ELSEVIER

Advances in Colloid and Interface Science
76–77 (1998) 389–443

ADVANCES IN COLLOID AND INTERFACE SCIENCE

Porous media transport descriptions — non-local, linear and non-linear against effective thermal/fluid properties

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Abstract

The momentum and scalar transport equations obtained using volume-averaging theory (VAT) involve additional terms which quantify the influence of the medium morphology. There are many mathematical models currently in use which are actually competing without comparison or analysis. The few most common and the VAT-based models are analyzed along with effective coefficients conventional equations. The random morphology fluctuations are incorporated into the VAT-based transport equations by means of randomly varying morpho-convective and morpho-diffusive terms. Methods for closure of the morpho-fluctuation terms in the governing transport equations are outlined. Statistical and numerical techniques were applied to classical irregular morphologies to treat the morpho-diffusive and morpho-convective terms along with integral terms. At present there are few well-developed closure expressions for the VAT-based transport equations in porous media. Some of them exploit the properties of available solutions to transport problems for individual morphological elements (F. Zanotti, R.G. Carbonell, Chem. Eng. Sci. 39 (1984) 263; C.T. Hsu, P. Cheng, Int. Comm. Heat Mass Transfer 15 (1988) 689; M. Quintard, S. Whitaker, Advances in Heat Transfer, vol. 23, Academic Press, 1993) and others are based on the natural morphological data of porous media (V.S. Travkin, I. Catton, Proceedings of the 28th National Heat Transfer Conference, San Diego, CA, August 1992, ASME HTD, vol. 193, 1992; L. Gratton, V.S. Travkin, I. Catton, Heat Transfer in Porous Media, ASME HTD, vol. 240, 1993; H. Ma, D.W. Ruth, Trans. Porous Media 13 (1993) 139). The challenging problem in irregular and random morphologies is to produce an analytical or numerical evaluation of the deviations in scalar or vector fields. In previous work, the authors have presented a few exact closures for predetermined regular and random porous

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PII S0001-8686(98)00054-2

medium morphologies. The questions related to effective coefficient dependencies, boundary conditions and porous media experiment analysis are discussed. A few issues particularly related to mass transport in different scale adsorbing media analysed with VAT techniques.

Keywords: Porous media; Modeling; Equations; Experiments; Effective coefficients; Adsorption; Mass transport

Contents

1. Introduction

The formulation of heterogenous medium transport equations has evolved a great deal since the 1950s [1–3]. Even so, the proper form of the governing equations for a porous media is still a source of frequent discord.

Determination of the flow variables and the magnitude of the scalar transport for problems involving heterogeneous porous media is difficult, even when subject to simplifications allowing specification of the medium periodicity or regularity. Linear or linearized models fail to intrinsically account for transport phenomena, requiring dynamic coefficient models to correct for shortcomings in the governing models. Additionally, when attempting to describe processes in a heterogeneous media, the correct form of the governing equations remains an area of debate among various researchers (see, for example [4,7–11]). Allowing inhomogeneities

to be of random or stochastic character further compounds the already daunting task of properly identifying pertinent transport mechanisms and predicting transport phenomena.

Mathematical simulation of physical processes in a highly non-homogeneous media, in general, calls for obtaining averaged characteristics of the medium and, consequently, the averaged equations. The averaging of processes in a randomly-organized media can be performed in many different ways. If a physical model has several interdependent structurally-organized levels of processes underway, it is expedient to employ one of the hierarchical methods of simulation (for example [12,13], among others). The hierarchical principle of simulation consists of successively studying the processes at a number of structural levels.

One first deals with the smallest-scale element, for example a small smooth capillary or globular media. Next, various types of capillary wall morphology are incorporated. This is followed by studies of a range of diameters, first smooth then rough, and then networking. Regular variations of the parameters are treated first, followed by random. This is done at each level. This approach is underway for capillary morphologies as well as granular or other morphologies. The process leads one to find ways to deal with the large number of closure expressions that result from the volume-averaging theory (VAT) used to obtain the original governing set of equations. Although of a common form, the resulting usable form depends on the media morphology and the local boundary conditions at the each level of the hierarchy. A particular closure expression will be different for energy, mass or momentum transfer between the fluid and the solid matrix, in part because of their different boundary conditions.

There are many disagreements about the applicability of models based on conventional diffusivity type of models of transport phenomena in porous media to media with the following features: (1) multi-scaled media; (2) media with non-linear physical characteristics; (3) polydisperse morphologies; (4) materials with phase anisotropy; (5) media with non-constant or field-dependent phase properties; (6) transient problems; (7) presence of imperfect interface surfaces; and (8) presence of internal (mostly at the interface) physico-chemical phenomena, etc.

The most common way to treat such problems has been to seek a solution by doing numerical experiments over more or less the exact morphology of interest. This leads to heavy use of large computers to solve large algebraic statements. The treatment and analysis of the results of such a direct numerical modeling (DNM) is both unappealing and difficult.

Meanwhile, the VAT presents an incredibly powerful tool for dealing with complex heterogeneous media problems having features like those enumerated above. The equations resulting from the use of VAT have strange additional terms that are not usually seen. One needs to ask whether or not these new terms are small enough to ignore. In what follows, it will be shown that they are not. In fact, they are of the same order of magnitude as the terms that are normally kept.

An important aspect of porous medium transport theory is the development of appropriate boundary-condition equations in addition to the equations governing transport in the internal region. Most existing treatments conveniently rely upon

first (I), second (II) or third (III) kind boundary conditions for heat or mass transfer. However, the I, II and III kind boundary statements are insufficient in portions of the near-boundary regions. A heat transfer boundary condition for the interface between a porous medium and the free stream was developed by Ochoa-Tapia and Whitaker [14] as a flux-jump condition. There are numerous ways to account for the additional (jump) terms between phases (porous medium–homogeneous fluid, or two porous media) that need to be addressed.

Many researchers make errors in developing the VAT-based equations or repeated use of existing basic models in spite of the fundamental work by Whitaker (for example, see [8,10]) that presents a comprehensive analysis, and derivation, of numerous laminar linear porous media VAT-based transport governing equations. An example is the energy equation developed by Plumb [15] for a flat channel filled with a porous media,

$$\tilde{U}\frac{\partial \tilde{T}_f}{\partial x} = \frac{\partial}{\partial y}\left[\frac{k_f}{c_{pf}\varrho_f\langle m\rangle}\frac{\partial \tilde{T}_f}{\partial y}\right] + \frac{\alpha_T S_w}{c_{pf}\varrho_f\langle m\rangle}\left(\{T_s\}_s - \tilde{T}_f\right),$$

which should be

$$\tilde{U}\frac{\partial \tilde{T}_f}{\partial x} = \frac{k_f}{c_{pf}\varrho_f}\left(\frac{\partial^2 \tilde{T}_f}{\partial y^2}\right) + \frac{\alpha_T S_w}{c_{pf}\varrho_f\langle m\rangle}\left(\{T_s\}_s - \tilde{T}_f\right),$$

for constant porosity and thermo-physical properties and for variable porosity it should be

$$c_{pf}\varrho_f\langle m\rangle\tilde{U}\frac{\partial \tilde{T}_f}{\partial x} = k_f\frac{\partial}{\partial y}\left[\langle m\rangle\frac{\partial \tilde{T}_f}{\partial y}\right] + \alpha_T S_w\left(\{T_s\}_s - \tilde{T}_f\right).$$

Here $\langle m\rangle$ is the mean (or constant) porosity in a representative elementary volume (REV), $\{T\}_s$ is an intrinsic average in the solid phase, $\{T\}_f$ or $\tilde{T}_f$ is the intrinsic average value in the fluid phase, α_T is the heat transfer coefficient between solid and fluid phase and S_w is the specific surface. The subscripts s and f refer to solid and fluid, respectively. For variable thermo-physical properties as well as the consistent retention of the morphology descriptors $\langle m\rangle$ and S_w, the equation differs even more, as shown in work by Travkin and Catton [16] and Travkin et al. [17].

1.1. Non-linear convection characteristics in porous media laminar transport

The assumptions used in various studies to obtain linear dependence of the field fluctuations from a field-averaged quantity are the following: (1) the problem is stated for linear equations and boundary conditions; and (2) in the derivation of the linear dependence of a function on the gradient of an averaged variable, many, for example Koch et al. [18], neglect any possible form of mass flux through the

interfacial surface. Volume or ensemble averaging with these two simplifications leads to the following form of the right-hand side of the diffusion equation [18],

$$\nabla[-\langle C'U'\rangle + D\nabla\langle C\rangle]. \tag{1}$$

This form of the diffusion equation leads to a much simplified right-hand side of the fluctuation equation,

$$\nabla[C'U - D\nabla C' + \langle C\rangle U'].$$

Carbonell and Whitaker [19] accounted for the same conditions with a different form of the right-hand side of the diffusion equation

$$\nabla\left[-\langle m\rangle\left\{\hat{C}_f\hat{U}\right\}_f + \langle m\rangle D\nabla\{C_f\}_f + \frac{D}{\Delta\Omega}\int_{\partial S_w}\hat{C}_f\cdot\vec{ds}\right], \tag{2}$$

where $\tilde{u}$ designates a fluctuation variable. Even neglecting differences between the form of the averaged values, this expression has one more term than Eq. (1). By accounting for non-linear coefficients and species interfacial fluxes, the full version of this part of equation becomes more complex and has more terms to deal with. Taking into account the non-zero boundary conditions on the interfacial surface adds at least one more averaged flux term to Eq. (2).

$$\nabla\left[-\langle m\rangle\left\{\hat{C}_f\hat{U}\right\}_f + \langle m\rangle D\nabla\{C_f\}_f + D\langle\hat{C}_f\rangle_{\partial S_w}\right] + \langle\vec{q}\rangle_{\partial S_w}, \tag{3}$$

where $\langle\rangle_{\partial Sw}$ is the interface-averaging term much like the last term in Eq. (2). The next step is to include the non-linear character of the transport coefficient which adds a new term to this expression [16,17,20]

$$\nabla\left[-\langle m\rangle\left\{\hat{C}_f\hat{U}\right\}_f + \langle m\rangle\tilde{D}\nabla\{C_f\}_f + \tilde{D}\langle\hat{C}_f\rangle_{\partial S_w} + \langle\tilde{D}\nabla\hat{C}_f\rangle_f\right] + \langle\vec{q}\rangle_{\partial S_w}, \tag{4}$$

where the brackets $\langle\rangle_f$ is the phase-average value. The last equation is practically never found in work on laminar transport in porous media. The only known works containing it is by Crapiste et al. [21] and in publications on turbulent transport in highly porous media by Primak et al. [22], Shcherban et al. [23].

Turbulent transport equations for porous media based on the generalized VAT approach were developed by Primak et al. [22], Shcherban et al. [23] and Travkin and Catton [4,16,20], based on a field integrated over a some REV similar to the work on laminar flow by Whitaker [8,9]. The governing transport equations for the momentum and multi component, two- or three-temperature media were derived from the initial turbulent transport equation sets using VAT to include averaging of the non-linearities in the right-hand-side morpho-diffusive terms.

