tilde{C}_\mu}{\partial^2 x} + \tilde{\Phi}\tilde{D}_s\frac{\partial^2 \tilde{C}_\mu}{\partial^2 x} - \bar{D}_s\frac{\overline{\tilde{\Phi}\partial^2 \tilde{C}_\mu}}{\partial^2 x} \qquad (12)
\end{aligned}$$

$$\begin{aligned}
M = &\, C_{\mu s}\left(\tilde{K}\bar{C} + \tilde{K}\tilde{C} - \overline{\tilde{K}\tilde{C}}\right) - \bar{C}\bar{C}_\mu\tilde{K} - \bar{K}\tilde{C}_\mu\tilde{C} - \bar{C}_\mu\tilde{K}\tilde{C} - \bar{C}\tilde{K}\tilde{C}_\mu \\
&+ \overline{\tilde{K}\tilde{C}}\bar{C}_\mu + \overline{\tilde{C}_\mu\tilde{C}}\bar{K} + \overline{\tilde{C}_\mu\tilde{K}}\bar{C} \qquad (13)
\end{aligned}$$

As stated earlier, the fluctuations are assumed to be Gaussian random numbers with zero mean, (i.e., $\overline{\tilde{C}} = \overline{\tilde{C}_\mu} = \overline{\tilde{D}} = \overline{\tilde{D}_s} = \overline{\tilde{K}} = \overline{\tilde{\Phi}} = \overline{\tilde{\alpha}_1} = \overline{\tilde{\alpha}_2} = \overline{\tilde{\alpha}'} = 0$); however, their auto– and cross–correlations (e.g., $\overline{\tilde{\alpha}_1\tilde{\alpha}_1}$ and $\overline{\tilde{\alpha}_1\tilde{D}}$) are non-trivial.

The assumption of small-perturbations was implemented. Accordingly, the porosity fluctuations are small such that the terms including fluctuation correlations higher than second order are neglected. Also, $\tilde{C}(x, t = 0) = \tilde{C}_\mu(x, t = 0) = 0$ are taken. The upscaled governing equations describing gas behavior in the heterogeneous matrix can be obtained by substituting explicit expressions for the auto– and cross–correlation terms in the mean equations (7–8). We approached the problem by first finding the general solutions for the free and adsorbed gas fluctuations, $\tilde{C}(k, s)$ and $\tilde{C}_\mu(k, s)$ in Fourier–Laplace domain. Next the correlation terms, which appear in the mean equation (7), are obtained by multiplying the proper spatial and temporal derivative of the concentration fluctuations (free or adsorbed) with the fluctuating term and keeping only up to second-order terms. Further, the correlation terms which appear in the mean equation (8) are obtained by multiplying the concentration fluctuations with the fluctuating term and keeping only up to second-order terms. The auto- and cross-correlation terms include a set of convolution integral terms in Fourier–Laplace domain. In order to evaluate these integrals, spatial correlation function is defined as $\overline{\tilde{\phi}(x)\tilde{\phi}(y)} = \sigma_\phi^2 f(|x - y|)$. We assume Gaussian model for the spatial covariance of porosity, characterized by correlation length λ: $f_x = \exp\left(-x^2/2\lambda^2\right)$. The model can be written as $f_Q = \sqrt{2\pi}\lambda\exp\left(-Q^2\lambda^2/2\right)$ in the spectral domain. Complete details of the mathematical procedure are presented in Appendix A. Details on the methodology and the correlation functions can be found in Forster (1977), Gelhar (1993), L'Heureux (2004) and more recently in Fathi and Akkutlu (2009).

4 Upscaled Governing Equations for the Nonlinear Problem with Surface Diffusion

The upscaled governing equations describing gas mass transport and nonlinear sorption kinetics are given in Eqs. 73–74 in the Appendix A. Using the definitions of $\bar{\alpha}_1, \bar{\alpha}_2, \bar{\Phi}, \bar{\alpha}'$, and β, in these upscaled equations and after simplifying and re-arranging, the following new form of the upscaled equations are obtained:

$$\bar{\phi}\frac{\partial \bar{C}}{\partial t} + (1-\bar{\phi})\frac{\partial \bar{C}_\mu}{\partial t} = \frac{\partial}{\partial x}\left(\bar{\phi}\mathcal{D}_{\text{eff}}\frac{\partial \bar{C}}{\partial x}\right) + \frac{\partial}{\partial x}\left(\bar{\phi}\bar{C}\frac{B_0}{\mu}\frac{\partial \bar{p}}{\partial x}\right) + \frac{\partial}{\partial x}\left[(1-\bar{\phi})\,\bar{D}_{s,\text{eff}}\frac{\partial \bar{C}_\mu}{\partial x}\right] + \Gamma_{\text{tr}} \tag{14}$$

$$\frac{\partial \bar{C}_\mu}{\partial t} = k_r\left[\bar{K}(\bar{C}_{\mu s} - \bar{C}_\mu)\bar{C} - (\bar{C}_\mu + \Gamma_{kn})\right] \tag{15}$$

Here, importantly, new quantities appear reflecting the macro-effects of local porosity heterogeneities. These are defined as follows:

$$\mathcal{D}_{\text{eff}} = \bar{D} - D'\sigma_\phi^2\left\{\frac{\dfrac{2D' + \beta g' + \dfrac{\bar{D}+\beta g}{\bar{\phi}}}{\bar{D}+2\beta g}}{1 + \dfrac{\upsilon_1\bar{\Phi}\bar{D}_s\bar{K}}{\bar{D}+2\beta g}} + \frac{\bar{K}\upsilon_1\left[1/\bar{\phi}(D_s' + \bar{D}_s) + \bar{D}_s\right]}{\bar{D}+2\beta g + \upsilon_1\bar{\Phi}\bar{D}_s\bar{K}}\right\} \tag{16}$$

$$\mathcal{D}_{s,\text{eff}} = \bar{D}_s - \frac{\sigma_\phi^2}{\bar{\Phi}}\left\{\begin{array}{l}\dfrac{2D'D_s'\bar{\Phi} + (\bar{\Phi}D_s' - \bar{D}_s)\left(\beta g' + \dfrac{\bar{D}+\beta g}{\bar{\phi}}\right)}{\bar{D}+2\beta g + \upsilon_1\bar{\Phi}\bar{D}_s\bar{K}} \\ + \dfrac{\bar{K}\upsilon_1\left[\left(D_s' + \dfrac{\bar{D}_s}{\bar{\phi}}\right)(\bar{\Phi}D_s' - \bar{D}_s) + (\bar{\Phi}D_s' + \bar{D}_s)^2\right]}{\bar{D}+2\beta g + \upsilon_1\bar{\Phi}\bar{D}_s\bar{K}}\end{array}\right\} \tag{17}$$

$$\Gamma_{\text{tr}} = \left\{\frac{\beta g' + \left(\dfrac{\bar{D}+\beta g}{\bar{\phi}}\right) + \bar{K}\upsilon_1\left[D_s' + (\bar{D}_s - D_s')\bar{\Phi}\right]}{\bar{D}+2\beta g + \upsilon_1\bar{K}\bar{\Phi}\bar{D}_s}\right\}\left(1 - \upsilon_2\upsilon_1\bar{C}\right)\bar{\phi}\sigma_\phi^2\bar{C}_{\mu 0} + \frac{K'\upsilon_1\left[D_s' + \left(\bar{D}_s - D_s'\right)\right]}{\lambda^2}\bar{\phi}\sigma_\phi^2\bar{C} \tag{18}$$

$$\Gamma_{kn} = \left(\frac{\upsilon_1\sigma_\phi^2\lambda^2\bar{C}_{\mu 0}K'}{\bar{D}+2\beta g + \upsilon_1\bar{K}\bar{\Phi}\bar{D}_s}\right)\left(1 + \upsilon_2\upsilon_1\bar{C} + \frac{2\bar{\Phi}\bar{D}_s\bar{K}^2\upsilon_1\bar{C}}{\bar{D}+2\beta g + \upsilon_1\bar{K}\bar{\Phi}\bar{D}_s}\right) \tag{19}$$

In the above equations, we defined $D' = \mathrm{d}\bar{D}/\mathrm{d}\bar{\phi} > 0$, $D_s' = \mathrm{d}\bar{D}_s/\mathrm{d}\bar{\phi} > 0$ and $K' = d\bar{K}/d\bar{\phi} < 0$. In addition, assuming the free gas amount is replaced by its value averaged over a large space domain L and time interval τ, we introduced g and g' as follows: $\bar{\bar{C}} = \int_0^\tau\int_0^L C(x,t)\mathrm{d}x\mathrm{d}t/L\tau \equiv g$ and $\partial\bar{\bar{C}}/\partial\overline{\bar{\phi}} = g'$. $\bar{C}_{\mu 0}$ is the average initially adsorbed gas amount that can be found using Langmuir equilibrium condition at $t = 0$. Finally, υ_1 and υ_2 are identified as new common parameters of our analysis:

$$\upsilon_1 = \frac{C_{\mu s} - \bar{C}_\mu}{1 + \bar{K}\bar{C}} \tag{20}$$

$$\upsilon_2 = \frac{(1-\bar{\phi})\bar{D}_s K'}{\bar{\phi}\lambda^2 \bar{C}_{\mu 0}} \tag{21}$$

These appear in the upscaled formulation purely due to the introduction of adsorption nonlinearity and surface diffusion, respectively.

5 Discussion

Based on the analytical part of our investigation, the following fundamental observations can be made in regards to structure of the upscaled differential equations :

(1) Upscaling introduces clearly defined new terms into the governing equations. These are the diffusive terms (involving apparent pore diffusivity $\mathcal{D}_{\text{eff}}$ and apparent surface diffusivity $\mathcal{D}_{s,\text{eff}}$) and the source/sink terms Γ_{tr}, and Γ_{kn}. The latter may also be considered as decay terms during the gas release from the matrix because they depend on the gas amounts in porous medium.

(2) Upscaled equations show gas amount dependency of pore and surface diffusion in the presence of nonlinear adsorption kinetics. It also shows that change in the adsorbed gas amount in time is related to the average of initially adsorbed gas amount $\bar{C}_{\mu 0}$. This effect is known as loading effect, as discussed earlier by Do (1998).

