General Approach for Modelling of Reactive Transport in Porous Media

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Abstract—This work presents a relatively new approach designed for modelling reacting flows in porous media by using conditional expectations. Similar methods, aimed at obtaining, closing and using conditional expectations in reacting fluid flows, were previously developed for and successfully used in turbulent combustion (e.g. conditional moment closure or CMC) are now generalised and adapted to perform simulations of reacting flows in porous media. Different versions of the porous models PCMC (porous CMC) variations of PDCMC (distance conditioned moment closure) have been proposed and are now summarised in this work. These approaches utilise single-conditioned expectations and the closure of the equations is obtained by using diffusion approximations conventional in CMC.

Fractal properties of a porous medium can be used to evaluate the coefficients of the conditional equations. A new approach for investigating transport phenomena in irregularly-connected pore networks and obtaining corresponding transport coefficients has also been suggested. This approach combines a generalised effective medium approximation with a macroscopic continuum model and allows us to explicitly obtain analytical expressions for the transport coefficients for both unconditional and conditional models.

As demonstrated, the proposed general approach is capable of emulating various regimes of reactive transport in porous media, while permitting accurate reproduction of the experimental results.

Index Terms—Conditional moment closure, fractality, generalised effective medium approximation, porous media, reacting flows.

I. INTRODUCTION

Conventional models based on unconditional averaging of the flow properties over varying pore configuration and sizes are likely to suffer from being insufficiently detailed to represent the whole complexity of the flow. It is common that, while spatial transport occurs mainly in the largest pores, *heterogeneous reactions* take place mainly in the smallest pores accessible only through a *cascade of pores* of different

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sizes. Distinguishing a limited number of different pore sizes (e.g. fractures and pores) may improve accuracy but is also likely to be insufficient for accurate treatment of reacting flows in porous media. *Conditional methods* allow us to formulate consistent transport equations while taking into account the whole spectrum of possible pore sizes.

The *Conditional Moment Closure* (CMC) methodology has been proposed in the earlier nineties [1], [2] for more accurate (compared to previously used, unconditionally averaged models) but still computationally affordable (in contrast to direct numerical simulations or DNS) modelling of turbulent reacting flows. The model based on conditional averaging contains much more detail than unconditional models. At the same time, the conditional approach is still much more computationally affordable than DNS. Conditional averaging, however, brought a new series of questions related to model consistency, preservation of conservation properties, accurate specification of the model coefficients, etc. These questions were mostly resolved over time and the results were presented in the comprehensive review of earlier studies on conditional methods [3].

The CMC methodology has been successfully applied to a variety of problems in turbulent reacting flows. This success encouraged the present authors to apply CMC methodology for modelling of reactive flows through porous media.

Both turbulent flows and those in porous media involve *multi-cascade processes*. These processes, however, represent physically different phenomena that should be reflected in conditional modelling. In turbulent non-premixed combustion, fluctuations of the reactive species concentrations correlate with fluctuations of the mixture fraction. The latter can be described statistically with a presumed *probability density function* (PDF) of the mixture fraction. In porous media, the laminar variations in the gas species concentrations correlate with the diffusive distance to the reactive surface. This distance can also be described statistically with a presumed PDF.

Transport in complex porous media, such as coal, involves cascade processes of diffusion through pores of different sizes (micro-, meso- and macro-pores), while convective transport predominantly occurs through the largest pores and fractures. Heterogeneous gas-solid reactions bring additional complexity to this process. In coal, which exhibits fractal properties [4], the reactive surface is predominantly located in the smallest pores and variations in gas species concentrations become of prime importance. The unconditional approach [5], [6], which is based on unconditional averages, is unable to take these variations into account.