In most physically realistic cases, highly complex integro-differential equations result [9,24,25]. When additional terms in the two- and three-phase statements are encountered, the level of difficulty in attempting to obtain closure and, hence, effective coefficients, increases greatly. The greatest challenge is surmounting the

lack of understanding of the new, advanced equations and insufficient development of closure theories, especially for integro-differential equations of the type encountered here.

2. Transport equations for different flow regimes

2.1. Linear and semi-linear averaged laminar regime transport equations in porous media

2.1.1. Creeping flow

The transport equations will be developed based on creep flow using Stokes equations with a permeable interface surface between the phases and two-phase mass and heat convective transport.

The linear Stokes equations are

$$\nabla V = 0,$$
$$0 = -\nabla p + \mu \nabla^2 V + \varrho_f \vec{g}. \tag{5}$$

Although the Stokes equation is adequate for many problems, linear as well as non-linear processes will result in different equations and modeling features.

The general averaged form of these transport equations with permeable interface boundaries between the phases will be developed with application of the following forms of the right-hand-side Laplacian term. First, one can have the two forms of diffusive flux in gradient form which could be taken independently as

$$\langle \mu \nabla V \rangle_f = \mu \nabla \langle V \rangle_f + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} V \vec{ds}, \tag{6}$$

or

$$\langle \mu \nabla V \rangle_f = \mu \langle m \rangle \nabla \tilde{V} + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} \hat{V} \vec{ds}, \tag{7}$$

and these forms will be explored in greater extent later in the heat and mass-transport equations. This development was pointed out first by Whitaker [8,9]. Following the averaged forms of velocity gradient, Eqs. (6) and (7), one can obtain the two averaged versions of the diffusion term in the Eq. (5), namely

$$\langle \mu \nabla (\nabla V) \rangle_f = \mu \nabla \cdot (\nabla \langle m \rangle \tilde{V}) + \mu \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} V \vec{ds} \right] + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} \nabla V \cdot \vec{ds}, \tag{8}$$

where the production $\nabla V \cdot \vec{ds}$ is the tensorial variable and with fluctuation in the

second integral term

$$\langle \mu\nabla(\nabla V)\rangle_f = \mu\nabla\cdot(\langle m\rangle\nabla\tilde{V}) + \mu\nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{V}\vec{ds}\right] + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds}. \tag{9}$$

Using these two forms of momentum viscous diffusion term, one can write down the two versions of the averaged Stokes equations. The first is

$$\nabla\langle V\rangle_f + \frac{1}{\Delta\Omega}\int_{\partial S_w} U_i\cdot\vec{ds} = 0, \quad U_i \equiv V, \tag{10}$$

$$0 = -\nabla\langle p\rangle_f - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} + \mu\nabla\cdot(\nabla\langle m\rangle\tilde{V}) + \mu\nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w} V\vec{ds}\right] + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}. \tag{11}$$

The second form of the averaged Stokes equations are found by using transformations of the averaged relations for the pressure gradient and the diffusion term (as shown in [9,23,20]) to yield

$$-\nabla\langle p\rangle_f - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} = -\langle m\rangle\nabla\tilde{p} - \frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds}, \tag{12}$$

and

$$\frac{1}{\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds} = -\nabla\langle m\rangle\cdot\nabla\{V\}_f + \frac{1}{\Delta\Omega}\int_{\partial S_w}\nabla\hat{V}\cdot\vec{ds}. \tag{13}$$

The legitimacy of the latter relation has been demonstrated by Whitaker [9]. It is a very important and useful relation. Using the developed formalism of the averaging rules developed by Shcherban et al. [23] and Travkin and Catton [16] facilitated the development of momentum equation. Combining Eqs. (9) and (12), (13), one is able to write the momentum transport equations in the second form with velocity fluctuations

$$\nabla\langle V\rangle_f - \{V\}_f\nabla\langle m\rangle + \frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{U}_i\cdot\vec{ds} = 0, \tag{14}$$

obtained due to relationships

$$V = \{V\}_f + \hat{V},$$
$$\frac{1}{\Delta\Omega}\int_{\partial S_w} V\vec{ds} = -\{V\}_f\nabla\langle m\rangle + \frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{U}_i\cdot\vec{ds}, \tag{15}$$

and the momentum equation

$$0 = -\langle m\rangle\nabla\tilde{p} - \frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} + \mu\nabla\cdot(\langle m\rangle\nabla\tilde{V}) + \mu\nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{V}\vec{ds}\right] - \mu\nabla\langle m\rangle\cdot\nabla\tilde{V} + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla\hat{V}\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}. \tag{16}$$

It can be shown that the latter equation can take a reduced form where the deviation of velocity represents the entire velocity field,

$$0 = -\langle m\rangle\nabla\tilde{p} - \frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} + \mu\nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{V}\vec{ds}\right] + \frac{\mu}{\Delta\Omega}\int_{\partial Sw}\nabla\hat{V}\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}. \tag{17}$$

2.1.2. Laminar flow with constant coefficients

The transport equations in a fluid phase with linear diffusive terms are

$$\frac{\partial U_i}{\partial x_i} = 0, \tag{18}$$

$$\frac{\partial U_i}{\partial t} + U_j\frac{\partial U_i}{\partial x_j} = -\frac{1}{\varrho_f}\frac{\partial p}{\partial x_j} + \nu\frac{\partial}{\partial x_j}\left(\frac{\partial U_i}{\partial x_j}\right) + S_u, \tag{19}$$

$$\frac{\partial\Phi_f}{\partial t} + U_j\frac{\partial\Phi_f}{\partial x_j} = D_f\frac{\partial}{\partial x_j}\left(\frac{\partial\Phi_f}{\partial x_j}\right) + S_{\Phi_f}. \tag{20}$$

Here Φ represents any scalar field (for example, concentration C) that might be transported into either of the porous medium phases and last terms on the right-hand side of Eqs. (19) and (20) are source terms. In the solid-phase diffusion equation is

$$\frac{\partial\Phi_s}{\partial t} = D_s\frac{\partial}{\partial x_j}\left(\frac{\partial\Phi_s}{\partial x_j}\right) + S_{\Phi_s}. \tag{21}$$

The averaged convective operator term in divergence form becomes, after phase averaging

$$\left\langle\frac{\partial}{\partial x_j}(U_jU_i)\right\rangle_f = \langle\nabla(U_jU_i)\rangle_f = \nabla\langle U_jU_i\rangle_f + \frac{1}{\Delta\Omega}\int_{\partial S_w}U_jU_i\cdot\vec{ds} = \nabla\left[\langle m\rangle\tilde{U}_j\tilde{U}_i + \langle m\rangle\{\hat{u}_j\hat{u}_i\}_f\right] + \frac{1}{\Delta\Omega}\int_{\partial S_w}U_jU_i\cdot\vec{ds}. \tag{22}$$

Decomposition of the first term on the right-hand side of Eq. (22) yields fluctuation types of terms that need to be treated in some way.

The non-divergent version of the averaged convective term in the momentum equation is

$$\left\langle \frac{\partial}{\partial x_j}(U_jU_i) \right\rangle_f = \langle m\rangle \tilde{U}_j \nabla \tilde{U}_i + \tilde{U}_i \nabla \langle U_j \rangle_f + \nabla \langle \hat{u}_j \hat{u}_i \rangle_f + \frac{1}{\Delta\Omega} \int_{\partial S_w} U_jU_i \cdot \vec{ds}$$

$$= \langle m\rangle \tilde{U}_j \frac{\partial}{\partial x_j} \tilde{U}_i - \tilde{U}_i \frac{1}{\Delta\Omega} \int_{\partial S_w} U_j \cdot \vec{ds} + \nabla \langle \hat{u}_j \hat{u}_i \rangle_f + \frac{1}{\Delta\Omega} \int_{\partial S_w} U_jU_i \cdot \vec{ds}. \tag{23}$$

The divergent and non-divergent forms of the averaged convective term in the diffusion equation are

$$\langle \nabla (CU_i) \rangle_f = \nabla \langle CU_i \rangle_f + \frac{1}{\Delta\Omega} \int_{\partial S_w} CU_i \cdot \vec{ds}$$

$$= \nabla \left[\langle m\rangle \tilde{C} \tilde{U}_i + \langle m\rangle \{\hat{c}\hat{u}_i\}_f \right] + \frac{1}{\Delta\Omega} \int_{\partial S_w} CU_i \cdot \vec{ds}$$

$$= \langle m\rangle \tilde{U}_i \frac{\partial}{\partial x_i} \tilde{C} - \tilde{C} \frac{1}{\Delta\Omega} \int_{\partial S_w} U_i \cdot \vec{ds} + \nabla \langle \hat{c}\hat{u}_i \rangle_f + \frac{1}{\Delta\Omega} \int_{\partial S_w} CU_i \cdot \vec{ds}. \tag{24}$$

Other averaged versions of this term can be obtained using impermeable interface conditions [9,24]. For the constant diffusion coefficient, D, the averaged diffusion term becomes

$$\langle \nabla \cdot (D \nabla C) \rangle_f = D \nabla \cdot (\langle m\rangle \nabla \tilde{C}) + D \nabla \cdot \left[\frac{1}{\Delta\Omega} \int_{\partial S_w} \hat{c} \vec{ds} \right] + \frac{D}{\Delta\Omega} \int_{\partial S_w} \nabla C \cdot \vec{ds}, \tag{25}$$

or

$$\langle \nabla \cdot (D \nabla C) \rangle_f = D \nabla \cdot \nabla (\langle m\rangle \tilde{C}) + D \nabla \cdot \left[\frac{1}{\Delta\Omega} \int_{\partial S_w} C \vec{ds} \right] + \frac{D}{\Delta\Omega} \int_{\partial S_w} \nabla C \cdot \vec{ds}, \tag{26}$$

or

$$\langle \nabla \cdot (D \nabla C) \rangle_f = D \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{c} \vec{ds} \right] + \frac{D}{\Delta \Omega} \int_{\partial S_w} \nabla \hat{c} \cdot \vec{ds}. \tag{27}$$

Other forms of Eq. (25), using the averaging operator for constant diffusion coefficient, constant porosity and absence of interface surface permeability and transmissivity, can be found in works by Whitaker [9], Plumb and Whitaker [24], as well as by Levec and Carbonell [26].