(3) In the homogeneous limit Γ terms all disappear and the apparent diffusion coefficients reduce to their homogeneous form due to the fact that the variance σ_ϕ^2 of the porosity field becomes nil. Hence, the upscaled equations (14–15) become identical with the local equations (3–4), i.e., the homogeneous case.

(4) Nonlinearity in sorption kinetics and surface diffusion are represented in the upscaled formulation by two new terms υ_1 and υ_2. Interestingly, when both υ_1 and υ_2 go to zero, the equations are reduced to the form earlier reported by Fathi and Akkutlu (2009), i.e., the linear case.

Second part of the work involves numerical analysis of the upscaled governing equations describing gas adsorption and transport in heterogeneous porous medium using a time-implicit finite difference approach based on Newton method and using gas/matrix system parameters given in Table 1. The data set includes the local (or measured) values of viscous flow and diffusive transport, and kinetics parameters for a symmetric matrix block (slab) with a half-length of 10.0 cm. In addition, the data set introduces a mildly heterogeneous matrix porosity as a base-case for the sensitivity analysis. For the purpose, gas release from a matrix is considered and presented as a one-dimensional initial/boundary value problem shown in Fig. 1. Results reflecting the influence of porosity heterogeneity on gas release rates are demonstrated using fractional gas recovery curves and comparing with the equivalent homogeneous case. Below, we take a closer look at the influence of local porosity fluctuations on the system behavior in terms of macro-transport and -kinetics effects.

The sensitivity analysis on the ultimate gas recovery showed that the heterogeneity does not have any significant impact on the effective pore and surface diffusivity values. Therefore $\mathcal{D}_{\text{eff}}$ and $\mathcal{D}_{s,\text{eff}}$, can be safely reduced to their local mean values of $\bar{D}$ and $\bar{D}_s$. We use the local mean values for the latter quantities in our analysis.

Table 1 Problem parameters for the heterogeneous gas/matrix system

Parameter	Unit	Value
$\bar{\phi}$	–	1.0E−2
σ_{ϕ}^{2}	–	5.3E−7
$\bar{C}_0$	mol/cc	2.0E−3
k_r	1/s	1.0E−5
$\bar{K}$	–	0.1
$\bar{C}_{\mu s}$	mol/cc	0.9
g	mol/cc	2.028E−4
B_0	cm^2	4.934E−14
μ_g	kg/cm s	2.0E−7
K'	–	−5.0E2
$\bar{D}$	cm^2/s	1.0E−3
$\bar{D}_s$	cm^2/s	2.5E−5
D'	cm^2/s	3.3E−2
D'_s	cm^2/s	3.3E−5
g'	mol/cc	−0.00835
λ	cm	1.0
L	cm	10.0
R_g	$\mathrm{kg\,cm}^2/(\mathrm{s}^2\,\mathrm{K\,mol})$	8.314E−4
T	K	293.15

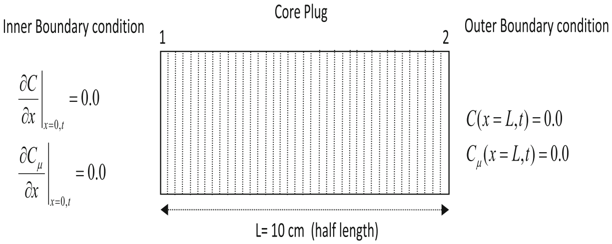


Fig. 1 A schematic showing the setup for numerical simulation. $\delta x_i = 10/500$ cm and $\delta t_i = 1.4$ minutes for $i = 1, 2, \ldots, 500$, $C(x, t = 0) = 2.0E{-}3$, $C_\mu(x, t = 0) = 2.0E{-}4$mol/cc

5.1 Macro-Kinetics Effects

Our numerical investigation based on the sensitivity of the upscaled quantities to gas release dynamics showed that the expression of macro-kinetics, Γ_{kn}, i.e., the right-hand-side of Eq. 19 can be simplified. The last term in second parenthesis takes small values during the simulation so that it can be ignored for the analysis. Furthermore, substituting definition of β, we obtain:

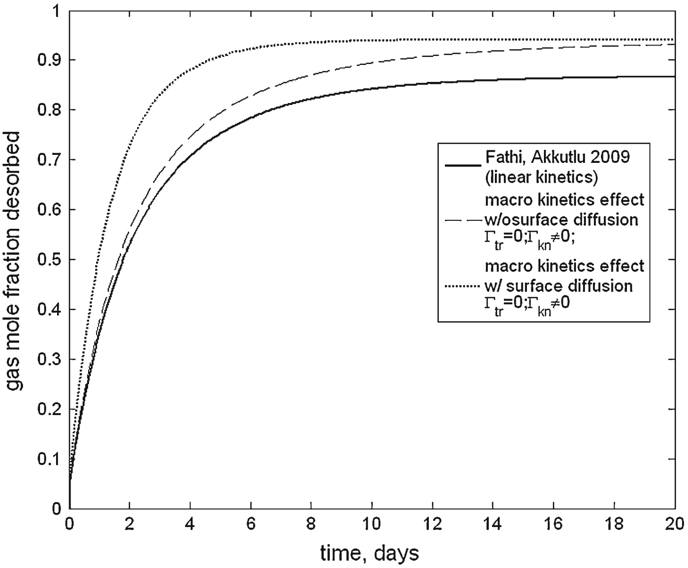


Fig. 2 The effect of macro-kinetics on matrix gas release

$$\begin{aligned}\mathit{\Gamma}_{kn} &\cong \upsilon_1\left(\frac{K'\sigma_\phi^2\lambda^2\bar{C}_{\mu0}}{\bar{D}+\dfrac{2B_0\bar{\bar{p}}}{\mu}}\right)\left(1+\upsilon_1\upsilon_2\bar{C}\right)=\upsilon_1\left[\frac{N_{Th}\sigma_\phi^2\bar{C}_{\mu0}}{k_r(1+2N_{Pe})}\right]\left(1+\upsilon_1\upsilon_2\bar{C}\right)\\ &=\upsilon_1\left(1+\upsilon_1\upsilon_2\bar{C}\right)\mathit{\Gamma}_{kn,\text{linear}}\end{aligned} \tag{22}$$

Here, $\mathit{\Gamma}_{kn,\text{linear}}$ has previously been introduced by Fathi and Akkutlu (2009) in their study on convection–diffusion with linear adsorption in the absence of adsorbed-phase transport. Also, in their study they have introduced N_{Th} and N_{Pe} as Thiele modulus and Peclet number, respectively,

$$N_{Th}=\frac{k_r\lambda^2}{\bar{D}}\frac{d\bar{K}}{d\bar{\phi}}$$

$$N_{Pe}=\frac{B_0\bar{\bar{p}}}{\mu\bar{D}}$$

Note that quantity $\bar{\bar{p}}=R_gT\bar{\bar{C}}$ is average pore pressure across the matrix.

$\mathit{\Gamma}_{kn}$ increases with the initially adsorbed gas amount and with the porosity variance. Equation 22 includes the effects related to the sorption nonlinearity and the adsorbed-phase transport through two new factors υ_1 and υ_2. In Fig. 2, the contributions of these factors are investigated. The new contributions improve the ultimate recovery up to 93.7% and decrease the time it takes to reach this recovery from more than 20 days (for linear case) to about 6 days. This is a significant improvement in gas production rate specifically due to macro kinetics effect.

If we were to include into our numerical analysis only the nonlinearity in sorption kinetics in the absence of surface diffusion, i.e., $\upsilon_2=0$, the macro-kinetics equation (22) then simplifies to

$$\Gamma_{kn} \cong \upsilon_1 \Gamma_{kn,\text{linear}} \tag{23}$$

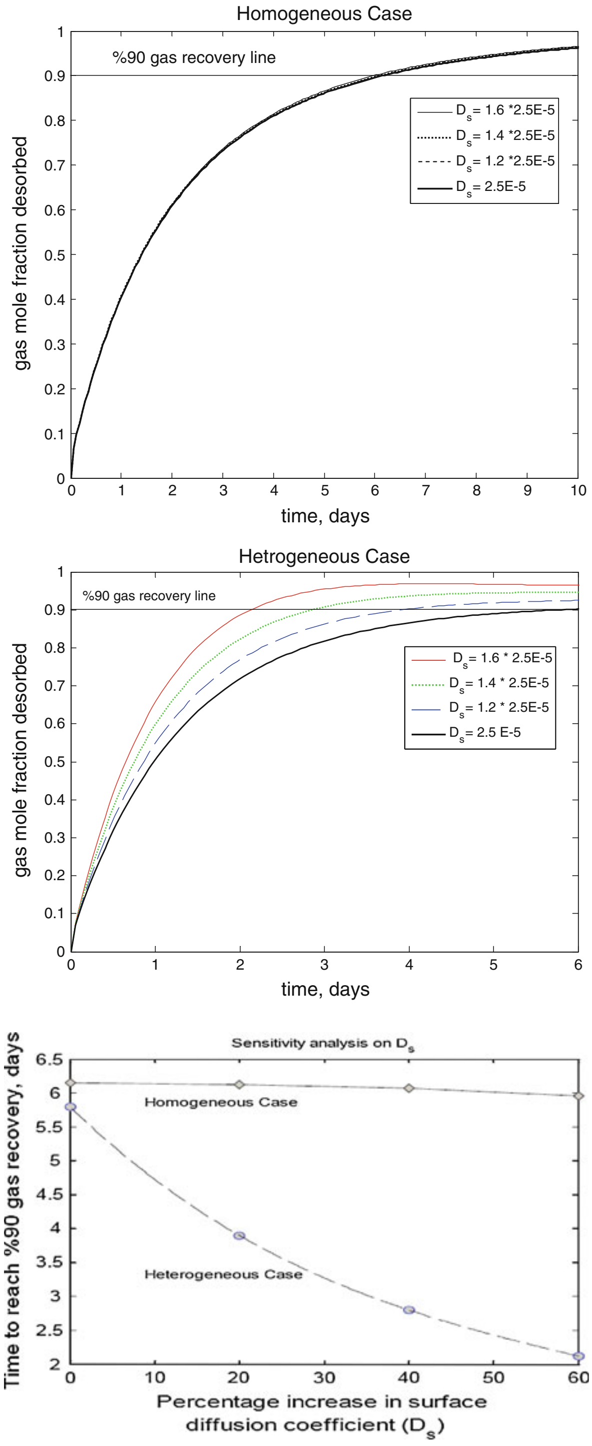
The dashed line in Fig. 2 shows this isolated effect. Clearly, the improvement in ultimate recovery is primarily due to nonlinearity in sorption kinetics. In the presence of surface diffusion, however, the gas release takes place at significantly higher rates. (e.g., 6 days for 93.7% recovery instead of 20 days in the absence of D_s), see the dotted line in the figure. Note that, for the simulations, the input values of the diffusivities are $\bar{D} = 1.0E{-}3\,\text{cm}^2/\text{s}$ for the pore diffusion and $\bar{D}_s = 2.5E{-}5\,\text{cm}^2/\text{s}$ for the surface diffusion. Given the fact that the adsorbed-phase diffusivity has two orders of magnitude smaller value, the enhancement in the gas release rate due to heterogeneity effect is a somewhat unexpected behavior. To find the source of this significant impact on the gas release, we revisited the mathematical formulation and back-traced the derivation of Γ_{kn}. In Eq. 8, it is the $(C_{\mu s} - \bar{C}_\mu)\overline{\tilde{K}\tilde{C}} - \bar{C}\,\overline{\tilde{K}\tilde{C}_\mu}$ terms that cause the impact on gas release, i.e., the nonlinearity effect (first term) and the cross-correlations between partition coefficient, K, and the molar densities. In essence, we theoretically observe new transport effects of heterogeneity in the presence of adsorbed-phase. This may explain the earlier experimental observations suggesting that the gas release cannot be accounted for only by free gas diffusion and there must be an additional transport associated with the adsorbed phase. Figure 3 further confirms this fundamental observation numerically by showing sensitivity of gas recovery to the changes in surface diffusivity values, for both homogeneous and heterogeneous cases. Figure 3 (top) shows the sensitivity to the surface diffusion in the homogeneous matrix. In this case, obviously the surface diffusion does not play any important role on the gas release dynamics. However, Figure 3 (middle), with the heterogeneous case, shows significant improvement on the gas release rate. Furthermore, the gas release rate is also sensitive to the changes in the surface diffusivity. Figure 3 (bottom) compares the times required to reach 90% gas recovery for both homogeneous and heterogeneous cases. It clearly shows that the adsorbed-phase transport is significantly important in the heterogeneous system. We also note that, unlike the linear case presented by Fathi and Akkutlu (2009), the contributions of nonlinearity and surface diffusion to the overall macro-kinetics effect are not constant. Therefore macro-kinetics effect of heterogeneity is now dependent on the free and adsorbed gas amounts and hence varies in time and space.