As discussed above, an additional variable that describes the variations in species concentrations needs to be introduced for accurate treatment of heterogeneous reactions. Two such variables have been proposed so far: the *diffusive* tracer and the distance tracer. Porous Conditional Moment Closure (PCMC) model for the diffusive tracer is presented in [7] and properties of such tracers in fractal porous media are comparatively analysed in [8]. Treatment of the case where the pore structure substantially changes due to heterogeneous reactions is given in [9]. The model for distance tracer, which is called Porous Distance Conditioned Moment Closure or PDCMC, is formulated in [10], where the interplay between interface and network fractalities of the porous medium in question is also analysed. The coefficients of the transport equations still need to be approximated. This problem has been solved [11] for arbitrary random networks of pores by combining a generalisation of the effective medium approximation [12] with a continuum approximation governed by equations similar to Fokker-Planck equations. This novel approach allows derivation of explicit analytical expressions for the transport coefficients.

Conditional methods become most effective when *volume averaging*, which is conventional in porous media, is replaced by more mathematically convenient *ensemble averaging*. The *ensemble-spatial averaging theorem*, which is the ensemble analogue of the *spatial averaging theorem* [6], has been proven in [8]. This enables the use of ensemble averaging, both conditional and unconditional, in porous media applications.

This paper presents a spectrum of models that can be effectively used to accurately model a wide range of reacting flows through porous media. We summarise theoretical developments of the previous studies and present some results of calculations. Note that the presented approach is general and independent of the sub-models used to describe diffusive characteristics of a porous medium or kinetics of heterogeneous and homogeneous reactions. In fact, one can use virtually any sub-models, which are dictated by real conditions or regarded as appropriate from separate considerations. The approach is applicable to a variety of reacting flows through porous media including, for example, methane replacement by CO_2 in coal. This opens the possibility to apply the successful CMC methodology for modelling and optimisation of such technologies as geological CO₂ sequestration and enhanced coal bed methane recovery, which are of particular importance in the modern carbon-constrained world.

II. MODELLING OF REACTIVE TRANSPORT IN POROUS MEDIA

A porous medium is conventionally characterised by two phases: the gaseous β -phase and the solid matrix or σ -phase. The reactive flow within the β -phase is governed by the continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{1}$$

and, for each gaseous species "i", by the species transport equations

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{v} Y_i) - \nabla \cdot (\rho D Y_i) = \rho W_i \qquad (2)$$

Here, ρ and **v** are the gas density and velocity, respectively; Y_i are the mass fractions of the gaseous species; while W_i are the species production rates in homogeneous (β -phase) reactions. To simplify the formulae, the diffusion coefficient D is assumed to be the same for all gaseous species. Note that heterogeneous reactions, which occur on the reactive surface or β/σ -interface, are treated with the help of boundary conditions as described below.

Traditionally [5], [6], the above equations are averaged using *intrinsic* (over the β -phase) or *superficial* (over the entire porous medium) averages. The averaging is performed by taking the convolution integral with a bell-shaped weighting function. The characteristic length scale of this function is much larger than the characteristic pore size but much smaller than the length scale of flow parameter variations. In terms of averages, the momentum balance is given by the *Darcy law* [13].

Since the characteristic length scale of the weighting function is much larger than the size of pores, models based on conventional averaging disregard the variations in species concentrations within a pore and variations between pores of different sizes. This poses no significant problems if the heterogeneous reaction is in the kinetics controlled regime, which is characterised by small *Damkohler numbers (Da <<* 1). In this regime, the gaseous reactant is transported to the reactive surface much faster than it is consumed on the surface. As a result, the concentration of the gaseous reactant does not vary significantly within a pore as schematically presented in Fig. 1 by a dashed line.



Fig. 1. Schematic view of the variations in a gaseous reactant concentration within a pore.

For large Damkohler numbers (Da >> 1), however, all the gaseous reactant that arrives at the reactive surface reacts almost instantaneously with the surface. In this case, the reactant concentration varies significantly within a pore as shown in Fig. 1 by a solid line. In the vicinity of the surface, the concentration is approximately zero and rapidly increases towards the centre of a pore. The conventional approach, which is based on unconditional averages, is independent of Da and does not consider such variations. As a result, the conventional approach gives unacceptable predictions for the diffusion controlled regime and poor predictions for the intermediate regimes ($Da \approx 1$) of the heterogeneous reaction (see Fig. 3 in [7]).