A similar derivation can be carried out for the momentum equation to treat cases where Stokes flow is invalid. Two versions of the momentum equation will result. The equation without fluctuation terms is

$$\begin{aligned} \varrho_f \Bigg(& \langle m \rangle \frac{\partial \tilde{V}}{\partial t} + \langle m \rangle \tilde{V} \cdot \nabla \tilde{V} - \tilde{V} \frac{1}{\Delta \Omega} \int_{\partial S_w} V \cdot \vec{ds} + \nabla \langle \hat{v} \hat{v} \rangle_f + \frac{1}{\Delta \Omega} \int_{\partial S_w} VV \cdot \vec{ds} \Bigg) \\ & = -\nabla (\langle m \rangle \tilde{p}) - \frac{1}{\Delta \Omega} \int_{\partial S_w} p \vec{ds} + \mu \nabla \cdot \nabla (\langle m \rangle \tilde{V}) \\ & \quad + \mu \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} V \cdot \vec{ds} \right] + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} \nabla V \cdot \vec{ds} + \langle m \rangle \varrho_f \vec{g}. \end{aligned} \tag{28}$$

With the fluctuation diffusion terms it becomes

$$\begin{aligned} \varrho_f \Bigg(& \langle m \rangle \frac{\partial \tilde{V}}{\partial t} + \langle m \rangle \tilde{V} \cdot \nabla \tilde{V} - \tilde{V} \frac{1}{\Delta \Omega} \int_{\partial S_w} V \cdot \vec{ds} \\ & + \nabla \langle \hat{v} \hat{v} \rangle_f + \frac{1}{\Delta \Omega} \int_{\partial S_w} VV \cdot \vec{ds} \Bigg) \\ & = -\langle m \rangle \nabla \tilde{p} - \frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{p} \vec{ds} + \mu \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{v} \cdot \vec{ds} \right] \\ & \quad + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} \nabla \hat{v} \cdot \vec{ds} + \langle m \rangle \varrho_f \vec{g}. \end{aligned} \tag{29}$$

The steady-state momentum transport equations for systems with impermeable interfaces can be readily derived from Eqs. (28), (29). They are

$$\begin{aligned} \varrho_f \Big(\langle m \rangle \tilde{V} \cdot \nabla \tilde{V} + \nabla \langle \hat{v} \hat{v} \rangle_f \Big) = & -\nabla (\langle m \rangle \tilde{p}) - \frac{1}{\Delta \Omega} \int_{\partial S_w} p \vec{ds} \\ & + \mu \nabla \cdot \nabla (\langle m \rangle \tilde{V}) + \frac{\mu}{\Delta \Omega} \int_{\partial S_w} \nabla V \cdot \vec{ds} + \langle m \rangle \varrho_f \vec{g}, \end{aligned} \tag{30}$$

or

$$\varrho_f\left(\langle m\rangle\tilde{V}\cdot\nabla\tilde{V}+\nabla\langle\hat{v}\hat{v}\rangle_f\right)=-\langle m\rangle\nabla\tilde{p}-\frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds}+\mu\nabla\cdot(\tilde{V}\nabla\langle m\rangle)+\frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla\hat{v}\cdot\vec{ds}+\langle m\rangle\varrho_f\vec{g}. \tag{31}$$

2.2. Non-linear fluid medium equations in laminar flow

To properly account for Newtonian fluid flow phenomena within a porous media in a general way, modeling should begin with the Navier–Stokes equations for variable fluid properties

$$\varrho_f\left(\frac{\partial V}{\partial t}+V\cdot\nabla V\right)=-\nabla p+\nabla\cdot\left[\mu(\nabla V+(\nabla V)^*)\right]+\varrho_f\vec{g},\qquad \mu=\mu(V,C_i,T), \tag{32}$$

rather than the constant viscosity Navier–Stokes equations. The negative stress tensor σ_{ij} in this equation is

$$N_{ij}=-\sigma_{ij}=2\mu(\nabla V)^s=2\mu S, \tag{33}$$

where the symmetrical tensor, S, is the deformation tensor

$$S=(\nabla V)^s=\tfrac{1}{2}(\nabla V+(\nabla V)^*), \tag{34}$$

and $(\nabla V)^*$ is the transposed diade ∇V. The following form of the momentum equation will be used in further developments:

$$\varrho_f\left(\frac{\partial V}{\partial t}+V\cdot\nabla V\right)=-\nabla p+\nabla\cdot(2\mu S)+\varrho_f\vec{g},\qquad \mu=\mu(V,C_i,T). \tag{35}$$

The homogeneous phase diffusion equations are

$$\frac{\partial\Phi_f}{\partial t}+U_j\frac{\partial\Phi_f}{\partial x_j}=\frac{\partial}{\partial x_j}\left(\lambda_f\left(\vec{x},\Phi_f,V\right)\frac{\partial\Phi_f}{\partial x_j}\right)+S_{\Phi_f}. \tag{36}$$

and

$$\frac{\partial \Phi_s}{\partial t} = \frac{\partial}{\partial x_j}\left(\lambda_s \frac{\partial \Phi_s}{\partial x_j}\right) + S_{\Phi_s}. \tag{37}$$

Here Φ_f and λ are the scalar fields and non-linear diffusion coefficients for these fields. The averaging procedures for transport equation convective terms were established above. The averaged non-linear diffusion term yields

$$\langle \nabla \cdot (D\nabla C)\rangle_f = \nabla \cdot (\langle m\rangle \tilde{D}\nabla \tilde{C}) + \nabla \cdot \left[\tilde{D}\frac{1}{\Delta\Omega}\int_{\partial S_w} \hat{c}\vec{ds}\right] + \nabla \cdot \left(\langle \hat{D}\nabla \hat{c}\rangle_f\right) + \frac{1}{\Delta\Omega}\int_{\partial S_w} D\nabla C \cdot \vec{ds}. \tag{38}$$

The other version of the diffusive terms with the full value of concentration on the interface surface is

$$\langle \nabla (D\nabla C)\rangle_f = \nabla \cdot (\tilde{D}\nabla(\langle m\rangle \tilde{C})) + \nabla \cdot \left[\tilde{D}\frac{1}{\Delta\Omega}\int_{\partial S_w} C\vec{ds}\right] + \nabla \cdot \left(\langle \hat{D}\nabla \hat{c}\rangle_f\right) + \frac{1}{\Delta\Omega}\int_{\partial S_w} D\nabla C \cdot \vec{ds}, \tag{39}$$

or the third form of the non-linear diffusion term gets much more complicated appearance

$$\langle \nabla \cdot (D\nabla C)\rangle_f = \nabla \cdot \left[\tilde{D}\frac{1}{\Delta\Omega}\int_{\partial S_w} \hat{c}\vec{ds}\right] + \nabla \cdot \left(\langle \hat{D}\nabla \hat{c}\rangle_f\right) + \tilde{D}\frac{1}{\Delta\Omega}\int_{\partial S_w} \nabla \hat{c} \cdot \vec{ds} + \nabla \tilde{C}\frac{1}{\Delta\Omega}\int_{\partial S_w} \hat{D}\vec{ds} + \frac{1}{\Delta\Omega}\int_{\partial S_w} \hat{D}\nabla \hat{c} \cdot \vec{ds}. \tag{40}$$

One will derive general forms of the non-linear transport equations in two major classes, namely for impermeable and permeable interface surfaces. The averaged momentum diffusion term is

$$\left\langle \frac{\partial}{\partial x_j}(2\mu S)\right\rangle_f = \langle \nabla \cdot (2\mu S)\rangle_f = \nabla \cdot (\langle 2\mu S\rangle_f) + \frac{1}{\Delta\Omega}\int_{\partial S_w} 2\mu S \cdot \vec{ds} = \nabla \cdot 2\left[\langle m\rangle \tilde{\mu}\tilde{S} + \langle m\rangle\{\hat{u}\hat{S}\}_f\right] + \frac{2}{\Delta\Omega}\int_{\partial S_w} \mu S \cdot \vec{ds}. \tag{41}$$

The general non-linear averaged momentum equation for a porous medium is

$$\varrho_f\Bigg(\langle m\rangle\frac{\partial\tilde{V}}{\partial t} + \langle m\rangle\tilde{V}\cdot\nabla\tilde{V} - \tilde{V}\frac{1}{\Delta\Omega}\int_{\partial S_w} V\cdot\vec{ds} + \nabla\langle\hat{v}\hat{v}\rangle_f + \frac{1}{\Delta\Omega}\int_{\partial S_w} VV\cdot\vec{ds}\Bigg)$$
$$= -\nabla(\langle m\rangle\tilde{p}) - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} + \nabla\cdot 2\Big[\langle m\rangle\tilde{\mu}\tilde{S} + \langle m\rangle\big\{\hat{\mu}\hat{S}\big\}_f\Big] + \frac{2}{\Delta\Omega}\int_{\partial S_w}\mu S\cdot\vec{d}\,s + \langle m\rangle\varrho_f\vec{g}. \tag{42}$$

The steady-state momentum transport equation for systems with impermeable interface follows from Eq. (42),

$$\varrho_f\Big(\langle m\rangle\tilde{V}\cdot\nabla\tilde{V} + \nabla\langle\hat{v}\hat{v}\rangle_f\Big) = -\nabla(\langle m\rangle\tilde{p}) - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} + \nabla\cdot 2\Big[\langle m\rangle\tilde{\mu}\tilde{S} + \langle m\rangle\big\{\hat{\mu}\hat{S}\big\}_f\Big] + \frac{2}{\Delta\Omega}\int_{\partial S_w}\mu S\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}. \tag{43}$$

The averaged non-linear mass transport equation in porous medium is as follows

$$\langle m\rangle\frac{\partial\tilde{C}_f}{\partial t} + \langle m\rangle\tilde{U}_i\nabla\tilde{C}_f - \frac{\tilde{C}_f}{\Delta\Omega}\int_{\partial S_w} U_i\cdot\vec{ds} + \nabla\langle\hat{c}_f\hat{u}_i\rangle_f + \frac{1}{\Delta\Omega}\int_{\partial S_w} C_f U_i\cdot\vec{ds}$$
$$= \nabla\cdot(\tilde{D}\nabla(\langle m\rangle\tilde{C})) + \nabla\cdot\left[\tilde{D}\frac{1}{\Delta\Omega}\int_{\partial S_w} C\vec{ds}\right] + \nabla\cdot\Big(\langle\hat{D}\nabla\hat{c}\rangle_f\Big) + \frac{1}{\Delta\Omega}\int_{\partial S_w} D\nabla C\cdot\vec{ds} + \langle m\rangle S_{c_f}. \tag{44}$$

In the last section of the present survey will be given some more simple mass-transport equations, which could be readily used while presenting fundamental relationships in heterogeneous medium transport description.