5.2 Macro-Transport Effect

Based on the sensitivity analysis, we omit last term in Eq. 18. Furthermore, typically $\bar{\phi} g' \ll g$ condition is satisfied across the matrix block. Substituting the definitions of β and g in Eq. 18, re-arranging and using the definitions of υ_1 and υ_2, the macro-transport effect Γ_{tr} is written in the following simple form:

$$\begin{aligned}
\Gamma_{\text{tr}} &\cong \left(1 - \upsilon_1 \upsilon_2 \bar{C}\right) \left(\frac{\bar{D}}{\bar{D} + 2\beta g} + \frac{\beta g}{\bar{D} + 2\beta g} \right) \bar{\phi} \sigma_\phi^2 \bar{C}_{\mu 0} \\
&= \left(1 - \upsilon_1 \upsilon_2 \bar{C}\right) \left(\frac{1}{1 + \dfrac{2B_0 \bar{\bar{p}}}{\bar{D}\mu}} + \frac{1}{2 + \dfrac{\bar{D}\mu}{B_0 \bar{\bar{p}}}} \right) \bar{\phi} \sigma_\phi^2 \bar{C}_{\mu 0} \\
&= \left(1 - \upsilon_1 \upsilon_2 \bar{C}\right) \frac{1}{1 + N_{Pe}/(1 + N_{Pe})} \bar{\phi} \sigma_\phi^2 \bar{C}_{\mu 0} \\
&= \left(1 - \upsilon_1 \upsilon_2 \bar{C}\right) \Gamma_{\text{tr,linear}}
\end{aligned} \tag{24}$$

Fig. 3 Effect of adsorbed-phase transport in homogeneous (*top*) and heterogeneous (*middle*) porous media



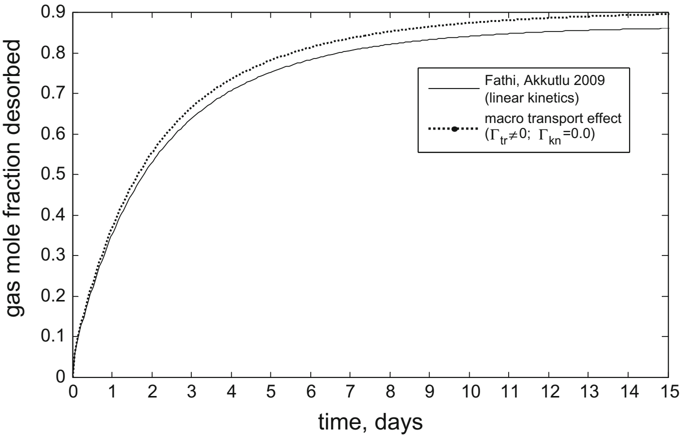


Fig. 4 Effect of macro-transport on matrix gas release

In this form, we can clearly identify the contribution of sorption nonlinearity and surface diffusion as a correction term to the linear-case earlier obtained by Fathi and Akkutlu (2009). Note that the bracket term in the last line of Eq. 24 is larger than unity, because $K' < 0$ taken; therefore $\Gamma_{\mathrm{tr}} > \Gamma_{\mathrm{tr,linear}}$. Also note that Γ_{tr} is dependent on the Peclet number and, hence, increases with the matrix permeability. It does not disappear in the zero permeability limit, however; instead, it changes with the average initial adsorbed gas amount, with the porosity and with the porosity variance. If we were to include in our numerical analysis only the nonlinearity in sorption kinetics in the absence of surface diffusion then Γ_{tr} in upscaled equation (14) simplifies to

$$\Gamma_{\mathrm{tr}} \cong \Gamma_{\mathrm{tr,linear}} \tag{25}$$

suggesting that contribution of heterogeneity is a combined effect and by removing the surface diffusion the sorption non-linearity effect in macro-transport diminishes too. Figure 4 shows the contribution of only the macro-transport term (i.e., $\Gamma_{\mathrm{tr}} \neq 0$ and $\Gamma_{kn} = 0$) on the gas release by comparing the numerical results with respect to the linear case. Based on the simulation, it is predicted that the ultimate gas recovery is increased slightly, to nearly 90%, due to pure macro-transport effect. However, no significant improvement on the recovery time is observed.

5.3 Sensitivity Analysis on Sorption Nonlinearity and Adsorbed-phase Transport

Auto- and cross– correlations in the mean equations (7–8) regarding the adsorbed-phase transport and nonlinearity in sorption kinetics leads to common parameters υ_2 and υ_1 in the upscaled equations (14–15). In this section, sensitivity to these parameters will be studied numerically using the gas release problem. In Fig. 5 the solid line is related to gas release according to Table 1 based on the results with linear sorption kinetics of Fathi and Akkutlu (2009). Note that in this case $\upsilon_1 = 0$. The dotted line corresponds to the heterogeneous base-case. The dashed line, on the other hand, presents the heterogeneous case where the nonlinearity effect has been reduced 90%. Two distinct observations can be made based on Fig. 5. First, comparison of the solid line with dotted line shows significant improvement on gas release rate and ultimate

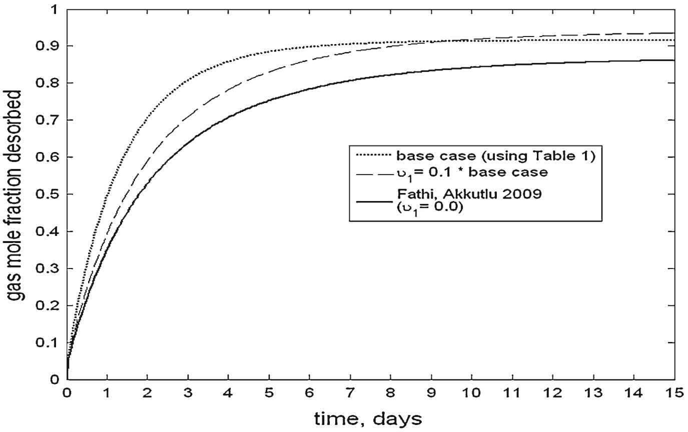


Fig. 5 Sensitivity analysis of υ_1

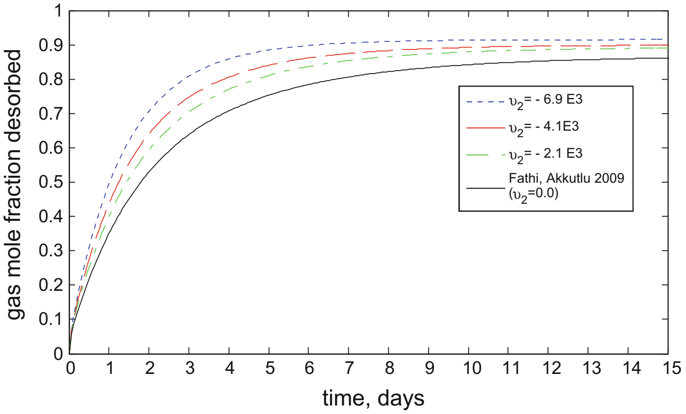


Fig. 6 Sensitivity analysis of υ_2

gas recovery due to presence of the adsorbed-phase transport and nonlinear sorption kinetics.

Second, the nonlinearity in sorption kinetics, i.e., υ_1, has a significant effect on the gas release rate, while its effect on the ultimate gas recovery is minimal. It is also important to notice that υ_1 has a dynamic effect on gas recovery as it changes with the average free gas and adsorbed-phase amounts (Eq. 20). υ_2, on the other hand, i.e., the adsorbed-phase transport effect, is a constant and does not change during the gas release. Figure 6 illustrates the sensitivity analysis of the υ_2. As mentioned earlier υ_2 appears in the up-scaled formulation purely due to introduction of surface diffusion on gas release behavior from the matrix. It is clear that both the rate of gas release and the ultimate gas recovery decrease significantly as the adsorb-phase transport effect is decreased. These observations also highlights the importance of the adsorbed-phase transport and its combined effects with nonlinearity in sorption kinetics on the gas release dynamics in heterogeneous porous medium.