The regime of the heterogeneous reaction is not known *a priori*. We note, however, that the diffusion controlled and intermediate regimes are generally more likely than kinetics

controlled regime in high temperature processes. Therefore, variations in species concentrations with pore size need to be considered for accurate modelling of such processes. In the CMC paradigm, this is achieved by introducing an additional variable which parameterises the distance to the reactive surface (which also serves as a proxy for pore size), and solving equations based on averages conditioned on this variable. Two variables have been used for conditioning: the diffusive tracer and the distance tracer. These variables and the corresponding models are considered in the next sections. In this study, we present only major equations of these models in their simplified form, while referring a reader to the previous papers [7], [8], and [10] for general formulations and more details. Unlike in the previous publications, we give only the conservative form of the conditional equations (but not the *convective form*).

III. DIFFUSIVE TRACER (PCMC)

The diffusive tracer Z is introduced in [7] as follows. The tracer Z is assumed to be produced with the constant rate W_Z in the β -phase. It is transported in the same way as gaseous species. That is, Z satisfies the conventional species transport equation

$$\frac{\partial \rho Z}{\partial t} + \nabla \cdot (\rho \mathbf{v} Z) - \nabla \cdot (\rho D Z) = \rho W_Z.$$
(3)

Similarity of (2) and (3) (with the same diffusion coefficient *D*) ensures that *Z* resembles transport of gaseous species, The value of the constant source term W_Z can be arbitrarily selected without loss of generality. As demonstrated in [8], the diffusive tracer can be interpreted as a distance from a given point in the β -phase to the reactive surface measured by the average time required for a random walk process to reach the surface.

The tracer is instantaneously consumed at the reactive surface, so that Z is positive in the β -phase and monotonically decreases to zero at the reactive surface. In this way, Z parameterises the distance from the reactive surface and the condition Z=0 defines the surface (in this case we say that conditioning on Z resolves the phase interface). Furthermore, the instantaneous consumption of Z on the surface emulates the diffusion controlled regime of heterogeneous reactions.

The equations of the PCMC model are expressed in terms of conditional *Favre averages*. For an arbitrary function *F*, the conditional Favre average $(\overline{F})_z$ is defined as $(\overline{F})_z \equiv \langle F \rho \beta | Z = z \rangle / \langle \rho \beta | Z = z \rangle$. The angular brackets conventionally denote superficial averages and *z* is the variable in *Z*-dimension, while $\beta(x)$ is the indicator of the β -phase so that $\beta = 1$ in the β -phase and $\beta = 0$ elsewhere. If *Z* resolves the interface, the indicator β does not affect conditional averaging and can be omitted there.

Averaging (1) and (2) with the help of the technique described in [3], while omitting the terms which are conventionally neglected in CMC approach [7], and conventionally denoting $Q_i \equiv (\overline{Y_i})_z$, we arrive at the following equations of the PCMC model:

$$\frac{\partial \rho_z P_z}{\partial t} + \nabla \cdot \left((\overline{\mathbf{v}})_z \rho_z P_z \right) . \quad (4)$$

$$+ \frac{\partial W_z \rho_z P_z}{\partial z} + \frac{\partial^2 (\overline{N})_z \rho_z P_z}{\partial z^2} = 0$$

$$\frac{\partial \rho_z P_z Q_i}{\partial t} + \nabla \cdot \left((\overline{\mathbf{v}})_z \rho_z P_z Q_i \right)$$

$$+ \frac{\partial (\overline{N})_z \rho_z P_z Q_i}{\partial z} Q_i - (\overline{N})_z \rho_z P_z \frac{\partial Q_i}{\partial z} \right) \quad (5)$$

$$+ \frac{\partial W_z \rho_z P_z Q_i}{\partial z} = \rho_z P_z (\overline{W_i})_z$$

where P_Z is the PDF of Z and $(\overline{N})_z \equiv (\overline{D(\nabla Z)^2})_z$ is the conditional dissipation of the tracer. In this work we give the conservative form of the conditional equation (5), while the convective form of the PCMC equation [7] can be easily obtained with the use of the PDF equation (4).