2.3. Porous medium turbulent VAT equations

After averaging over the REV the basic initial set of turbulent transport equations (see, for example [27])

$$\frac{\partial \overline{U}_i}{\partial t} + \overline{U}_j \frac{\partial \overline{U}_i}{\partial x_j} = -\frac{1}{\varrho_f}\frac{\partial \overline{p}}{\partial x_i} + \frac{\partial}{\partial x_j}\left(\nu \frac{\partial \overline{U}_i}{\partial x_j} - \overline{u'}_i \overline{u'}_j\right) + S_{U_i}, \tag{45}$$

$$\frac{\partial \overline{\Phi}_f}{\partial t} + \overline{U}_j \frac{\partial \overline{\Phi}_f}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D_f \frac{\partial \overline{\Phi}_f}{\partial x_j} - \overline{u'}_i \overline{\varphi'}_f\right) + S_{\Phi_f}, \tag{46}$$

$$\frac{\partial \overline{U}_i}{\partial x_i} = 0, \tag{47}$$

and using the averaging formalism developed in the works by Primak et al. [22], Shcherban et al. [23], Primak and Travkin [28], one obtains the following equations for mass conservation

$$\frac{\partial}{\partial x_i}\langle \overline{U}_i \rangle_f + \frac{1}{\Delta\Omega}\int_{\partial S_w} \overline{U}_i \cdot \vec{ds} = 0, \tag{48}$$

for turbulent filtration (with molecular viscosity terms neglected for the simplicity)

$$\begin{aligned}\langle m \rangle \frac{\partial \tilde{\overline{U}}_i}{\partial t} + \frac{\partial}{\partial x_j}\left(\langle m \rangle \tilde{\overline{U}}_j \tilde{\overline{U}}_i\right) = &-\frac{1}{\varrho_f}\frac{\partial}{\partial x_i}(\langle m \rangle \tilde{\bar{p}}) + \frac{\partial}{\partial x_j}\langle -\overline{u'_j u'_i}\rangle_f + \frac{\partial}{\partial x_j}\langle -\hat{\bar{u}}_j \hat{\bar{u}}_i \rangle_f \\ &- \frac{1}{\varrho_f \Delta\Omega}\int_{\partial S_w} \bar{p} \cdot \vec{ds} - \frac{1}{\Delta\Omega}\int_{\partial S_w} \overline{U}_j \overline{U}_i \cdot \vec{ds} \\ &- \frac{1}{\Delta\Omega}\int_{\partial S_w} -\overline{u'_j u'_i} \cdot \vec{ds} \\ &+ \langle m \rangle \tilde{S}_{v_i}, \quad i,j = 1-3,\end{aligned} \tag{49}$$

and for scalar diffusion (with molecular diffusivity terms neglected)

$$\begin{aligned}\langle m \rangle \frac{\partial \tilde{\overline{\Phi}}_f}{\partial t} + \frac{\partial}{\partial x_i}\left(\langle m \rangle \tilde{\overline{U}}_i \tilde{\overline{\Phi}}_f\right) = &\frac{\partial}{\partial x_i}\langle -\overline{u'_i \varphi'_f}\rangle_f + \frac{\partial}{\partial x_i}\langle -\hat{\bar{u}}_i \hat{\bar{\varphi}}_f \rangle_f \\ &- \frac{1}{\Delta\Omega}\int_{\partial S_w} \overline{U}_i \overline{\Phi}_f \cdot \vec{ds} - \frac{1}{\Delta\Omega}\int_{\partial S_w} \overline{u'_i \varphi'_f} \cdot \vec{ds} + \langle m \rangle \tilde{S}_{\Phi_f}, \quad i = 1-3.\end{aligned} \tag{50}$$

Many details and possible variants of the above written equations with tensorial terms can be found in Primak et al. [22], Shcherban et al. [23], Travkin and Catton [16,17]. The volume-averaging procedures were applied in the work by Masuoka and Takatsu [29] to derive the VAT turbulent-transport equations. Like in numerous other studies pertaining to multiphase transport modeling, the major difficulty in averaging right-hand-side terms has been overcome using assumed artificial-closure models for stress-component terms. As a result, the averaged turbulent-

momentum equations, for example, have conventional additional resistance terms like the momentum-averaged equation developed by Vafai and Tien [30] for laminar regime transport in porous medium.

One-dimensional mathematical statements will be used in what follows for simplicity. Admission of specific types of medium irregularity or randomness requires that complicated additional expressions be included in the generalized governing equations. Treatment of these additional terms becomes a crucial step once the governing averaged equations are written. An attempt to implement some basic departures from a porous medium with strictly regular morphology descriptions into a method for evaluation of some of the less tractable, additional terms is explained below.

The one-dimensional momentum equation with terms representing a detailed description of the medium morphology is depicted as follows

$$\begin{aligned}
&\frac{\partial}{\partial x}\left(\langle m\rangle\left(\tilde{K}_m+\upsilon\right)\frac{\partial\tilde{\bar{U}}}{\partial x}\right)+\frac{\partial}{\partial x}\left(\langle\hat{K}_m\frac{\partial\hat{\bar{u}}}{\partial x}\rangle_f\right)+\frac{\partial}{\partial x}\left(\langle-\hat{\bar{u}}\hat{\bar{u}}\rangle_f\right)\\
&\quad=\langle m\rangle\tilde{\bar{U}}\frac{\partial\tilde{\bar{U}}}{\partial x_j}-\frac{1}{\Delta\Omega}\int_{\partial S_w}(K_m+\upsilon)\frac{\partial\bar{U}}{\partial x_i}\cdot\vec{ds}+\frac{1}{\varrho_f\Delta\Omega}\int_{\partial S_w}\bar{p}\vec{ds}\\
&\qquad+\frac{1}{\varrho_f}\frac{\partial}{\partial x}(\langle m\rangle\tilde{\bar{p}})\\
&\quad=\langle m\rangle\tilde{\bar{U}}\frac{\partial\tilde{\bar{U}}}{\partial x_j}+u^2_{*rk}S_w(x)+\frac{1}{\varrho_f\Delta\Omega}\int_{\partial S_w}\bar{p}\vec{ds}+\frac{1}{\varrho_f}\frac{\partial}{\partial x}(\langle m\rangle\tilde{\bar{p}}),
\end{aligned}\tag{51}$$

where K_m is the turbulent eddy viscosity, u^2_{*rk} is the square friction velocity at the upper boundary of surface roughness layer, h_r, averaged over interface surface ∂S_w.

General statements for energy transport in a porous medium require two-temperature treatments. Travkin et al. [31] showed that the proper form for the turbulent heat transfer equation in the fluid phase using K-theory one-equation closure with primarily one-dimensional convective heat transfer is

$$\begin{aligned}
c_{pf}\varrho_f\langle m\rangle\tilde{\bar{U}}\frac{\partial\tilde{\bar{T}}_f}{\partial x}&=\frac{\partial}{\partial x}\left[\langle m\rangle\left(\tilde{K}_T+k_f\right)\frac{\partial\tilde{\bar{T}}f}{\partial x}\right]\\
&\quad+\frac{\partial}{\partial x}\left(\langle\hat{K}_T\frac{\partial\hat{\bar{T}}_f}{\partial x}\rangle_f\right)+c_{pf}\varrho_f\frac{\partial}{\partial x}\left[\langle m\rangle\left\{-\hat{\bar{T}}_f\hat{\bar{u}}\right\}_f\right]\\
&\quad+\frac{\partial}{\partial x}\left[\frac{\left(\tilde{K}_T+k_f\right)}{\Delta\Omega}\int_{\partial S_w}\hat{\bar{T}}_f\vec{ds}\right]+\frac{1}{\Delta\Omega}\int_{\partial S_w}(K_T+k_f)\frac{\partial\bar{T}_f}{\partial x_i}\cdot\vec{ds},
\end{aligned}\tag{52}$$

while in the neighboring solid phase, the corresponding equation is

$$\frac{\partial}{\partial x}\left[(1-\langle m\rangle)\{K_{sT}\}_s\frac{\partial\{T_s\}_s}{\partial x}\right]+\frac{\partial}{\partial x}\left(\langle\hat{K}_{sT}\frac{\partial\hat{T}_s}{\partial x}\rangle_s\right)$$
$$+\frac{\partial}{\partial x}\left[\frac{\{K_{sT}\}_s}{\Delta\Omega}\int_{\partial S_w}\hat{T}_s\vec{ds}_1\right]+\frac{1}{\Delta\Omega}\int_{\partial S_w}K_{sT}\frac{\partial T_s}{\partial x_i}\cdot\vec{ds}_1. \tag{53}$$

The generalized longitudinal one-dimensional mass-transport equation in the fluid phase, including description of potential morpho-fluctuation influences, for a medium morphology with only one-dimensional fluctuations is written

$$\frac{\partial}{\partial x}\left[\langle m\rangle\left(\tilde{K}_c+D_f\right)\frac{\partial\bar{\bar{C}}_f}{\partial x}\right]+\frac{\partial}{\partial z}\left(\langle\hat{K}_c\frac{\partial\hat{\bar{C}}_f}{\partial x}\rangle_f\right)$$
$$+\frac{\partial}{\partial x}\left[\langle m\rangle\left\{-\hat{\bar{c}}_f\hat{\bar{u}}\right\}_f\right]+\frac{\partial}{\partial x}\left[\frac{\left(\tilde{K}_c+D_f\right)}{\Delta\Omega}\int_{\partial S_w}\hat{\bar{c}}_f\vec{ds}\right]$$
$$+\frac{1}{\Delta\Omega}\int_{\partial S_w}(K_c+D_f)\frac{\partial\overline{C}_f}{\partial x_i}\cdot\vec{ds}+\langle m\rangle\tilde{S}_c=\langle m\rangle\tilde{\bar{U}}\frac{\partial\bar{\bar{C}}_f}{\partial x}, \tag{54}$$

while the corresponding non-linear equation for the solid phase is

$$\frac{\partial}{\partial x}\left[(1-\langle m\rangle)\{D_s\}_s\frac{\partial\{C_s\}_s}{\partial x}\right]+\frac{\partial}{\partial x}\left(\langle\hat{D}_s\frac{\partial\hat{c}_s}{\partial x}\rangle_s\right)$$
$$+\frac{\partial}{\partial x}\left[\frac{\{D_s\}_s}{\Delta\Omega}\int_{\partial S_w}\hat{C}_s\vec{ds}_1\right]+\frac{1}{\Delta\Omega}\int_{\partial S_w}D_s\frac{\partial C_s}{\partial x_i}\cdot\vec{ds}_1. \tag{55}$$

3. Closure theories and approaches for transport in porous media

Closure theories for transport equations in heterogeneous media have been the primary measure of advancement and for measuring success in research on transport in porous media. It is believed that the only way to achieve substantial gains is to maintain the connection between porous medium morphology and the rigorous formulation of mathematical equations for transport. There are only two well-known types of porous media morphologies for which researchers have had major successes. But even for these morphologies, namely straight parallel pores and equal-size spherical inclusions, not enough evidence is available to state that the closure problems for them 'are closed'.

In one of the few existing VAT direct closure application studies, Hsu and

Cheng [2,32] used the averaged one-temperature equation (Eq. 40a in [32]) without the next morpho-diffusive term

$$\nabla\cdot\left[(k_f - k_s)\tilde{T}(-\nabla\langle m\rangle)\right] = \nabla\cdot\left[(k_s - k_f)\tilde{T}(\nabla\langle m\rangle)\right].$$

In our previous efforts we have obtained some results for both morphologies and demonstrated the strength of morphological closure procedures. A model of turbulent flow and two-temperature heat transfer in a highly-porous medium was evaluated numerically for a layer of regularly-packed particles [4,5,17,33] with heat exchange from the side surfaces. Non-linear two-temperature heat- and momentum-turbulent transport equations were developed on the basis of VAT, requiring the evaluation of transport-coefficient models. This approach required that the coefficients in the equations, as well as the form of the equations themselves, be consistent to accurately model the processes and morphology of the porous medium. The integral terms in the equations were dropped or transformed in a rigorous fashion consistent with physical arguments regarding the porous medium structure-, flow- and heat-transfer regimes [17,20]. The form of the Darcy term as well as the quadratic term was shown to depend directly on the assumed version of the convective and diffusion terms. More importantly, both diffusion (Brinkman) and drag-resistance terms in the final forms of the flow equations were proven to be directly connected. These relations follow naturally from the closure process. The resulting necessity for transport-coefficient models for forced, single-phase fluid convection led to their development for non-uniformly and randomly structured highly-porous media.