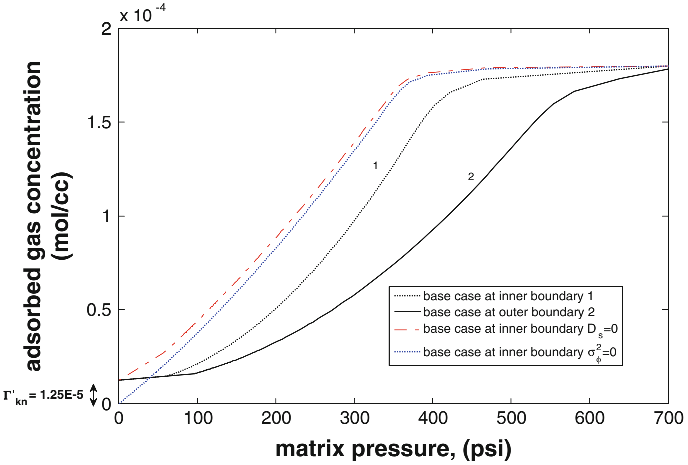


Fig. 7 Time evolution of matrix pressure versus adsorbed-phase molar densities at fixed locations of the matrix block during the gas release. Free gas amount is shown in terms of matrix pore pressure at the fixed points

5.4 Adsorption Equilibrium Limit

One can have a more insightful look at the importance of macro-kinetics effect in the equilibrium adsorption limit. Note that under the equilibrium conditions, we now have $\partial \bar{C}_\mu / \partial t = 0$, thus:

$$\bar{K}(C_{\mu s} - \bar{C}_\mu)\bar{C} - \left(\bar{C}_\mu + \Gamma_{kn}\right) = 0 \tag{26}$$

which gives the well-known expression for the Langmuir adsorption isotherm with an additional term purely related to the heterogeneity of the matrix block:

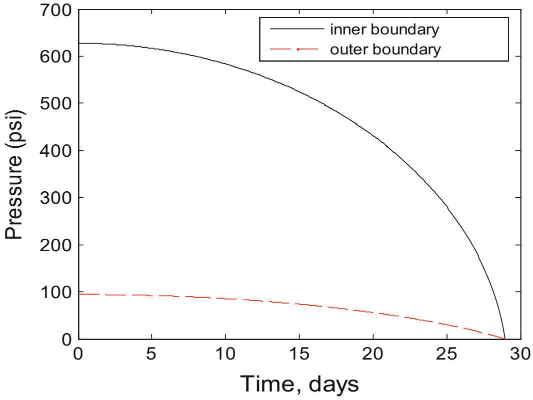
$$\bar{C}_\mu = \frac{\bar{K} C_{\mu s} \bar{C}}{1 + \bar{K}\bar{C}} - \frac{\Gamma_{kn}}{1 + \bar{K}\bar{C}} \tag{27}$$

Accordingly, the macro-kinetics effect of heterogeneity appears in equation (27) as a gas trapping mechanism that leads to residual adsorbed gas in the matrix.

Figure 7 shows the time evolution of the estimated free gas versus adsorbed-phase densities at two fixed locations of the matrix block (points 1 and 2) during the gas release. The x-coordinate represents the pore pressure associated with the free gas at a location in the matrix. In Fig. 7, first, the nonlinear sorption kinetics case with and without surface diffusion is compared. The dotted blue line is obtained using Eqs. 3–4 for the homogeneous Langmuir kinetics, the solid black line corresponds to the heterogeneous case using the upscaled equations (14–15), and the dashed red line is the heterogeneous case where adsorbed-phase transport is ignored (i.e., $\bar{D}_s = 0$). Clearly, the isotherm is more like the homogeneous case in the absence of surface diffusion with the only exception that the heterogeneity acts as trapping mechanism. Consequently, at significantly large times, when the pore pressure goes to zero, some adsorbed gas is trapped in the matrix. In the presence of surface diffusion, on the other hand, the heterogeneity leads to accelerated transport of the adsorbed phase at high pressures although its trapping effect persists at large times.

Figure 7 shows a significant difference between the numerically predicted isotherms at different locations in the porous medium. At the outer boundary the derivative of the adsorbed

Fig. 8 Comparison of the pressure profiles at the inner and outer boundaries



phase with respect to the free gas is less than that at the inner boundary, in particular at early times:

$$\left(\frac{\partial \bar{C}_{\mu}}{\partial \bar{C}}\right)_{\text{innerboundary}} > \left(\frac{\partial \bar{C}_{\mu}}{\partial \bar{C}}\right)_{\text{outerboundary}}$$

The effect can be discussed easily, if one considers the pressure transient at the inner and outer boundary conditions. Using the definition of $\frac{\partial \bar{C}_{\mu}}{\partial \bar{C}}$, based on the Langmuir kinetics, we have:

$$\frac{\partial \bar{C}_{\mu}}{\partial \bar{C}} = \frac{\bar{K} C_{\mu s}}{(1 + \bar{K}\bar{C})^2} \tag{28}$$

Here, for clarity in the discussion we ignored the derivative of the macro-kinetic term in Eq. 28. Figure 8 shows that the free gas amount drops much faster at the inner boundary. This means that the gradient must be larger at that location.

Figure 7 shows that, once the system reaches the residual gas saturation, the difference between homogeneous and heterogenous case is not a function of free gas amount and it reduces to the constant, i.e., Γ'_{kn}. The residual adsorbed gas amount in nonlinear case is much less than the linear case purely due to presence of surface diffusion. When the free gas amount approaches to zero, i.e., $\bar{C} \to 0$, Eq. 27 reduces to:

$$\left(\bar{C}_{\mu}\right)_{\bar{C}=0} = \Gamma'_{kn} = -\left(\Gamma_{kn}\right)_{\bar{C}=0} = \left(-\upsilon_1 \Gamma_{kn,\text{linear}}\right)_{\bar{C}=0} \tag{29}$$

substituting the definitions of υ_1 and Γ_{kn} at $\bar{C} = 0$, and rearranging the equation leads to

$$\Gamma'_{kn} = -\frac{C_{\mu s}\Gamma'_{\text{linear}}}{1 - \Gamma'_{\text{linear}}} \tag{30}$$

where Γ'_{linear} is defined as

$$\Gamma'_{\text{linear}} = \left(\Gamma_{\text{linear}}\right)_{\bar{C}=0} = \frac{N_{Th}\sigma_{\phi}^2 \bar{C}_{\mu 0}}{k_r\left(1 + 2N_{Pe}\right)} \tag{31}$$

6 Conclusion

In this article, gas flow, diffusive transport, and adsorption in heterogeneous porous media with low permeability and porosity is investigated using a theoretical approach. Unlike previous theoretical works, the sorption rates are explicitly introduced to the mathematical framework.

Random local variations in matrix pore structure is considered and their influence on gas sorption and transport are investigated using small perturbations theory, a proven technique widely used in various other disciplines where analysis of multi-physics problems are required in the presence of a priori fluctuations induced by non-uniform fields. In conclusion, the homogenized gas–matrix system behavior can be described using the following upscaled governing equations.

$$\bar{\phi}\frac{\partial \bar{C}}{\partial t} + (1-\bar{\phi})\frac{\partial \bar{C}_{\mu}}{\partial t} = \frac{\partial}{\partial x}\left(\bar{\phi}\mathcal{D}_{\text{eff}}\frac{\partial \bar{C}}{\partial x}\right) + \frac{\partial}{\partial x}\left(\bar{\phi}\bar{C}\frac{B_0}{\mu}\frac{\partial \bar{p}}{\partial x}\right) + \frac{\partial}{\partial x}\left[(1-\phi)\,\bar{D}_s\frac{\partial \bar{C}_{\mu}}{\partial x}\right] + \frac{\bar{\phi}\sigma_{\phi}^{2}\bar{C}_{\mu 0}}{1+N_{Pe}/(1+N_{Pe})}(1-\upsilon_1\upsilon_2\bar{C}) \tag{32}$$

$$\frac{\partial \bar{C}_{\mu}}{\partial t} = k_f\left(C_{\mu s}-\bar{C}_{\mu}\right)\bar{C} - k_r\bar{C}_{\mu} - \frac{N_{Th}}{1+2N_{Pe}}\sigma_{\phi}^{2}C_{\mu 0}\upsilon_1(1+\upsilon_1\upsilon_2\bar{C}) \tag{33}$$

Further, it is found that the matrix heterogeneity defined by random porosity field generates non-trivial macro-transport and macro-kinetics effects on the system that includes well known dimensionless numbers, i.e., Peclet number and Thiele modulus. It is also shown that the heterogenous porosity field leads to a significant improvement in adsorbed-phase transport when nonlinear sorption kinetics is considered, that can explain earlier experimental observations suggesting significant adsorbed phase transport in microporous materials such as carbon and coal (Carman and Raal 1951; Ash et al. 1963; Aylmore and Barrer 1966; Do and Wang 1998; Siemons et al. 2007). Our upscaling approach clearly shows the importance of initially adsorbed amount of gas on macro-transport and macro kinetics, known as the loading effect on gas sorption and adsorbed-phase transport (Do 1998). The system behavior is investigated numerically and it is found that macro–kinetics significantly increases the gas release rate and macro–transport increases the ultimate gas recovery compared to the case where adsorbed-phase transport is ignored. Most importantly, our theoretical investigation shows that the nonlinear gas dynamics does not allow the system to reach equilibrium adsorption limit, even at large times.