If the reactive surface is not resolved by the conditioning variable, the source terms W_i involve the effect of both volumetric and surface reactions. If the surface is resolved by Z=0 (or by a similar condition), then the surface reactions are treated separately by boundary conditions for the Z-dimension [10]. This case of the phase interface resolved by Z=0 is specifically considered this section. The boundary conditions are obtained using the ensemble averaging [7], which generalises the spatial averaging theorem [14]. Following [7], we assume that the reactive surface is quasi-stationary and the Z-field is developed. Then, the boundary conditions for $Z\rightarrow0$ read

$$\left(W_{Z}\rho_{z}P_{Z} + \frac{\partial(\overline{N})_{z}\rho_{z}P_{Z}}{\partial z}\right)_{z=+0} = A_{z}M, \quad (6)$$

$$\left(A_{z}\stackrel{\bullet}{M}Q_{i}-\rho_{z}(\overline{N})_{z}P_{Z}\cdot\frac{\partial Q_{i}}{\partial z}\right)_{z=+0}=A_{z}\Psi_{i}.$$
 (7)

Here, A_{z} is the interface surface area per unit volume,

$$\dot{M} = \sum_{i} \Psi_{i}(Q_{1}, Q_{2}, ...)$$
 (8)

is the mass production rate per unit area at the interface surface and Ψ_i are the mass rates of the heterogeneous reactions per unit surface area. While the flow is considered only in the β -phase, the PDF P_Z and all other PDFs in this work are understood as *superficial* and normalised by

$$\int_{+0}^{\infty} P_Z(z) dz = \left< \beta \right> \tag{9}$$

where β is the indicator function of the β -phase and the average $\langle\beta\rangle$ is the *porosity* of the medium. Intrinsic PDFs, which are not used here, are normalised to unity and these PDFs need to be multiplied by porosity in the equations. Note also that left part in (7) represents mass fluxes of the gaseous reactants to the reactive surface.

Thus, (7) takes into account the heterogeneous reactions and provides one of the major advances of CMC models over the conventional (unconditional) approach. In (7), the surface reaction rates Ψ_i are functions of Q_i , which are linked to the distance to the reactive surface via conditioning on Z. In contrast, only unconditional averages, which are independent of that distance, are available in conventional models. With this advantage, the PCMC model demonstrated a good match with the results of DNS performed for a test case of carbon oxidation [7], specifically for the diffusion controlled and intermediate regimes of the surface reaction.

Note that consistent modelling of both P_Z and $(N)_z$ is required to close (4) and (5). Generally, P_Z is not known and needs to be reasonably approximated. In the test case considered in [7], such an approximation was obtained by matching the DNS results. This approach, however, is computationally expensive and requires additional modelling of the structure of a porous medium, which can be an extremely difficult problem by itself. A more practical method for a medium with fractal properties is suggested in [9]. Such a medium is characterised by geometrical similarity of pore structures at different scales (micro-, meso- and macro-pores) and by the predominant location of the reactive surface within the smallest pores. As demonstrated in [8], P_Z asymptotically follows the power law for such media $P_Z = c(z-a)^{-\alpha}$. See [8] and [9] for details.

IV. DISTANCE TRACER (PDCMC)

Alternatively, the distance to the phase interface can be parameterised by the distance tracer R, which is linked to the stochastic geometry of a porous medium and is defined as the minimal distance from a point within a pore to the reactive surface [8]. The sample variable in R-dimension is r. The distance tracer seems to be a more natural parameterisation and averages conditioned on this tracer do not depend on the flow. The PDCMC model equations, however, involve the additional velocity component u corresponding to the R-direction and other additional terms.

The PDCMC model equations are formulated in terms of conditional averages [10]. For an arbitrary function F we define $\langle F \rangle_r \equiv \langle F | R = r \rangle$ and $(\overline{F})_r \equiv \langle F \rho \rangle_r / \rho_r$ where $\rho_r = \langle \rho | R = r \rangle$ is conditional average of the density. As demonstrated in [8], P_R asymptotically follows the power-law $P_R \sim 1/r^a$. Similarly to the diffusive tracer, R is positive in the β -phase and the condition R=0 defines the reactive surface.