A regular morphology structure was used to determine the characteristic morphology functions (porosity, $\langle m\rangle$; specific surface, S_w) that were used in the equations in the form of analytically calculable functions. A first approximation for the coefficients, e.g. drag resistance or heat transfer, was obtained from experimentally-determined coefficient correlations. Existing models for variable morphology functions, such as porosity and specific surface, were used by Travkin and Catton [17] and Gratton et al. [5] to obtain comparisons with other work in a relatively high Reynolds number range.

All the coefficient models they used were strictly connected to assumed (or admitted) porous-medium morphology models, meaning that the coefficient values are determined in a manner consistent with the selected geometry. Comparison of modeling results was sometimes difficult because other models utilized mathematical treatments, models that do not allow a complete description of the medium morphology, see Travkin and Catton [4]. Closures were developed for capillary and globular medium-morphology models [4,5,17,33]. It was shown that the approach taken to close the integral resistance terms in the momentum equation for a regular structure allows the second-order terms for the laminar and turbulent regimes to naturally occur. These terms were taken to be analogous to the Darcy or Forchheimer terms for different flow velocities. Numerical evaluations of the models show distinct differences in the overall drag coefficient among the straight capillary and globular models for both the regular and simple cubic morphologies.

Though so far several different closure models for the source terms for uniform, non-uniform, non-isotropic and specifically random non-isotropic highly-porous layers had been extensively developed and tested, unique situations arise when a process is occurring in irregular or random morphologies. Some further points of interest are outlined below.

The reasoning often applied to the morpho-convective term-closure problem in averaged scalar and momentum-transport equations is that it may be negligible. The basis for this reasoning is (see [12])

$$\hat{c} \approx |\nabla C| d_{ch} \quad \text{and} \quad \hat{j} = D|\nabla C|, \quad \text{so} \quad \nabla \langle \hat{c}\hat{j} \rangle_f \approx D \langle |\nabla C|^2 \rangle_f \frac{d_{ch}}{l},$$

where l is the characteristic length associated with averaging volume (see, for example [34] and others) and d_{ch} is the mean diameter of pores in a REV. It is not obvious that the length scale, d_{ch}, taken for the approximation of $\hat{c}$ follows from the use of l as a scale for the second derivative. Furthermore, assuming that the variable to be averaged over the REV changes very slowly over the REV does not mean that it changes very slowly in the neighborhood of the primary REV.

Different heterogeneous media transport equations closure attempts resulted in various final equations. One needs to know what those equations are all about. Treatment of the one-dimensional heat-conduction equation with a stochastic function for the thermal diffusivity in a article by Fox and Barakat [35] yielded a spatially fourth-order partial differential equation to be solved. Gelhar et al. [36], after having eliminated the second-order terms in the species-conservation equation for a stochastic media, were able to develop an interesting procedure for deriving a mean concentration transport equation. The equation form includes an infinite series of derivatives on the right-hand side of the equation. Analysis of this equation allows the derivation of the final form of the mass-transport equation

$$\frac{\partial \tilde{C}^*}{\partial t} + U \frac{\partial \tilde{C}^*}{\partial x} = (A + a_L) U \frac{\partial^2 \tilde{C}^*}{\partial x^2} - B \frac{\partial^3 \tilde{C}^*}{\partial t \partial x^2} - BU \frac{\partial^3 \tilde{C}^*}{\partial x^3},$$

where the most important term is the second term on the right-hand side. In the derivation of this equation, the stochastic character of the existing assigned fields of velocity, concentration and dispersion coefficients were assumed.

A simple form of the advective diffusion equation with constant diffusion coefficients was developed without sorption effects by Tang et al. [37]

$$\frac{\partial \langle m \rangle C}{\partial t} + \langle m \rangle V_i \cdot \nabla C = D \nabla \cdot (\langle m \rangle \nabla C).$$

They transformed the equation with the help of ensemble averaging into a

stochastic transport equation,

$$\frac{\partial\langle m\rangle\tilde{C}^*}{\partial t} + \langle m\rangle\tilde{u}_j^*\nabla\tilde{C}^* = D\nabla\cdot(\langle m\rangle\nabla\tilde{C}^*) + \langle m\rangle\varrho_{jk}\frac{\partial^2\tilde{C}^*}{\partial x_j\partial x_k},$$

where the tensor of the ensemble dispersion coefficient is a correlation function denoted by

$$\varrho_{jk} = \frac{1}{2}\frac{\left\{\overline{u'_j\,u'_k}\right\}^*}{\left\{\vec{u}\right\}^*\left\{\vec{u}\right\}^*}\vec{x}\cdot\left\{\vec{u}\right\}^*,$$

with $\{\vec{u}\}^*$ being the ensemble-averaged velocity. The additional term, reflecting the influence of the stochastic or inhomogeneous nature of the spatial velocity and concentration fluctuations in the ensemble-averaged stochastic equation developed by Tang et al. [37], has the dispersivity coefficient fully dependent on the velocity fluctuations. As can be seen by this equation, the effect of concentration fluctuations was eliminated.

Torquato and co-workers (see, for example [38–40]) has been developing means to characterize the various mathematical dependencies of a composite medium microstructure in a statistically homogeneous media. Some of the quantities considered by Torquato are useful in obtaining resolution to certain closure problems for VAT-developed mathematical models of globular morphologies. In particular, the different near-neighbor distance distribution density functions deserve special mention [38,41].

Carbonell and Whitaker [19] combined the methods of volume averaging and the morphology approach to specify the dispersion tensor for the problem of convective diffusion for cases where there is no reaction or adsorption on the solid phase surface,

$$-D\frac{\partial C}{\partial n} = 0, \quad \vec{x}\epsilon\partial S_w,$$

and considered a constant diffusion coefficient and constant porosity, $\langle m\rangle$, which greatly simplifies the closure problems. They expressed the spatial deviation function as

$$\hat{c} = \vec{f}(\vec{r})\cdot\nabla\tilde{C},$$

where $\vec{f}$ is a vector function of position in the fluid phase. Averaged equations of convective diffusion are the same as the convective heat-transfer equation given by Levec and Carbonell [26] with the exclusion of the flux surface integral term. The closure technique used in their article is an analog to a turbulence theory scheme,

helping them to derive the closure equation for the spatial deviation function in the form of a partial differential equation,

$$\hat{V} + (\tilde{V} + \hat{V})\nabla\vec{f} = D\nabla^2\vec{f}, \quad -\vec{n}\cdot\nabla\vec{f} = \vec{n}, \quad \vec{x}\epsilon\partial S_w.$$

One should note that the spatial deviation functions defined for a periodic media are periodic themselves.

Nozad et al. [42], for a transient heat conduction problem with constant coefficients in a two-phase system (stationary), suggested that the same closure scheme be used to represent the fluctuation terms, $\hat{T}_f$ and $\hat{T}_s$, for the one-temperature model by using

$$\hat{T}_f = \vec{f}\nabla\{T\} + \psi, \quad \hat{T}^s = \vec{g}\nabla\langle T\rangle + \xi.$$

Partial differential equations for $\vec{f}$, $\vec{g}$, ψ and ξ are found. They obtained excellent predictions of the effective thermal conductivity for conductivity ratios $k = k_s/k_f \leq 100$.

Carbonell [43] attempted to obtain an averaged convective-diffusion equation for a straight tube morphological model and obtained an equation with three different concentration variables. This demonstrates that the averaging procedures, being taken too literally, can result in incorrect expressions or conclusions.

A common form of the averaged governing equations for closure of multiphase laminar transport in porous media was obtained by Crapiste et al. [21]. They developed a closure approach that led to a complex integro-differential equation for the spatial deviations of a substance in the void or fluid phase volume of the macro REV. This means that solving the boundary value problem for spatial concentration fluctuations, for example, requires that one obtain a solution to second-order partial differential or coupled integro-differential equations in a real geometric volume within the porous medium.

For a heterogeneous porous medium, this means that the coupled integro-differential equation sets for the averaged spatial deviation variables must be solved for at least two scales. For averaged variables the scales are the external scale or L-domain and for the spatial deviations it is the volume of the fluid phase considered at the local (pore) scale. This presents a great challenge and has not yet been resolved by a real mathematical statement.

To close the reaction-diffusion problem, Crapiste et al. [21] made a series of assumptions: (1) the diffusion coefficient D and the first-order reaction rate coefficient k_r are constant; (2) diffusion is linear in the solid part of the porous medium; (3) the spatial concentration fluctuation is linearly dependent on the gradient of the intrinsic averaged concentration and the averaged concentration itself; (4) the intrinsic averaged concentration and solid surface averaged concentration are equal; (5) the following restriction should be satisfied,

$$\frac{k_r d_p}{D} \ll 1;$$

and (6) spatial fluctuations of the intrinsic concentration and the surface concentration fluctuations are equal. The fourth and sixth assumptions are equivalent to an equality of surface and intrinsic concentrations, which means that the adsorption mechanisms are taken to be volumetric phenomena.

4. Applications of the transport equations and closure

4.1. Capillary morphologies with regular and random morphological characteristics

Consistent research and development in porous medium morphology reveals that more and more realistic structures in the pore network image must be treated (see, for example [44]). Inasmuch as each of the significant morphology structure elements can be randomly assigned ([44] and other studies), workers have gradually developed a more sophisticated, randomized, network morphology, with up to 5 levels of randomness: (1) pore surface roughness; (2) pore diameter; (3) pore length; (4) pore pathway between modes (for tortuosity); and (5) pore cross-sectional shape.

In the work by Sahimi [45], diffusion-controlled reaction and transport of species is being modeled as a network of branching pores, with no closed loops. It is called the wood approximation and does not allow the study of real pore networks. Another drawback to this kind of approach is a fixed pore-length resulting because diffusion along the pore from one node to another has been approximated by a finite difference scheme, often based on constant internode spacing. These are very serious restrictions and have been noted elsewhere [12].

Contemporary technology can measure, with certain confidence, many of the pore's media characteristics, the total void fraction, the density of the solid phase, the relative pore size distribution for pores larger than 30 Å in diameter and the equilibrium adsorption characteristics of the porous medium solid phase [46]. There is a problem of how to connect porous medium morphology characteristics, that can and are being measured, to the transport equation being considered and their coefficients.