Appendix A

Upscaling Approach Using Small Perturbation Theory

Space-Fourier and time-Laplace transform of the mean equations (7–8) are taken. This process gives the following algebraic equations for the mean free gas and the adsorbed phase in the Fourier–Laplace domain:

$$(s+k^2\bar{D})\bar{C}_{ks}-\bar{C}_{k,t=0}+(s\bar{\Phi}+k^2\bar{\Phi}\bar{D}_s)(\bar{C}_\mu)_{ks}-\bar{\Phi}(\bar{C}_\mu)_{k,t=0}=\bar{R}_{ks} \tag{34}$$

$$(\bar{C}_\mu)_{ks}=\frac{(\bar{C}_\mu)_{k,t=0}+k_r\left[\bar{K}\bar{C}(C_{\mu s})-\bar{C}_\mu+(C_{\mu s}-\bar{C}_\mu)\overline{\tilde{K}\tilde{C}}-\bar{C}\overline{\tilde{K}\tilde{C}_\mu}-\bar{K}\overline{\tilde{C}_\mu\tilde{C}}\right]_{ks}}{s\,+\,k_r} \tag{35}$$

where k is the wave number, s the Laplace transform variable, $\bar{C}_{k,t=0}$ and $(\bar{C}_\mu)_{k,t=0}$ are the Fourier transform of the initial amounts of free and adsorbed gas respectively. Substituting Eq. 35 into the Eq. 34 leads to the formal solution of the free gas mass in Fourier–Laplace domain as follow:

$$\bar{C}_{ks}=\hat{G}_{ks}^{-1}\bar{R}_{ks}+\hat{G}_{ks}^{-1}X_{ks} \tag{36}$$

where $\hat{G}_{ks}$ and X_{ks} are defined as

$$\hat{G}_{ks}=\left[s+k^2D+\frac{\bar{\Phi}k_r\bar{K}(s+k^2\bar{D}_s)C_{\mu s}}{s+k_r}\right]_{ks} \tag{37}$$

$$\begin{aligned}X_{ks}=&\,\bar{C}_{k,t=0}+\left(\bar{\Phi}-\frac{\bar{\Phi}(s+k^2\bar{D}_s)}{s+k_r}\right)\bar{C}_{\mu(k,t=0)}\\&-\frac{\bar{\Phi}k_r(s+k^2\bar{D}_s)}{s+k_r}\left[\overline{\tilde{K}\tilde{C}}(C_{\mu s}-C_\mu)-\bar{K}\bar{C}\bar{C}_\mu-\bar{K}\overline{\tilde{C}_\mu\tilde{C}}-\bar{C}\overline{\tilde{K}\tilde{C}_\mu}\right]_{ks}\end{aligned} \tag{38}$$

In order to find the equivalent expression for free gas fluctuation $\tilde{C}$ in Fourier–Laplace domain, we use the mean-field approximation for the terms $\beta\bar{C}\partial^2\tilde{C}/\partial x^2$ and $\beta\tilde{C}\partial^2\bar{C}/\partial x^2$. Assuming the average gas amount is replaced by its value averaged over a large space domain L and time interval τ: $\bar{\bar{C}}=\int_0^\tau\int_0^L C(x,t)dxdt/L\tau\equiv g$ and $\partial\bar{\bar{C}}/\partial\overline{\phi}=g'$. Equivalently, we take $\bar{C}_{ks}=g$ in Fourier–Laplace domain. In homogeneous porous media, $\bar{\alpha}_1$, $\bar{\alpha}_2$ and $\bar{\alpha}'$ are defined as (L'Heureux 2004)

$$\bar{\alpha}_1\cong\frac{\overline{\tilde{D}\partial\tilde{\phi}}}{\partial x}-\left(\frac{\bar{D}}{\bar{\phi}}\right)\frac{\overline{\tilde{\phi}\partial\tilde{\phi}}}{\partial x}$$

$$\bar{\alpha}_2\cong\frac{\Phi\overline{\tilde{D}_s\partial\tilde{\phi}}}{\partial x}-\left(\frac{\bar{D}_s}{\bar{\phi}}\right)\frac{\overline{(1-\tilde{\phi})\partial\tilde{\phi}}}{\partial x}$$

$$\bar{\alpha}'\cong\frac{\overline{\tilde{C}\partial\tilde{\phi}}}{\partial x}-\left(\frac{\bar{C}}{\bar{\phi}}\right)\frac{\overline{\tilde{\phi}\partial\tilde{\phi}}}{\partial x}$$

These are already second order in porosity fluctuations; therefore, $\bar{\alpha}_1\partial\tilde{C}/\partial x\ \cong\ 0$, $\bar{\alpha}_2\partial\tilde{C}_\mu/\partial x\cong 0$ and $\bar{\alpha}'\partial\tilde{C}/\partial x\cong 0$ are taken. Next we apply Fourier–Laplace transform to the perturbation equations (10–11):

$$\left(s+k^2\bar{D}+2\beta gk^2\right)\tilde{C}_{ks}+\left(\bar{\Phi}s+\bar{\Phi}D_sk^2\right)\tilde{C}_{\mu ks}=\tilde{R}_{ks} \tag{39}$$

$$\tilde{C}_{\mu,ks}=\frac{k_r\bar{K}\left(C_{\mu s}-\bar{C}_{\mu ks}\right)\tilde{C}_{ks}}{\left(s+k_r+k_r\bar{K}\bar{C}_{ks}\right)}+\frac{k_rM_{ks}}{\left(s+k_r+k_r\bar{K}\bar{C}_{ks}\right)} \tag{40}$$

Substituting Eq. 40 into Eq. 39 leads to the formal solution for $\tilde{C}_{ks}$ in Fourier–Laplace domain as

$$\tilde{C}_{ks}=G_{ks}^{-1}\tilde{R}_{ks}-L_{ks}M_{ks} \tag{41}$$

where G_{ks}, and L_{ks} is defined as follow

$$G_{ks} = \left[s + (\bar{D} + 2\beta g)k^2 + \frac{\bar{\Phi} k_r \bar{K} (s + \bar{D}_s k^2)(C_{\mu s} - \bar{C}_\mu)_{ks}}{s + k_r + k_r \bar{K} \bar{C}_{ks}} \right] \tag{42}$$

$$L_{ks} = \left[\frac{\bar{\Phi} k_r (s + \bar{D}_s k^2)}{s + k_r + k_r \bar{K} \bar{C}_{ks}} \right] G_{ks}^{-1} \tag{43}$$

In the space–time domain, the fluctuating free gas mass is given by the convolution integral

$$\begin{aligned} \tilde{C}(x,t) &= \int_0^t \int G^{-1}\left(x - x', t - t'\right) \tilde{R}\left(x', t'\right) \mathrm{d}x' \mathrm{d}t' \\ &\quad - \int_0^t \int L\left(x - x', t - t'\right) M\left(x', t'\right) \mathrm{d}x' \mathrm{d}t' \\ &\equiv G^{-1}_{x-x',t-t'} * \tilde{R}_{x',t'} - L_{x-x',t-t'} * M_{x',t'} \end{aligned} \tag{44}$$

Next we substitute Eq. 41 into Eq. 40. Now $\tilde{C}_\mu$ can be expressed in space–time domain as follows

$$\begin{aligned} \tilde{C}_\mu(x,t) &= \int_0^t \int \breve{G}^{-1}\left(x - x', t - t'\right) \tilde{R}\left(x', t'\right) \mathrm{d}x' \mathrm{d}t' \\ &\quad - \int_0^t \int \breve{L}\left(x - x', t - t'\right) M\left(x', t'\right) \mathrm{d}x' \mathrm{d}t' \\ &\equiv \breve{G}^{-1}_{x-x',t-t'} * \tilde{R}_{x',t'} - \breve{L}_{x-x',t-t'} * M_{x',t'} \end{aligned} \tag{45}$$

Here, we introduced

$$\breve{G}_{ks}^{-1} = \left[\frac{\bar{K} k_r (C_{\mu s} - \bar{C}_\mu)_{ks}}{s + k_r + k_r \bar{K} \bar{C}_{ks}} \right] G_{ks}^{-1} \quad \text{and} \quad \breve{L}_{ks} = \left(\frac{-\bar{K} k_r (C_{\mu s} - \bar{C}_\mu)_{ks}}{s + k_r + k_r \bar{K} \bar{C}_{ks}} L_{ks} - \frac{k_r}{s + k_r + k_r \bar{K} \bar{C}_{ks}} \right)$$

Having an analytical expressions for $\tilde{C}$ and $\tilde{C}_\mu$ the cross-correlation terms in mean equations (7–8) are obtained solving a series of convolution integrals. The summation term in Eq. 7 can be obtained by multiplying the proper spatial derivative of the molar density fluctuation $\tilde{C}$ with the fluctuating transport term $\xi_m(x)$ neglecting the third order porosity fluctuation terms and taking the expectation.

$$\sum_{m=1,2} \frac{\overline{\xi_m \partial^m \tilde{C}}}{\partial x^m} = \sum_{m=1,2} \frac{\partial^m G^{-1}_{x-x',t-t'}}{\partial x^m} * \overline{\xi_m \tilde{R}_{x',t'}} - \sum_{m=1,2} \frac{\partial^m L_{x-x',t-t'}}{\partial x^m} * \overline{\xi_m M_{x',t'}} \tag{46}$$

The rest of the cross correlation terms in Eq. 7 are obtained similarly using the definitions of $\tilde{C}$ and $\tilde{C}_\mu$:

$$\beta \frac{\overline{\tilde{\alpha}' \partial \tilde{C}}}{\partial x} = \frac{\partial G^{-1}_{x-x',t-t'}}{\partial t} * \beta \overline{\tilde{\alpha}' \tilde{R}} - \frac{\partial L_{x-x',t-t'}}{\partial t} * \beta \overline{\tilde{\alpha}' M} \tag{47}$$

$$\overline{\tilde{\alpha}_2 \frac{\partial \tilde{C}_\mu}{\partial x}} = \frac{\partial \breve{G}^{-1}_{x-x',t-t'}}{\partial x} * \overline{\tilde{\alpha}_2 \tilde{R}} + \frac{\partial \breve{L}_{x-x',t-t'}}{\partial x} * \overline{\tilde{\alpha}_2 M} \tag{48}$$

$$\overline{\frac{\tilde{\Phi}\partial\tilde{C}_{\mu}}{\partial t}} = \frac{\partial\breve{G}^{-1}_{x-x',t-t'}}{\partial t} * \overline{\tilde{\Phi}\tilde{R}} + \frac{\partial\breve{L}_{x-x',t-t'}}{\partial t} * \overline{\tilde{\Phi}M} \tag{49}$$

$$\bar{D}_s\overline{\tilde{\Phi}\frac{\partial^2\tilde{C}_{\mu}}{\partial x^2}} = \frac{\partial^2\breve{G}^{-1}_{x-x',t-t'}}{\partial x^2} * \bar{D}_s\overline{\tilde{\Phi}\tilde{R}} + \frac{\partial^2\breve{L}_{x-x',t-t'}}{\partial x^2} * \bar{D}_s\overline{\tilde{\Phi}M} \tag{50}$$

$$\bar{\Phi}\overline{\tilde{D}_s\frac{\partial^2\tilde{C}_{\mu}}{\partial x^2}} = \frac{\partial^2\breve{G}^{-1}_{x-x',t-t'}}{\partial x^2} * \bar{\Phi}\overline{\tilde{D}_s\tilde{R}} + \frac{\partial^2\breve{L}_{x-x',t-t'}}{\partial x^2} * \bar{\Phi}\overline{\tilde{D}_sM} \tag{51}$$