In terms of the averages conditioned on R, (1) reads

$$\frac{\partial P_R \rho_r}{\partial t} + \nabla \cdot \left(P_R \rho_r(\mathbf{v})_r \right) + \frac{\partial P_R \rho_r(u)_r}{\partial r} = 0. \quad (10)$$

A superficial PDF, normalised as in equation (9), is implied here. Using an over-tilde to distinguish the conditioning on *R* from that on *Z* and denoting $\tilde{Q}_i \equiv (\overline{Y}_i)_r$, (2) takes the form

$$\frac{\partial P_{R}\rho_{r}\tilde{Q}_{i}}{\partial t} + \nabla \cdot \left(P_{R}\rho_{r}(\mathbf{v})_{r}\tilde{Q}_{i}\right) - \nabla \cdot \left(P_{R}\rho_{r}D_{x}\nabla\tilde{Q}_{i}\right) + \frac{\partial}{\partial r}\left(P_{R}\rho_{r}\left((\mathbf{u})_{r}\tilde{Q}_{i} - D_{r}\frac{\partial\tilde{Q}_{i}}{\partial r}\right)\right) = P_{R}\rho_{r}(\overline{W_{i}})_{r}$$
(11)

The boundary conditions on the reactive surface (R=0) are given by

$$\rho_r(\overline{u_i})_r = \dot{M} , \qquad (12)$$

$$\rho_r\left(\bar{(u)}_r\tilde{Q}_i - D_r\frac{\partial\tilde{Q}_i}{\partial r}\right) = \Psi_i(\tilde{Q}_1, \tilde{Q}_2, \dots).$$
(13)

The PDCMC model was applied to simulate the process of CH_4 replacement by CO_2 in a coal sample [10] and the results of calculations were compared with the experimental data previously obtained at the University of Queensland. In this experiment, CO_2 was supplied at the pressure of 500 kPa on one side of the coal sample initially filled in with methane, while the mixture of CH_4 and CO_2 was drained from the other side at the pressure of 300 kPa. The methane fraction in the outflow was recoded as a function of time. The parameters of the model were selected to match the characteristics of the coal sample and the conditions of the experiment reported in [16]. The excess fractal dimension $\alpha = 0.71$ was taken from [4]. The experimental data and the computational results are presented in the Fig. 2.



As shown in this figure, the experimental results follow a power-law decay in CH₄ concentration with time. Clearly, such a behaviour cannot be explained only by kinetics considerations, which imply an exponential decay. Thus, the observed power-law decay indicates that the adsorption/desorption reactions are not kinetically limited, which confirms the results of the previous study [17]. The PDCMC model consistently treats diffusion of methane from smaller to larger pores and a counterflow of CO₂ induced by the pressure gradient coupled with the adsorption/desorption reactions. As a result, an excellent asymptotic match of the experimental data is achieved (see Fig. 2). The initial disagreement is believed to be due to a relatively large dead volume, which is initially filled in with CH4, between the coal sample and the sensor. This volume causes an apparent delay (not more than 100 seconds for the multi-hour experiment) in the breakthrough of CO₂. Its influence, however, vanishes with time and does not affect the long-term asymptote. It is important to note that the PDCMC model correctly predicts an exponential decay for kinetics controlled reactions.

Numerical experiments with the PDCMC model demonstrate that, depending on the values of the parameters characterising the gas flow and the medium, methane

recovery enhanced by CO2 injection may occur in two different major regimes. These are the ``diffusive exchange" and the ``wave-like" regimes. In the diffusive exchange regime, which has been observed in the experiments and calculations presented here, is shown in Fig. 2. In this regime, CO₂ quickly (within few seconds) breaks though the largest pores, while CH₄ initially remains stagnant mainly in the smallest pores. Then, CH₄ diffuses from the smallest pore into the stream over a substantial period of time. After the initial drop, the fraction of CH₄ in the outflow gradually decreases in time. In the wave-like regime, CO₂ does not break though. Instead, the interface between CO2 and CH4 stretches from smallest to largest pores, while forming a "wave" front that propagates downstream. The fraction of CH₄ in the outflow drops rapidly, when the front reaches the downstream end of the coal sample. Comparison of the diffusive exchange and the wave-like regimes is shown in Fig. 3. The ability of the PDCMC model to simulate both regimes provides a potential for optimising the gas injection parameters. Selecting the optimal gas injection regime is the major task in a successful enhanced coal bed methane recovery.