The method of effective medium approximation (EMA) is used in many previous works and shows excellent results, see Koplik [47]. Essential differences exist in our approach and the commonly-used EMA approach where the actual problem pore network is replaced by a network with artificial uniform morphology [45,47–49] and effective properties, such as the effective diffusivity, D_{eff}, or the effective reactivity, R_{eff}. An important consideration, most often not dealt with, is determining which network morphology properties can be assigned externally, or from an effective properties point of view, which can be justified. Some of the network characteristics should be calculated to match the problem features and not assigned.

Another important point is that much of the previous research results are based on substitution of porous medium properties and functions using artificial network simulation capabilities without satisfying the initial equations. The concern is that

the physical problem, which is simulated with the help of network modeling, must still be modeled on the basis of its initial physical and mathematical statements. The development of models of irregular and random networks of pores in the REV with consequent substitution of closed morpho-convective and morpho-diffusive terms into the transport equations is a part of current research. Numerical modeling and application of theoretical studies to this kind of closure approach is based on realities of medium morphologies.

It has been proven that the generalized momentum- and scalar-transport equations correctly involve additional terms which quantify the influence of the medium irregularity. Theoretical forms of these additional terms, derived from application of the closure methodology, were reviewed for both one- and two-dimensional cases in a porous medium morphology consisting of specified, stationary distributions of a polydisperse (including binary) system of straight, non-intersecting pores (Fig. 1). The differences among the modeling results, and their significance to the closure scheme, were increased by introducing specific kinds of non-regularity to the medium's morphology. In some cases, large deviations in the overall results were obtained by merely allowing small morphology non-regularities [50]. It was shown numerically that slight manipulations of these particular morphology descriptions can create large fluctuations in transport parameter values, signifying the potential for modeling errors if particular features of the morphology are neglected. Important physical behavior was extracted from the morphology model by illustrating how hydrodynamic flow-regime considerations also significantly effect the transport parameter values.

Variants of the one-dimensional creep-transport flow equations for systems with

Fig. 1. System of randomly distributed diameter straight pore morphology.

impermeable interface can be obtained from the next forms of the equations (some details of derivation and similar equations can be found in Whitaker's [9] work)

$$0 = -\nabla\langle p\rangle_f - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} + \mu\nabla\cdot(\nabla\langle m\rangle\tilde{V}) + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}, \tag{56}$$

or

$$\langle m\rangle\nabla\tilde{p} = -\frac{1}{\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} + \mu\nabla(\tilde{V}\nabla\langle m\rangle) + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla\hat{V}\cdot\vec{ds} + \langle m\rangle\varrho_f\vec{g}. \tag{57}$$

Using more common notations, these equations are written

$$\nu\frac{\partial}{\partial x}\left(\frac{\partial\langle m\rangle\tilde{U}}{\partial x}\right) + \frac{\nu}{\Delta\Omega}\int_{\partial S_w}\frac{\partial U}{\partial x_i}\cdot\vec{ds} - \frac{1}{\varrho_f\Delta\Omega}\int_{\partial S_w} p\vec{ds} + \langle m\rangle\vec{g} = \frac{1}{\varrho_f}\frac{\partial}{\partial x}(\langle m\rangle\tilde{p}), \tag{58}$$

or with fluctuation terms

$$\frac{\nu}{\Delta\Omega}\int_{\partial S_w}\frac{\partial\hat{U}}{\partial x_i}\cdot\vec{ds} + \nu\frac{\partial}{\partial x}\left(\tilde{U}\frac{\partial\langle m\rangle}{\partial x}\right) - \frac{1}{\varrho_f\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} + \langle m\rangle\vec{g} = \frac{\langle m\rangle}{\varrho_f}\frac{\partial}{\partial x}(\tilde{p}). \tag{59}$$

These two equations can be simplified for well-defined morphologies, such as, for example, straight pore morphology to a form more useful for comparisons with the published results of different workers. Dropping the gravitation force term for simplicity and expressing the interface stress term through the full velocity variable one can get

$$-\frac{\partial}{\partial x}\{p\}_f = \frac{1}{\langle m\rangle\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} - \frac{\mu}{\langle m\rangle\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds}. \tag{60}$$

Which differentiates from Eq. (3.1) found in the work by Ma and Ruth [6]

$$-\frac{\partial}{\partial x}\{p\}_f = \frac{1}{\langle m\rangle\Delta\Omega}\int_{\partial S_w} p\vec{ds} - \frac{\mu}{\langle m\rangle\Delta\Omega}\int_{\partial S_w}\frac{\partial U}{\partial x_i}\cdot\vec{ds} = -\frac{\tilde{p}}{\langle m\rangle}(\nabla\langle m\rangle) + \frac{1}{\langle m\rangle\Delta\Omega}\int_{\partial S_w}\hat{p}\vec{ds} - \frac{\mu}{\langle m\rangle\Delta\Omega}\int_{\partial S_w}\frac{\partial U}{\partial x_i}\cdot\vec{ds}, \tag{61}$$

by one term — the first term on the right-hand side of the Ma and Ruth [6] equation. The latter equation is the equation developed by Ma and Ruth for morphology of straight, periodically-contracted pores (tubes). This equation is correct only for constant porosity, $\langle m \rangle$, and that condition fortunately is satisfied.

The intrinsic averaging process used in this work for the momentum equation is inappropriate for vector quantity equations (Eq. (2.3) of Ma and Ruth [6]). One of the problems arises from the boundary conditions for vector quantities — velocity in this case. The correctly-averaged momentum equation for periodically-contracted straight-pore morphology has the form of Eq. (60). Despite the almost correct one-dimensional momentum equation form derived by Ma and Ruth [6], closure of the additional integral terms was not achieved. The authors found a way to represent the integral terms as outstanding constant values. Meanwhile, the closure of these terms can be obtained following the procedures described by Travkin and Catton [4], where the skin-friction term is treated as, for example, a laminar boundary layer.

$$\frac{\mu}{\Delta\Omega}\int_{\partial S_{wL}} \frac{\partial U}{\partial x_i}\cdot \vec{ds} = \frac{\varrho_f}{\varrho_f \Delta\Omega}\int_{\partial S_w} \tau_{wL}\cdot \vec{ds} = -\tfrac{1}{2} c_{fL}(\vec{x}) S_{wL}(\vec{x})\left[\varrho_f \tilde{U}^2(\vec{x})\right],$$

$$\tau_{wL} = \mu \frac{\partial U}{\partial x_i},\ u^2_{*rk} = \tfrac{1}{2} c_{fL}\tilde{U}^2(\vec{x}), \tag{62}$$

where τ_{wL} is the wall laminar shear stress, S_{wL} is the laminar part of the specific surface in the REV and c_{fL} is the mean skin friction coefficient in the REV laminar region. The form-drag integral term is approximated by

$$\frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds} = \tfrac{1}{2} c_{dp}(\vec{x}) S_{wp}(\vec{x})\left[\varrho_f \tilde{U}^2(\vec{x})\right]. \tag{63}$$

where c_{dp} is the mean form-resistance coefficient in the REV and S_{wp} is the ratio of the cross-flow projected area of obstacles to the representative elementary volume $\Delta\Omega$. One should note that these are well-established ideas used in different areas of fluid mechanics. Here they are applied to a separate elementary subarea on the interface surface ∂S_w, with consecutive averaging over the ∂S_w. Substituting these expressions into Eq. (60) yields

$$-\frac{\partial}{\partial x}\{p\}_f = \frac{1}{\langle m\rangle \Delta\Omega}\int_{\partial S_w} \hat{p}\vec{ds} - \frac{\mu}{\langle m\rangle \Delta\Omega}\int_{\partial S_w} \nabla V\cdot \vec{ds}$$

$$= \tfrac{1}{2} c_{dp}\frac{S_{wp}}{\langle m\rangle}\left[\varrho_f \tilde{U}^2\right] + \frac{\tilde{p}}{\langle m\rangle}(\nabla\langle m\rangle) + \tfrac{1}{2} c_{fL}\frac{S_{wL}}{\langle m\rangle}\left[\varrho_f \tilde{U}^2\right]. \tag{64}$$

Finally this equation yields a form for the constant bulk pressure loss for a constant porosity media that is quite applicable to many non-demanding problems,

as well as being appropriate for comparison with existing experimental data on drag resistance in porous media:

$$-\frac{\partial}{\partial x}\{p\}_f = (c_{fL}S_{wL} + c_{dp}S_{wp})\frac{\varrho_f \tilde{U}^2}{2\langle m\rangle}. \tag{65}$$

It is clear that the morphology which comprises directly a drag-resistance experimental data has obvious relief for final evaluation. Hsu and Cheng [32] have given an approach for closure of the resistance integral terms in dilute spherical particle suspensions which is based on a solution for a single particle in a cell. The expression for drag coefficient, c_d, they derived is

$$F = c_d\left(d_p^2\right)\frac{\left[\varrho_f \tilde{U}^2\right]}{2},$$

which is very close to what is usually assumed for globular morphologies

$$F = c_d\left(\pi R_p^2\right)\frac{\left[\varrho_f \tilde{U}^2\right]}{2}.$$

The authors managed to determine the constant coefficients in the drag-force relation and obtain an Ergun expression with two integral resistance terms in the averaged momentum Navier–Stokes equation.

The simplicity of Eq. (65) is achieved mainly because of the simplicity of straight-pore morphology. The integral drag-resistance terms in the creep or Stokes flow transport equations can be closed whenever theoretical or experimental values of the drag resistance are available.

There presently are only a few studies of large Reynolds number flows where constant-coefficient Navier–Stokes equations could be applied (see, for example [51,52]). It is unfortunate that when Jaiswall et al. [51] were describing the variances between their results and similar ones obtained by LeClair and Hamielec [52], they did not recognize that the morphologies of the media were different.

4.2. Globular morphologies — regular, irregular and random

Most investigations of globular (and capillary) porous media have a common source of error, the model used is not rich enough to fully represent the morphology of the media under investigation. This is a result of the complexity of the boundary value problem posed by the media and the difficulties associated with precise representation of the geometries within the heterogeneous structure.

As a result, the approximations made for a given media may not lead to improvement but rather to lessening of the modeling quality. It is intuitively clear that an approach which combines rather simple but specific features of a morphology has the best chance of successful modeling when used with an available rigorous method of obtaining a solution. However, the complexity is so high that

even for relatively simple and well-developed theories (heat conduction, linear elasticity), strict methods of solution for multiply-connected structures are not available.

Among the available approximate methods of analysis is one that is based on a priori assumptions about the nature of the physical fields in the phases and routinely ignores the field's fluctuations in all the phases or in some of them. This reduces the multi-particle problem to one for a space with a single inclusion and results in a solution (which, however, is not a solution of the initial problem) in a closed form. As a result of the limitations of the assumptions, accounting for particle pairwise interactions with a first approximation yields results that are applicable only to media where these interactions have little influence on the overall properties. Such media, for example, are porous media with a low-volume fraction of the dispersed phase and a moderate difference between the properties of the components as shown by Fig. 2. For this case, the majority of known methods of solution yield practically the same results. In a strongly heterogeneous highly-filled media, the interaction of phases has a decisive influence on transport phenomena. The physical fields in a such media are essentially non-uniform. In order to study these media, it is necessary to select a morphological model that can account for the real spatial distribution of inhomogeneities and an accurate method to evaluate their interactions.