The solution of the equations (46–51) are found, taking the space-Fourier and time-Laplace transformation of them and dropping the third order terms in the porosity fluctuations:

$$\begin{aligned}\left(\sum_{m=1,2}\overline{\frac{\xi_m\partial^m\tilde{C}}{\partial x^m}}\right)_{ks} &= P_{1,ks}\bar{C}_{\mu\,k,t=0} + P_{2,ks}\bar{C}_{ks} + P_{3,ks}\bar{C}_{ks} + P_{4,ks}\bar{C}_{\mu ks} + P_{5,ks}\bar{C}_{\mu ks}\\ &\quad + P_{6,ks}\bar{C}_{\mu ks} - P_{7,ks}\bar{C}_{ks} + P_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{52}$$

$$\begin{aligned}\left(\beta\overline{\frac{\tilde{\alpha}'\partial\tilde{C}}{\partial x}}\right)_{ks} &= Q_{1,ks}\bar{C}_{\mu\,k,t=0} + Q_{2,ks}\bar{C}_{ks} + Q_{3,ks}\bar{C}_{ks} + Q_{4,ks}\bar{C}_{\mu ks} + Q_{5,ks}\bar{C}_{\mu ks}\\ &\quad + Q_{6,ks}\bar{C}_{\mu ks} - Q_{7,ks}\bar{C}_{ks} + Q_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{53}$$

$$\begin{aligned}\left(\overline{\tilde{\alpha}_2\frac{\partial\tilde{C}_{\mu}}{\partial x}}\right)_{ks} &= T_{1,ks}\bar{C}_{\mu\,k,t=0} + T_{2,ks}\bar{C}_{ks} + T_{3,ks}\bar{C}_{ks} + T_{4,ks}\bar{C}_{\mu ks} + T_{5,ks}\bar{C}_{\mu ks}\\ &\quad + T_{6,ks}\bar{C}_{\mu ks} - T_{7,ks}\bar{C}_{ks} + T_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{54}$$

$$\begin{aligned}\left(\overline{\frac{\tilde{\Phi}\partial\tilde{C}_{\mu}}{\partial t}}\right)_{ks} &= U_{1,ks}\bar{C}_{\mu\,k,t=0} + U_{2,ks}\bar{C}_{ks} + U_{3,ks}\bar{C}_{ks} + U_{4,ks}\bar{C}_{\mu ks} + U_{5,ks}\bar{C}_{\mu ks}\\ &\quad + U_{6,ks}\bar{C}_{\mu ks} - U_{7,ks}\bar{C}_{ks} + U_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{55}$$

$$\begin{aligned}\left(\bar{D}_s\overline{\tilde{\Phi}\frac{\partial^2\tilde{C}_{\mu}}{\partial x^2}}\right)_{ks} &= V_{1,ks}\bar{C}_{\mu\,k,t=0} + V_{2,ks}\bar{C}_{ks} + V_{3,ks}\bar{C}_{ks} + V_{4,ks}\bar{C}_{\mu ks} + V_{5,ks}\bar{C}_{\mu ks}\\ &\quad + V_{6,ks}\bar{C}_{\mu ks} - V_{7,ks}\bar{C}_{ks} + V_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{56}$$

$$\begin{aligned}\left(\bar{\Phi}\overline{\tilde{D}_s\frac{\partial^2\tilde{C}_{\mu}}{\partial x^2}}\right)_{ks} &= W_{1,ks}\bar{C}_{\mu\,k,t=0} + W_{2,ks}\bar{C}_{ks} + W_{3,ks}\bar{C}_{ks} + W_{4,ks}\bar{C}_{\mu ks} + W_{5,ks}\bar{C}_{\mu ks}\\ &\quad + W_{6,ks}\bar{C}_{\mu ks} - W_{7,ks}\bar{C}_{ks} + W_{8,ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{57}$$

In order to evaluate these integrals, the porosity fluctuations $\tilde{\phi}$ around the mean porosity $\bar{\phi}$ assumed to be Gaussian random variable with zero mean and variance σ^2_{ϕ}, and the spatial correlation function defined as $\overline{\tilde{\phi}(x)\tilde{\phi}(y)} = \sigma^2_{\phi}f(|x-y|)$. Then auto- and cross-covariances appearing in the integrals can be defined using Gaussian correlation function, $f(x)$ and f_Q in space–time and spectral domain, respectively. For instance, one can write the auto correlation of the drift velocity α_1 as follows

$$\overline{\tilde{\alpha}_{1x}\tilde{\alpha}_{1x'}} = \left(D' + \bar{D}/\bar{\phi}\right)^2\overline{\partial_x\tilde{\phi}(x)\partial_{x'}\tilde{\phi}(x')} = -\left(D' + \bar{D}/\bar{\phi}\right)^2\sigma^2_{\phi}d^2f(x)/dx^2 \tag{58}$$

in space and time domain, that is $\overline{\xi_{Q1}\xi_{-Q1}} = \overline{\tilde{\alpha}_Q\tilde{\alpha}_{-Q}} = \left(D' + \bar{D}/\bar{\phi}\right)^2\sigma^2_{\phi}Q^2f_Q$ in Fourier space domain. Here, σ^2_{ϕ} is the variance of porosity and $f_Q = \sqrt{2\pi}\lambda\exp\left(-Q^2\lambda^2/2\right)$ is the Fourier transform of the porosity correlation function $f(x) = \exp\left(-x^2/2\lambda^2\right)$. We also defined $D' = \mathrm{d}\bar{D}/\mathrm{d}\bar{\phi} > 0$, $D'_s = d\bar{D}_s/d\bar{\phi} > 0$ and $K' = d\bar{K}/d\bar{\phi} < 0$. Using defined auto- and cross-covariances presented in Appendix B, Table 2, Eqs. 52–57) are obtained solving a series of convolution integrals introduced in Appendix B, Table 3. In the table, Q is dummy wave number label. Similar procedure is applied to obtain the explicit analytical solutions for the cross-correlations in Eq. 8. We can express the cross-correlation terms $\overline{\tilde{K}\tilde{C}}$, $\overline{\tilde{K}\tilde{C}_\mu}$ and $\overline{\tilde{C}\tilde{C}_\mu}$ in Eq. 8 using the definitions of $\tilde{C}$ and $\tilde{C}_\mu$(Eqs. 44–45) in the following form

$$\overline{\tilde{K}\tilde{C}} = G^{-1} * \overline{\tilde{K}\tilde{R}} - L * \overline{\tilde{K}M} \tag{59}$$

$$\overline{\tilde{K}\tilde{C}_\mu} = \breve{G}^{-1} * \overline{\tilde{K}\tilde{R}} - \breve{L} * \overline{\tilde{K}M} \tag{60}$$

$$\overline{\tilde{C}\tilde{C}_\mu} = \breve{G}^{-1} * G^{-1} * \overline{\tilde{R}\tilde{R}} - \breve{G}^{-1} * L * \overline{\tilde{R}M} - \breve{L} * G^{-1} * \overline{\tilde{R}M} + \breve{L} * L * \overline{MM} \tag{61}$$

Taking space–Fourier and time–Laplace transform of equations (59–61) leads to

$$\begin{aligned}\left(\overline{\tilde{K}\tilde{C}}\right)_{ks} &= S1_{ks}\bar{C}_{\mu\, k,t=0} + S2_{ks}\bar{C}_{ks} + S3_{ks}\bar{C}_{ks} + S4_{ks}\bar{C}_{\mu ks} + S5_{ks}\bar{C}_{\mu ks}\\ &\quad + S6_{ks}\bar{C}_{\mu ks} - S7_{ks}\bar{C}_{ks} + S8_{ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{62}$$

$$\begin{aligned}\left(\overline{\tilde{K}\tilde{C}_\mu}\right)_{ks} &= I1_{ks}\bar{C}_{\mu\, k,t=0} + I2_{ks}\bar{C}_{ks} + I3_{ks}\bar{C}_{ks} + I4_{ks}\bar{C}_{\mu ks} + I5_{ks}\bar{C}_{\mu ks}\\ &\quad + I6_{ks}\bar{C}_{\mu ks} - I7_{ks}\bar{C}_{ks} + I8_{ks}\bar{C}_{ks}\bar{C}_{\mu ks}\end{aligned} \tag{63}$$

$$\left(\overline{\tilde{C}\tilde{C}_\mu}\right)_{ks} = F1_{ks}\bar{C}_{\mu\, k,t=0}\bar{C}_{ks} \tag{64}$$

which also includes a set of integral terms given in Appendix B, Table 4. Using conventional approximations $s = k = 0$ in Q–dependent terms of the integrands, the following solutions are obtained for the integrals defined in Tables 3 and 4 and inserted in Eqs. 52–57 and Eqs. 62–64:

$$\begin{aligned}\left(\sum_{m=1,2}\overline{\frac{\xi_m\,\partial^m\tilde{C}}{\partial x^m}}\right)_{ks} &= \frac{(1+\bar{K}\bar{C}_{ks})\sigma_\phi^2\dfrac{\bar{D}}{\bar{\phi}}\ \ \bar{C}_{\mu\, k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\ &\quad - \frac{(1+\bar{K}\bar{C}_{ks})\sigma_\phi^2 D'\left(2D'+\dfrac{\bar{D}}{\bar{\phi}}\right)\ (ik)^2\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\ &\quad - \frac{(1+\bar{K}\bar{C}_{ks})\sigma_\phi^2 D'_s\bar{\Phi}\left(2D'+\dfrac{\bar{D}}{\bar{\phi}}\right)\ (ik)^2\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\ &\quad + \frac{(1+\bar{K}\bar{C}_{ks})\sigma_\phi^2\bar{D}_s\dfrac{\bar{D}}{\bar{\phi}}\ \ (ik)^2\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\ &\quad - \frac{\sigma_\phi^2\bar{\Phi}K'\bar{D}_s\dfrac{\bar{D}}{\bar{\phi}}(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{\lambda^2\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]}\end{aligned} \tag{65}$$