Fig. 3. Diffusive exchange and wave-like regimes.

V. CONDITIONING ON PORE SIZES

Two types of fractality - interface fractality and network fractality - should to be considered [8]. It has been demonstrated that, depending on the parameters of the porous medium, either interface or network fractality dominates (see Section 10 in [8] for more details). In the latter case, the distance tracer is also a proxy for pore sizes [9] (as explained in [8] the diffusive tracer can also serve as the indicator of pore sizes but this is not used here). Indeed distance R cannot be found in a pore much smaller than R while the probability of being located in a pore much larger than R is low since smaller pores contain most of the interface surface. Hence as deduced in [9], (11) can be interpreted as equations conditioned on the pore size. There is however an adjustment to make since r=0 no longer resolves the phase interface. In principle, conditional methods permit conditioning on two or more variables (e.g. on both distance to the interface and pore size) but this seems unnecessary at this stage of development. If *R* is interpreted as the pore size, equation (11) corresponds to neglecting reaction on the phase interface in all but the smallest pores. This can be corrected by introducing distributed heterogeneous reaction source terms into the conditional equations [9]. Using hat to denote conditioning on the pore size, the continuity and species transport equations take the form

$$\frac{\partial P_{\hat{R}}\rho_{\hat{r}}}{\partial t} + \nabla \cdot \left(P_{\hat{R}}\rho_{\hat{r}}(\mathbf{\bar{v}})_{\hat{r}}\right) + \frac{\partial P_{\hat{R}}\rho_{\hat{r}}(u)_{\hat{r}}}{\partial \hat{r}} \quad (14)$$

$$= A_{\hat{r}}P_{\hat{R}} \stackrel{\bullet}{M} \quad (14)$$

$$\frac{\partial P_{\hat{R}}\rho_{\hat{r}}\hat{Q}_{i}}{\partial t} + \nabla \cdot \left(P_{\hat{R}}\rho_{\hat{r}}(\mathbf{\bar{v}})_{\hat{r}}\hat{Q}_{i}\right) + \frac{\partial P_{\hat{R}}\rho_{\hat{r}}(u)_{\hat{r}}\hat{Q}_{i}}{\partial \hat{r}} \quad (15)$$

$$-\nabla \cdot \left(P_{\hat{R}}\rho_{\hat{r}}D_{x}\nabla\hat{Q}_{i}\right) - \frac{\partial}{\partial \hat{r}} \left(P_{\hat{R}}\rho_{\hat{r}}D_{\hat{r}}\frac{\partial \hat{Q}_{i}}{\partial \hat{r}}\right) \quad (15)$$

where $A_{\hat{r}}$ is interface area per volume of pore of size \hat{r} . Although these equations are formulated only for the β -phase, the PDF is understood as superficial and is normalised similar to (9).

Due to the additional velocity component u, the momentum balance in the PDCMC model is given by the following generalisation of the Darcy law for conditional averages.

$$(\bar{u})_{\hat{r}} = -\frac{\kappa_{\hat{r}}}{\mu} \frac{\partial p_{\hat{r}}}{\partial \hat{r}}, \quad (\bar{\mathbf{v}})_{\hat{r}} = -\frac{\kappa_x}{\mu} \nabla p_{\hat{r}}. \quad (16)$$

where μ is the dynamic viscosity of the gas, κ_x is the permeability of the medium in the physical space and $p_{\hat{r}}$ is the conditional pressure $p_{\hat{r}} = \langle p | \hat{R} = \hat{r} \rangle$, while the parameter $\kappa_{\hat{r}}$ plays the role of the permeability coefficient in the *r*-direction. Methods for evaluation of the diffusion coefficients in physical space D_x and in the pore size space $D_{\hat{r}}$ are discussed in section VI.