Derivation of the coefficient of effective diffusivity by Koch et al. [18], was accomplished by the explicit depletion of the following three assumptions:

1. the gradient of the mean concentration is equals to a constant value, $\nabla\langle C\rangle = const$;
2. the morpho-convective correlation is independent of position, $\nabla\langle c'u'\rangle = 0$; and
3. the concentrating fluctuations are steady state, $\dfrac{\partial c'}{\partial t} = 0$.

All three assumptions are important components of every problem under consideration. The latter two are valid for conservative solute dispersion.

The main results obtained by Edwards et al. [53] are interesting, as they are supposed to confirm that the 'configurational properties of the porous medium significantly influence the reactivity source coefficient in the diffusion equation'. This could also be anticipated from volume-averaging theory (VAT). Furthermore, it was theoretically confirmed that the interstitial velocity of the reactive solute depends on the chemical reaction in the medium.

There are a few regular morphologies for which a fair amount of theoretical and experimental results exist, for example, cubical location of spherical particles [54,55] or cubical and hexagonal cylinders in creeping cross-flow [56]. These works accommodate the large amount of experimental and theoretical drag-resistance correlations for pure outlined morphologies. Exact solutions of some drag-resistance-related creeping-flow problems in regular suspensions are given in such works as Happel [57], Happel and Brenner [58], Sangani and Acrivos [54,56], Zick and Homsy [55], and others evidently give the basis for closure equations, Eq. (68),

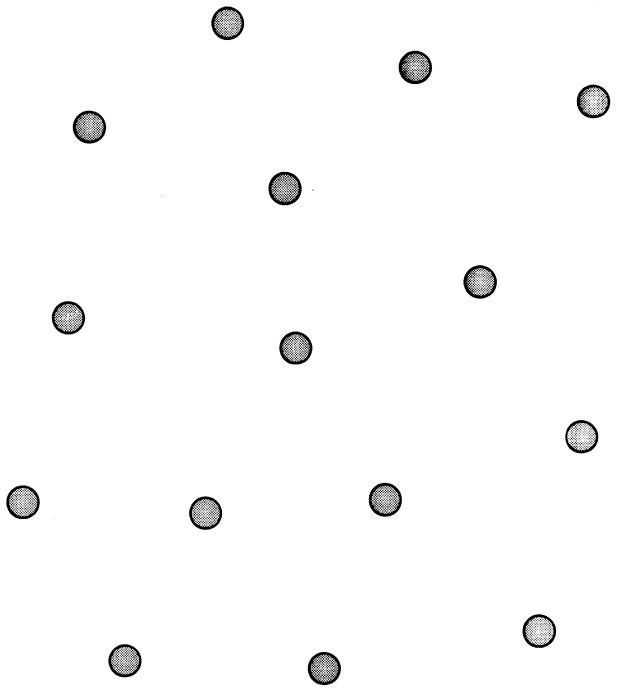

Fig. 2. Highly porous medium consisting of disperse spheres with inter-spherical spacing greater than five sphere diameters.

and even Eq. (59). The latter equation is a subject in the study by Travkin and Kushch [59] dealing with the Stokes flow and heat transport in regular and irregular conglomerates of spherical particles, Fig. 3, where a rigorous solution applied to porous-media problems in VAT statements.

Few equations of heat transfer with constant conductivities in porous media will depict the benefits of the specific morphologies that are now being used to deal with these problems. To develop a one-dimensional steady-state fluid phase equation of convective heat transfer in porous media, one needs to start from the equation in deviation form

$$\langle m\rangle \tilde{U}_i \nabla \tilde{T}_f = \nabla\langle - \hat{T}_f \hat{u}_i\rangle_f + a_f \nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w} \hat{T}_f \vec{ds}\right] + \frac{a_f}{\Delta\Omega}\int_{\partial S_w} \nabla \hat{T}_f \cdot \vec{ds} + \frac{\langle m\rangle}{(\varrho c_p)_f} S_{T_f}, \tag{66}$$

or the full value equation

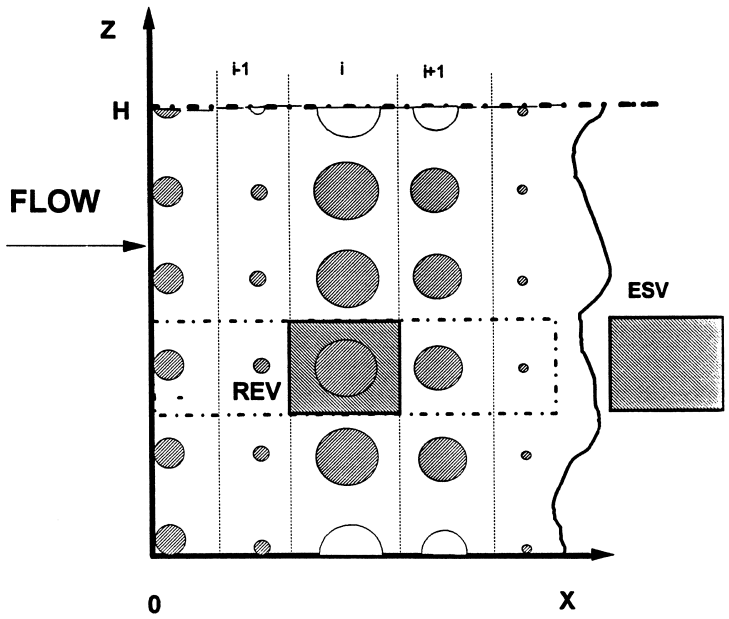

Fig. 3. Randomized series of spherical bead screens — one-dimensional globular morphology.

$$\langle m\rangle \tilde{U}_i \nabla \tilde{T}_f = \nabla\langle -\hat{T}_f \hat{u}_i\rangle_f + a_f \nabla\nabla\left(\langle m\rangle \tilde{T}_f\right) + a_f \nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w} T_f \vec{ds}\right] + \frac{a_f}{\Delta\Omega}\nabla T_f\cdot\vec{ds} + \frac{\langle m\rangle}{(\varrho c_p)_f} S_{T_f}. \quad (67)$$

It is interesting to note that Hsu and Cheng [32] dropped the morpho-convective term

$$\varrho_f \nabla\langle -\hat{u}_i\hat{u}_i\rangle_f$$

in the averaged Navier–Stokes momentum equation and at the same time acquired the analogous term

$$c_{pf\varrho f}\nabla\langle -\hat{T}_f\hat{u}_i\rangle_f$$

in the averaged heat-transfer equation. To close this term, Hsu and Cheng [32] used several assumptions to comply with the closure schemes developed by Zanotti and Carbonell [1] and Carbonell and Whitaker [19]. Numerical results were obtained using experimental measurements of the bulk stagnant conductivity, k_d, and the tensorial quantity of the porous medium bulk thermal dispersivity, k.

When the coefficient of thermal conductivity, k_f, is a constant value, the steady state conduction regime is described by

$$k_f \nabla^2 \left(\langle m \rangle \tilde{T}_f \right) + \nabla \cdot \left[\frac{k_f}{\Delta \Omega} \int_{\partial S_w} T_f \vec{ds} \right] + \frac{k_f}{\Delta \Omega} \int_{\partial S_w} \nabla T_f \cdot \vec{ds} + \langle m \rangle S_{T_f} = 0, \tag{68}$$

or written in fluctuation variables it is

$$k_f \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{T}_f \vec{ds} \right] + \frac{k_f}{\Delta \Omega} \int_{\partial S_w} \nabla \hat{T}_f \cdot \vec{ds} + \langle m \rangle S_{T_f} = 0. \tag{69}$$

The one-dimensional version of the equations, without a source in a motionless matrix in Cartesian coordinates, are

$$\frac{\partial}{\partial x} \left[\langle m \rangle \frac{\partial \tilde{T}_f}{\partial x} \right] + \frac{\partial}{\partial x} \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{T}_f \vec{ds} \right] + \frac{1}{\Delta \Omega} \int_{\partial S_w} \frac{\partial T_f}{\partial x_i} \cdot \vec{ds} = 0, \tag{70}$$

or

$$\frac{\partial}{\partial x} \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{T}_f \vec{ds} \right] + \frac{1}{\Delta \Omega} \int_{\partial S_w} \frac{\partial \hat{T}_f}{\partial x_i} \cdot \vec{ds} = 0, \tag{71}$$

or

$$\frac{\partial^2}{\partial x^2} \left[\langle m \rangle \tilde{T}_f \right] + \frac{\partial}{\partial x} \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} T_f \vec{ds} \right] + \frac{1}{\Delta \Omega} \int_{\partial S_w} \frac{\partial T_f}{\partial x_i} \cdot \vec{ds} = 0. \tag{72}$$

Meanwhile, in the solid phase with constant k_s, the equation yields the same form

$$\frac{\partial}{\partial x} \left[\langle s \rangle \frac{\partial \{T_s\}_s}{\partial x} \right] + \frac{\partial}{\partial x} \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{T}_s \vec{ds}_1 \right] + \frac{1}{\Delta \Omega} \int_{\partial S_w} \frac{\partial T_s}{\partial x_i} \cdot \vec{ds}_1 = 0, \tag{73}$$

or for the fluctuating variable

$$\frac{\partial}{\partial x} \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{T}_s \vec{ds}_1 \right] + \frac{1}{\Delta \Omega} \int_{\partial S_w} \frac{\partial \hat{T}_s}{\partial x_i} \cdot \vec{ds}_1 = 0. \tag{74}$$

Travkin and Catton [4,16,17] suggested that the integral heat-transfer terms in Eqs. (71)–(73) be closed in a natural way by III-type heat-transfer law. The second integral term reflects the changing averaged surface temperature along the x coordinate. Eqs. (72) and (73) can be treated using heat-transfer correlations for the heat-exchange integral term (the last term). Regular dilute arrangements of pores, spherical particles or cylinders have been studied much more than random

morphologies. Using separate element or 'cell' modeling methods [50,58] to finding the interface temperature field allows one to close the second-'surface' diffusion integral terms in Eqs. (72) and (73) along with Eq. (68).

Many forms of the energy equation are used in the analysis of transport phenomena in porous media. The primary difference between such equations and those resulting from a more rigorous development based on VAT are certain additional terms. The best way to evaluate the need for these additional more complex terms is to obtain an exact mathematical solution and compare the results with calculations using the VAT equations. This will clearly display the need for using the more complex VAT mathematical statements.