$$\begin{aligned}
\left(\beta\frac{\overline{\tilde{\alpha}'\partial\tilde{C}}}{\partial x}\right)_{ks} &= \frac{(1+\bar{K}\bar{C}_{ks})\sigma_{\phi}^{2}\beta(C'+\frac{\bar{C}}{\bar{\phi}})_{ks}\ \ \bar{C}_{\mu\,k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{(1+\bar{K}\bar{C}_{ks})\sigma_{\phi}^{2}\beta D'(C'+\frac{\bar{C}}{\bar{\phi}})_{ks}\ \ (ik)^{2}\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{(1+\bar{K}\bar{C}_{ks})\sigma_{\phi}^{2}\beta(C'+\frac{\bar{C}}{\bar{\phi}})_{ks}(\bar{\Phi}D'_{s}-\bar{D}_{s})\ \ (ik)^{2}\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\sigma_{\phi}^{2}\Phi K'\bar{D}_{s}\beta(C'+\frac{\bar{C}}{\bar{\phi}})_{ks}(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{\lambda^{2}\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]}
\end{aligned}\tag{66}$$

$$\begin{aligned}
\left(\overline{\tilde{\alpha}_{2}\frac{\partial\tilde{C}_{\mu}}{\partial x}}\right)_{ks} &= \frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})(D'_{s}+\frac{\bar{D}_{s}}{\bar{\phi}})\ \ \bar{C}_{\mu\,k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})D'(D'_{s}+\frac{\bar{D}_{s}}{\bar{\phi}})\ \ (ik)^{2}\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})(\bar{\Phi}D'_{s}-\bar{D}_{s})(D'_{s}+\frac{\bar{D}_{s}}{\bar{\phi}})\ \ (ik)^{2}\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\bar{K}K'\bar{\Phi}\bar{D}_{s}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})^{2}(D'_{s}+\frac{\bar{D}_{s}}{\bar{\phi}})\ \ \bar{C}_{ks}}{\lambda^{2}\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]} \\
&\quad +\frac{K'\sigma_{\phi}^{2}(D'_{s}+\frac{\bar{D}_{s}}{\bar{\phi}})(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{\lambda^{2}\left(1+\bar{K}\bar{C}_{ks}\right)}
\end{aligned}\tag{67}$$

$$\begin{aligned}
\left(\bar{D}_{s}\overline{\tilde{\Phi}\frac{\partial^{2}\tilde{C}_{\mu}}{\partial x^{2}}}\right)_{ks} &= -\frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})\bar{D}_{s}\ \ \bar{C}_{\mu\,k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})D'\bar{D}_{s}\ \ (ik)^{2}\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})} \\
&\quad -\frac{\bar{K}\sigma_{\phi}^{2}(C_{\mu s}-\bar{C}_{\mu ks})(\bar{\Phi}D'_{s}-\bar{D}_{s})\bar{D}_{s}\ \ (ik)^{2}\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_{s}\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}
\end{aligned}$$

$$
\begin{aligned}
&-\frac{\bar{K}K'\bar{\Phi}\bar{D}_s^2\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})^2\ \ \bar{C}_{ks}}{\lambda^2(1+\bar{K}\bar{C}_{ks})\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]}\\
&+\frac{K'\sigma_\phi^2\bar{D}_s(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{\lambda^2\left(1+\bar{K}\bar{C}_{ks}\right)}
\end{aligned}
\tag{68}
$$

$$
\begin{aligned}
\left(\overline{\bar{\Phi}\tilde{D}_s\frac{\partial^2\tilde{C}_\mu}{\partial x^2}}\right)_{ks}={}&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})\bar{\Phi}D_s'\ \ \bar{C}_{\mu k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})D'\bar{\Phi}D_s'\ \ (ik)^2\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})(\bar{\Phi}D_s'+\bar{D}_s)\bar{\Phi}D_s'\ \ (ik)^2\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&+\frac{\bar{K}K'\bar{\Phi}^2\bar{D}_sD_s'\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})^2\ \ \bar{C}_{ks}}{\lambda^2(1+\bar{K}\bar{C}_{ks})\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]}\\
&-\frac{\bar{\Phi}K'\sigma_\phi^2D_s'(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{\lambda^2\left(1+\bar{K}\bar{C}_{ks}\right)}
\end{aligned}
\tag{69}
$$

$$
\begin{aligned}
\left(\overline{\tilde{K}\tilde{C}}\right)_{ks}={}&-\frac{K'\sigma_\phi^2\lambda^2(1+\bar{K}\bar{C}_{ks})\ \ \bar{C}_{\mu k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{K'\sigma_\phi^2\lambda^2(1+\bar{K}\bar{C}_{ks})D'\ \ (ik)^2\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{K'\sigma_\phi^2\lambda^2(\bar{\Phi}D_s'-\bar{D}_s)(1+\bar{K}\bar{C}_{ks})\ \ (ik)^2\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{\Phi}\bar{D}_sK'^2\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})\ \ \bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}
\end{aligned}
\tag{70}
$$

$$
\begin{aligned}
\left(\overline{\tilde{K}\tilde{C}_\mu}\right)_{ks}={}&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})K'\lambda^2\ \ \bar{C}_{\mu k,t=0}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})D'K'\lambda^2\ \ (ik)^2\bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{K}\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})K'\lambda^2(\bar{\Phi}D_s'-\bar{D}_s)\ \ (ik)^2\bar{C}_{\mu ks}}{(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})}\\
&-\frac{\bar{K}K'^2\bar{\Phi}\bar{D}_s\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})^2\ \ \bar{C}_{ks}}{(1+\bar{K}\bar{C}_{ks})\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]}
\end{aligned}
\tag{71}
$$

$$
\left(\overline{\tilde{C}\tilde{C}_\mu}\right)_{ks}=\frac{2\bar{K}^2\bar{\Phi}\bar{D}_s\sigma_\phi^2(C_{\mu s}-\bar{C}_{\mu ks})K'\lambda^2\ \ \bar{C}_{\mu k,t=0}\bar{C}_{ks}}{\left[(1+\bar{K}\bar{C}_{ks})(\bar{D}+2\beta g)+\bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s}-\bar{C}_{\mu ks})\right]^2}
\tag{72}
$$

Taking the inverse Laplace-Fourier transform of equatios (65–72)and substituting to the governing mean equations (7–8)after rearranging and simplifying the new governing equations can be written as follow:

$$\begin{aligned}
\frac{\partial \bar{C}}{\partial t} &= -\bar{\Phi}\frac{\partial \bar{C}_\mu}{\partial t} + \bar{D}\frac{\partial^2 \bar{C}}{\partial x^2} + \bar{\Phi}\bar{D}_s\frac{\partial^2 \bar{C}_\mu}{\partial x^2} + \bar{\alpha}_1\frac{\partial \bar{C}}{\partial x} + \beta\bar{\alpha}'\frac{\partial \bar{C}}{\partial x} + \bar{\alpha}_2\frac{\partial \bar{C}_\mu}{\partial x} + \beta\bar{C}\frac{\partial^2 \bar{C}}{\partial x^2}\\
&\quad + \left(\frac{(1+\bar{K}\bar{C})\left[\frac{\bar{D}}{\bar{\phi}} + \beta(C' + \frac{\bar{C}}{\bar{\phi}})\right] + \bar{K}(C_{\mu s} - \bar{C}_\mu)[(1+\bar{\Phi})D'_s + \bar{\Phi}\bar{D}_s]}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\right)\sigma_\phi^2\bar{C}_{\mu 0}\\
&\quad - \left(\frac{(1+\bar{K}\bar{C})\left[2D' + \frac{\bar{D}}{\bar{\phi}} + \beta(C' + \frac{\bar{C}}{\bar{\phi}})\right] + \bar{K}(C_{\mu s} - \bar{C}_\mu)[(1+\bar{\Phi})D'_s + \frac{1+\bar{\phi}}{\bar{\phi}}\bar{D}_s]}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\right)D'\sigma_\phi^2\frac{\partial^2 \bar{C}}{\partial x^2}\\
&\quad - \left(\frac{(1+\bar{K}\bar{C})\left[2D'D'_s\bar{\Phi} + (\bar{\Phi}D'_s - \bar{D}_s)\left(\frac{\bar{D}}{\bar{\phi}} + \beta(C' + \frac{\bar{C}}{\bar{\phi}})\right)\right]}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\right.\\
&\quad \left. + \frac{\bar{K}(C_{\mu s} - \bar{C}_\mu)\left[(D'_s + \frac{\bar{D}_s}{\bar{\Phi}})(\bar{\Phi}D'_s - \bar{D}_s) + (\bar{\Phi}D'_s + \bar{D}_s)^2\right]}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\right)\sigma_\phi^2\frac{\partial^2 \bar{C}_\mu}{\partial x^2}\\
&\quad - \left(\frac{(1+\bar{K}\bar{C})\bar{\Phi}\bar{D}_s K'(C_{\mu s} - C_\mu)\left[\frac{\bar{D}}{\bar{\phi}} + \beta(C' + \frac{\bar{C}}{\bar{\phi}})\right] + \bar{K}(C_{\mu s} - \bar{C}_\mu)^2\bar{\Phi}\bar{D}_s K' C_{\mu s}[(1-\bar{\Phi})D'_s + \bar{\Phi}\bar{D}_s]}{\lambda^2(1+\bar{K}\bar{C})\left[(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)\right]}\right.\\
&\quad \left. + \frac{K'(C_{\mu s} - C_\mu)(D'_s + \frac{\bar{D}_s}{\bar{\Phi}} - \bar{\Phi}D'_s + \bar{D}_s)}{\lambda^2(1+\bar{K}\bar{C})}\right)\sigma_\phi^2\bar{C}
\end{aligned}\tag{73}$$

$$\begin{aligned}
\frac{\partial \bar{C}_\mu}{\partial t} &= k_r\left[\bar{K}\bar{C}(C_{\mu s} - \bar{C}_\mu) - \bar{C}_\mu\right]\\
&\quad - \frac{k_r(C_{\mu s} - \bar{C}_\mu)K'\sigma_\phi^2\lambda^2\bar{C}_{\mu 0}}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\\
&\quad \times\left[1 + \frac{\bar{\Phi}\bar{D}_s K'(C_{\mu s} - \bar{C}_\mu)\bar{C}}{(1+\bar{K}\bar{C})C_{\mu 0}\lambda^2} + \frac{2\bar{\Phi}\bar{D}_s\bar{K}^2(C_{\mu s} - \bar{C}_\mu)\bar{C}}{(1+\bar{K}\bar{C})(\bar{D}+2\beta g) + \bar{\Phi}\bar{D}_s\bar{K}(C_{\mu s} - \bar{C}_\mu)}\right]
\end{aligned}\tag{74}$$

Appendix B

See Tables 2, 3, 4.