These equations are conceptually similar to (10) and (11), where conditioning is performed on the distance to the reactive surface. However, heterogeneous reactions are treated differently in these two cases. In the case of conditioning on the distance to the reactive surface, heterogeneous reactions are taken into account by boundary conditions (12) and (13), which are formulated for the resolved phase interface. Such an approach is not applicable to (14) and (15), since the phase interface is not explicitly resolved, when conditioning is performed on the pore size. In this case, the heterogeneous reactions are taken into account by the additional source terms, which depend on the pore size \hat{r} . Generally, one can expect that gas-solid reactions are more intense in smaller pores. Note that the equations conditioned on the pore size (14) and (15) can be used for various porous media, including those with complex fractal properties. Note that the conditional equations considered here can be generalised for the free molecular regime [10].

VI. TRANSPORT COEFFICIENTS

As demonstrated [7], [10], the conditional models have proven to be successful in modelling a variety of reactive flows through porous media. However, the transport coefficients in these models were treated as adjustable parameters. Their values were mainly selected by fitting the available experimental data. In reality, the transport coefficients are determined by the properties of the porous media in question and need to be modelled in a physically realistic fashion. This problem has been recently addressed by a novel approach [11], which generalises and combines the *effective medium approximation* with a macroscopic continuum model that is expressed by equations similar to the *Fokker-Planck equation*.

The suggested approach is general and has the capacity to deal with various kinds of irregularity in porous media without the need for excessive detail or computational effort. Unlike previous effective medium approaches, the generalized effective medium approximation permits variation in coordination numbers, anisotropy, and macroscopic fluctuations. This is more representative of real porous media, which commonly exhibit such irregularities.

As demonstrated [11], the new model is able to account for effects related to the connectedness of the medium, most notably the existence of a percolation threshold. This results in much higher accuracy of the model for low coordination numbers, as is clearly illustrated in Fig.4. Moreover, the generalised effective medium technique can handle some cases where other approaches, such as a simple Fokker-Planck model, would give highly inaccurate or even infinite results [11].



Fig. 4. Comparison of normalized diffusion coefficients between the new model, a simple Fokker-Planck model, and direct simulations.

VII. CONCLUSION

The CMC methodology, which has been successfully used to model turbulent reactive flows, is extended to model reactive flows through porous media, including combustion of porous materials. Two conditional variables: the diffusive tracer and the distance tracer are introduced. Conditioning on these tracers takes into account variations in gas species concentrations and allow for a more accurate (compared to unconditional models) and consistent treatment of heterogeneous reactions. Various variants of the conditional model, which consistently simulate complex multi-cascade processes of reactive transport in complex porous media, are formulated for these tracers in terms of single-conditioned expectations.

Depending on the selection of the conditional variable, two versions of the conditional models are considered (i.e. PCMC and PDCMC). The models can be formulated either with the phase interface resolved by the conditioning variable or without the resolving interface (for example, conditioning on the pore size). Different versions of conditional models have their plusses and minuses and are intended to be used flexibly depending on the physics of the problems under consideration.

The PCMC model, in contrast to unconditional models, provides a good match to the results of DNS for the carbon oxidation test case, specifically for the diffusion controlled and intermediate regimes of the surface reaction. The PDCMC model, being applied for modelling of methane replacement by CO_2 in a coal sample, demonstrates excellent asymptotic agreement with the experimental data, which indicate a power-law decay in CH_4 concentration. The PDCMC model is also able to simulate various regimes of methane replacement by CO_2 in coal. This ability makes the model specifically useful for optimising the parameters of gas injection in such technologies as enhanced coal bed methane recovery and geological CO_2 sequestration.

A novel approach, enabling the derivation of analytical expressions for transport coefficients of irregular networks of pores, is suggested. This approach unifies two principal existing methods (the effective medium approximation and the Fokker-Planck equation) into a single general and powerful methodology.

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