Table 2 Auto- and cross-correlations

$$\overline{\tilde{\Phi}_{-Q}\tilde{\alpha}_{1Q}} = i\left(D' + \bar{D}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{\alpha}_{2Q}} = i\left(D'_{s} + \bar{D}_{s}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{D}_{sQ}} = D'_{s}\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{D}_{Q}} = D'\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\alpha}_{1Q}\tilde{\alpha}_{1-Q}} = \left(D' + \bar{D}/\bar{\phi}\right)^{2}\sigma_{\phi}^{2} Q^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\alpha}_{2Q}\tilde{\alpha}_{2-Q}} = \left(D'_{s} + \bar{D}_{s}/\bar{\phi}\right)^{2}\sigma_{\phi}^{2} Q^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{-Q}\tilde{\alpha}_{1Q}} = -iD'\left(D' + \bar{D}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{s-Q}\tilde{\alpha}_{1Q}} = -iD'_{s}\left(D'_{s} + \bar{D}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{s-Q}\tilde{\alpha}_{2Q}} = -iD'_{s}\left(D'_{s} + \bar{D}_{s}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{-Q}\tilde{D}_{Q}} = D'^{2}\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{s-Q}\tilde{D}_{sQ}} = D'^{2}_{s}\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{-Q}\tilde{D}_{sQ}} = D'D'_{s}\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{\alpha}'_{Q}} = i\left(C' + \bar{C}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{\Phi}_{Q}} = \sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\Phi}_{-Q}\tilde{K}_{Q}} = K'\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{K}_{-Q}\tilde{\alpha}'_{Q}} = iK'\left(C' + \bar{C}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\alpha}'_{Q}\tilde{\alpha}'_{-Q}} = \left(C' + \bar{C}/\bar{\phi}\right)^{2}\sigma_{\phi}^{2} Q^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\alpha}_{Q}\tilde{\alpha}'_{-Q}} = -\left(C' + \bar{C}/\bar{\phi}\right)\left(D' + \bar{D}/\bar{\phi}\right)\sigma_{\phi}^{2} Q^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{\alpha}_{2Q}\tilde{\alpha}'_{-Q}} = -\left(C' + \bar{C}/\bar{\phi}\right)\left(D'_{s} + \bar{D}_{s}/\bar{\phi}\right)\sigma_{\phi}^{2} Q^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{Q}\tilde{\alpha}'_{-Q}} = -iD'\left(C' + \bar{C}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{D}_{sQ}\tilde{\alpha}'_{-Q}} = -iD'_{s}\left(C' + \bar{C}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{K}_{-Q}\tilde{\alpha}_{1Q}} = iK'\left(D' + \bar{D}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{K}_{-Q}\tilde{\alpha}_{2Q}} = iK'\left(D'_{s} + \bar{D}_{s}/\bar{\phi}\right)\sigma_{\phi}^{2} Q\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

$$\overline{\tilde{K}_{-Q}\tilde{D}_{sQ}} = K'D'_{s}\sigma_{\phi}^{2}\sqrt{2\pi}\lambda\exp\left(-Q^{2}\lambda^{2}/2\right)$$

Table 3 Examples of convolution integrals (reset of the integrals are defined similarly)

$$P_{1,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\xi_{Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, \mathrm{d}Q$$

$$P_{2,ks} = \sum_{m,n=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\xi_{Qm} \xi_{-Qn}} \, [i(k-Q)]^m \, (ik)^n \mathrm{d}Q$$

$$P_{3,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \overline{\xi_{Qm} \tilde{\alpha}'_{-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$P_{4,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\xi_{Qm} \tilde{\alpha}_{2-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$P_{5,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \bar{\Phi} \overline{\xi_{Qm} \tilde{D}_{s-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$P_{6,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \bar{D}_s \overline{\xi_{Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$P_{7,ks} = \int \frac{1}{2\pi} L_{k-Q\,s} C_{\mu s} \overline{\xi_{Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

$$P_{8,ks} = \int \frac{1}{2\pi} L_{k-Q\,s} \overline{\xi_{Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

$$Q_{1,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \overline{\tilde{\alpha}'_{Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, \mathrm{d}Q$$

$$Q_{2,ks} = \sum_{m,n=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \overline{\xi_{Qm} \tilde{\alpha}'_{-Qn}} \, [i(k-Q)]^m \, (ik)^n \mathrm{d}Q$$

$$Q_{3,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta^2 \overline{\tilde{\alpha}'_{Qm} \tilde{\alpha}'_{-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$Q_{4,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \overline{\tilde{\alpha}'_{Qm} \tilde{\alpha}_{2-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$Q_{5,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \bar{\Phi} \overline{\tilde{\alpha}'_{Qm} \tilde{D}_{s-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$Q_{6,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \bar{D}_s \overline{\tilde{\alpha}'_{Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$Q_{7,ks} = \int \frac{1}{2\pi} L_{k-Q\,s} C_{\mu s} \beta \overline{\tilde{\alpha}'_{Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

$$Q_{8,ks} = \int \frac{1}{2\pi} L_{k-Q\,s} \beta \overline{\tilde{\alpha}'_{Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

$$T_{1,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\tilde{\alpha}_{2Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, \mathrm{d}Q$$

$$T_{2,ks} = \sum_{m,n=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\xi_{Qm} \tilde{\alpha}_{2-Qn}} \, [i(k-Q)]^m \, (ik)^n \mathrm{d}Q$$

$$T_{3,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \beta \overline{\tilde{\alpha}_{2Qm} \tilde{\alpha}'_{-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$T_{4,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\tilde{\alpha}_{2Qm} \tilde{\alpha}_{2-Q}} \, [i(k-Q)]^m \, (ik) \mathrm{d}Q$$

$$T_{5,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \bar{\Phi} \overline{\tilde{\alpha}_{2Qm} \tilde{D}_{s-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$T_{6,ks} = \sum_{m=1,2} \int \frac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \bar{D}_s \overline{\tilde{\alpha}_{2Qm} \tilde{\Phi}_{-Q}} \, [i(k-Q)]^m \, (ik)^2 \mathrm{d}Q$$

$$T_{7,ks} = \int \frac{1}{2\pi} \breve{L}_{k-Q\,s} C_{\mu s} \overline{\tilde{\alpha}_{2Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

$$T_{8,ks} = \int \frac{1}{2\pi} \breve{L}_{k-Q\,s} \overline{\tilde{\alpha}_{2Qm} \tilde{K}_{-Q}} \, [i(k-Q)] \, \mathrm{d}Q$$

Table 4

$$S_{1,ks} = \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{\Phi}_{-Q}} \mathrm{d}Q$$

$$S_{2,ks} = \textstyle\sum_{m=1,2} \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\xi_{Qm} \tilde{K}_{-Q}} (ik)^m \mathrm{d}Q$$

$$S_{3,ks} = \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \beta \overline{\tilde{K}_{Qm} \tilde{\alpha'}_{-Q}} (ik) \mathrm{d}Q$$

$$S_{4,ks} = \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{\alpha}_{2-Q}} (ik) \mathrm{d}Q$$

$$S_{5,ks} = \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \bar{\Phi} \overline{\tilde{K}_{Qm} \tilde{D}_{s-Q}} (ik)^2 \mathrm{d}Q$$

$$S_{6,ks} = \int \tfrac{1}{2\pi} G^{-1}_{k-Q\,s} \bar{D}_s \overline{\tilde{K}_{Qm} \tilde{\Phi}_{-Q}} (ik)^2 \mathrm{d}Q$$

$$S_{7,ks} = \int \tfrac{1}{2\pi} L_{k-Q\,s} C_{\mu s} \overline{\tilde{K}_{Qm} \tilde{K}_{-Q}} \mathrm{d}Q$$

$$S_{8,ks} = \int \tfrac{1}{2\pi} L_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{K}_{-Q}} \mathrm{d}Q$$

$$I_{1,ks} = \int \tfrac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{\Phi}_{-Q}} \mathrm{d}Q$$

$$I_{2,ks} = \textstyle\sum_{m=1,2} \int \tfrac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\xi_{Qm} \tilde{K}_{-Qn}} (ik)^m \mathrm{d}Q$$

$$I_{3,ks} = \int \tfrac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \beta \overline{\tilde{K}_{Qm} \tilde{\alpha'}_{-Q}} (ik) \mathrm{d}Q$$

$$I_{4,ks} = \int \tfrac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{\alpha}_{2-Q}} (ik) \mathrm{d}Q$$

$$I_{5,ks} = \int \tfrac{1}{2\pi} \breve{G}^{-1}_{k-Q\,s} \bar{\Phi} \overline{\tilde{K}_{Qm} \tilde{D}_{s-Q}} (ik)^2 \mathrm{d}Q$$

$$I_{6,ks} = \int \tfrac{1}{2\pi} \breve{G}_{k-Q\,s} \bar{D}_s \overline{\tilde{K}_{Qm} \tilde{\Phi}_{-Q}} (ik)^2 \mathrm{d}Q$$

$$I_{7,ks} = \int \tfrac{1}{2\pi} \breve{L}_{k-Q\,s} C_{\mu s} \overline{\tilde{K}_{Qm} \tilde{K}_{-Q}} (ik)^2 \mathrm{d}Q$$

$$I_{8,ks} = \int \tfrac{1}{2\pi} \breve{L}_{k-Q\,s} \overline{\tilde{K}_{Qm} \tilde{K}_{-Q}} (ik)^2 \mathrm{d}Q$$

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