Consider a two-phase heterogeneous medium consisting of an isotropic continuous (solid or fluid) matrix and an isotropic discontinuous phase (spherical particles or pores). The volume fraction of matrix, or f-phase, is $\langle m \rangle = m_f = \Delta\Omega_f/\Delta\Omega$, the volume fraction of fillet, or s-phase, is $m_s = 1 - m_f = \Delta\Omega_s/\Delta\Omega$, where $\Delta\Omega = \Delta\Omega_f + \Delta\Omega_s$ is the volume of the REV. The constant properties (phase conductivities, k_f and k_s), stationary (time-independent) heat conduction differential equations for T_f and T_s, the local phase temperatures,

$$k_f \nabla^2 T_f = 0, \quad k_s \nabla^2 T_s = 0,$$

with the IVth kind of interfacial $(f - s)$ thermal boundary conditions. No internal heat sources are present inside the composite sample so that the temperature field is determined by the boundary conditions at the external surface of the sample. After correct formulation of these conditions, the problem is completely stated and has a unique solution.

Two ways to realize a solution to this problem were compared by Travkin and Kushch [60]. The first is the conventional way of replacing the actual composite medium by an equivalent homogeneous medium with an effective thermal conductivity coefficient, $k = k_{eff}(\langle s \rangle, k_f, k_s)$, assuming one knows how to obtain or calculate it. The exact effective thermal coefficient was obtained using DNM based on the mathematical theory of globular morphology multiphase fields developed by Kushch (see, for example [61–63]).

The second way is to solve the problem using the VAT two-equation, three-term integro-differential equations, Eqs. (70) and (73) (see also, for example [4,20]). To evaluate and compare solutions to these equations with the DNM results, one needs to know the local solution characteristics, the averaged characteristics over the both phases in each cell and, in this case, the additional morpho-diffusive terms.

An infinite homogeneous isotropic medium containing a three-dimensional array of spherical particles is chosen for analysis. The particles are arranged so that their centers lie at the nodes of a simple cubic lattice with period a. The temperature field in this heterogeneous medium is caused by a constant heat flux, Q_z, prescribed at the sample boundaries, which, due to the absence of heat sources, leads to the equality of averaged internal heat flux, $\langle q \rangle = Q_z$.

The model composite medium consists of the three regions shown in Fig. 4. The

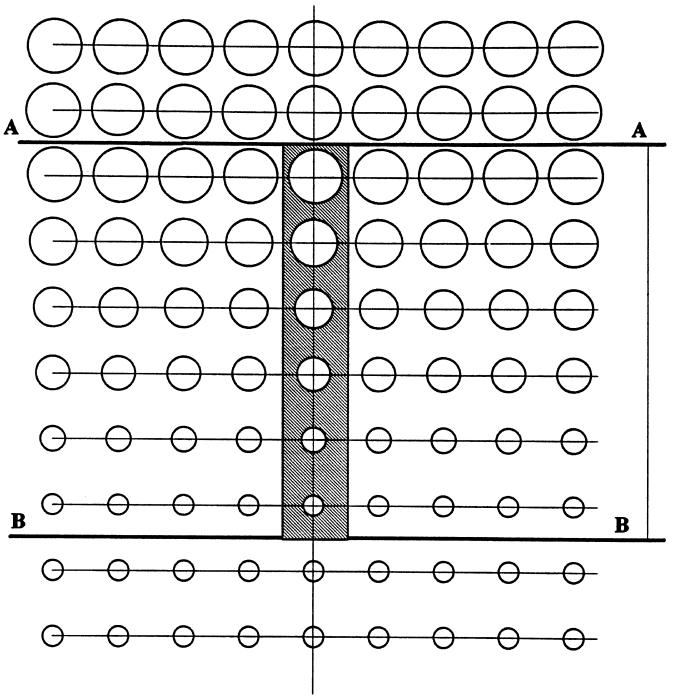

Fig. 4. Model of two-phase medium with variable volume fraction of disperse phase.

half-space lying above the A–A plane has a volume content of the disperse phase $m_s = m_A$ and for half-space below the B–B plane $m_s = m_B$. To define the problem, let $m_A > m_B$. The third part is the composite layer between the plane boundaries A–A and B–B containing N double periodic lattices of spheres (screens) with changing diameters.

The normalized solution of both models (VAT and DNM) for the case of linearly-changing porosity between A–A and B–B and with effective conductivity coefficients of $k_{eff} = 0$, 0.2, 1, 10 and 10 000, respectively, showed practically negligible difference ($< 10^{-3}$) supposedly because of numerical error accumulation [60]. Solutions of the VAT equations, Eqs. (70) and (73), for the composite with varying volume content of disperse phase with accurate DNM closure of the micro model VAT integro-differential terms were obtained implicitly, meaning that each term was calculated independently using the results of DNM calculations.

The coincidence of the results of the exact calculation of the two-equation, three-term energy transport VAT model, Eqs. (70) and (73), with the exact DNM solution and the one-temperature effective coefficient model for heterogeneous media with non-constant spatial morphology clearly demonstrates the need for using all the terms in the VAT equations. The need for the morpho-diffusive terms in the energy equation are further demonstrated by noting that their magnitudes are all of the same order.

4.3. Effective transport coefficient modeling

Determination of effective transport coefficients for a heterogeneous media have received considerable attention by researchers who are studying the transport of heat (or a conservative solute) through a fully-saturated porous media by advection and diffusion. Careful notation procedures are necessary when the turbulent thermal dispersivity is being studied. To evaluate an experiment, it is typical to use a solution obtained analytically or by the moment method. This was done, for example, by Han and Carbonell [64], Gunn and Sabri [65] and Somerton and Catton [66]. Han and Carbonall [64] defined the longitudinal thermal diffusivity coefficient using the equation

$$\frac{\partial \varrho}{\partial x} + u\frac{\partial \varrho}{\partial x} = K_{cx}\frac{\partial^2 \varrho}{\partial x^2},$$

and the lateral thermal dispersivity coefficient uses the equation

$$u\frac{\partial \varrho}{\partial x} = K_{cy}\frac{\partial^2 \varrho}{\partial y^2}.$$

Gunn and Sabri [65] used analytical solutions of the two-dimensional equation with constant coefficients to treat experimental data from packed columns and tubes. The results of their work should to be treated with caution and not too many conclusions drawn about their results because the model and equation are weak.

A deterministic unit-cell model was used Adnani et al. [67] to calculate the effective thermal conductivity (k_m) of a packed bed of spherical particles with stagnant gas for various particle sizes, single and binary, and gas pressures. It was shown by Adnani et al. [67] and others that previously-developed models tend to be unreliable in the regions of high solid/fluid conductivity ratios (k_s/k_f) and low porosities. The unit-cell model developed by Adnani et al. [67] can be used to calculate k_m in these regions. The model can be used in situations where the solid/fluid conductivity ratio is less than 1300. As the solid/fluid conductivity ratio gets larger than 1300, however, the contact resistance and area characteristics become more and more important. A set of correlations was derived for binary mixtures of particles at 15% and 18% porosity. Results from these correlations are shown to be in good agreement with experimental data.

One of the methods of closure of mathematical models of diffusion processes in a heterogeneous media is the quasi-homogeneous method. In this case, the transfer process is modeled as an ideal continuum with homogeneous effective transport characteristics instead of the real heterogeneous characteristics of a porous medium. This method of closure of the diffusive terms in the heat- and mass-diffusion equations results in certain limitations: (a) the two-phase medium components are without fluctuations of the type $\hat{T}$, $\hat{c}$ in each of the phases; and (b) the transfer coefficients being constant in each of the phases [68,69] results in reducing them to

additional algebraic equations. These equations relate to the unknown averaged diffusion flows in each of the phases in the following form

$$\langle \vec{j} \rangle_f + \langle \vec{j} \rangle_s = -K^*_{c(ij)} \langle \nabla \overline{C} \rangle, \tag{75}$$

$$\langle \nabla \overline{C} \rangle = \nabla [\langle m \rangle \{\overline{C}\}_f + (1 - \langle m \rangle)\{\overline{C}\}_s] + \frac{1}{\Delta \Omega} \int_{\partial S_w} (\overline{C}^+ - \overline{C}^-) \vec{ds}, \tag{76}$$

$$\left(K^f_{c(ij)}\right)^{-1} \langle \vec{j} \rangle_f + (K^s_{c(ij)})^{-1} \langle \vec{j} \rangle_s = -\langle \nabla \overline{C} \rangle. \tag{77}$$

Here, unlike the work of Khoroshun [68], Kudinov and Moyzes [70] and Hadley [71], $\overline{C}^+$ and $\overline{C}^-$ are the values of the concentrations (or temperatures) at both sides of the phase transition surface ∂S_w (they do not have to be equal), $K^f_{c(ij)}$ $K^s_{c(ij)}$ are the transfer coefficient tensors in each of the phases and $K^*_{c(ij)}$ is the effective diffusion coefficient. Thus, at least in this case, the problem of closure has been reduced to finding $K^*_{c(ij)}$ and integrals across the interface of the difference of the values of limits of admixture concentrations (or temperature) at both its sides. For temperature fields, the above relationships will be similar (neglecting the heat resistance of the interface boundary)

$$\langle \nabla \overline{T} \rangle_f + \langle \nabla \overline{T} \rangle_s = \langle \nabla \overline{T} \rangle, \quad -K^f_{T,eff} \langle \nabla \overline{T} \rangle_f - K^s_{T,eff} \langle \nabla \overline{T} \rangle_s = -K^*_T \langle \nabla \overline{T} \rangle. \tag{78}$$

Applying the closure relation, for example

$$K^f_{T,eff} \langle \nabla \overline{T} \rangle_f = K^s_{T,eff} \langle \nabla \overline{T} \rangle_s, \tag{79}$$

yields the effective stagnant coefficient

$$K^*_T = \frac{2K^f_{T,eff} K^s_{T,eff}}{\left(K^f_{T,eff} + K^s_{T,eff}\right)}, \tag{80}$$

that represents the lower bound of the effective stagnant conductivity for a two-phase material from the known boundaries of Hashin-Shtrikman (see, for example [70,72]) for equal volume fraction of phases. Other closure equations for calculating the stagnant effective conductivity are found in work by Hadley [71] and by Kudinov and Moyzes [70]. The quasi-homogeneous approach has several defects: (a) the basis for the quasi-homogeneous equations is in question; (b) the local fluctuation values, as well as inhomogeneity and dispersivity of the medium, are neglected; and (c) the interdependence of the correlated coefficients and arbitrary adjustment to fit data significantly reduce the generality of the results.

Finding effective parameters for heterogeneous medium using a perturbation expansion to derive the higher-order exact bounds of a composite's properties has many difficulties. Torquato's approach (see, for example [38,39]) is an application

of the perturbation expansion method to a composite medium using advanced statistical information about medium morphology based on the n-point probability functions. The difficulty in this approach is in the determination of the n-point morphological characteristics that should be considered. Torquato [73] provided a comparison of his predictions with experimental data of Turner [74] for a medium (composite) with periodic and randomly located spherical inclusions. Excellent agreement was obtained for regular morphology. However, for a composite with a random disperse phase spatial distribution, the calculated values were not in good agreement with the experimental data of Turner. The two first terms of the perturbation expansion and three-point probability distribution functions were used in the simulation.

Rather comprehensive analysis of the same problem is presented by Sangani and Yao [75] where the random microstructure of the composite was approximated by a spatially-periodic array with a unit cell containing N (16) arbitrary placed inclusions. In other words, the spatial model consists N periodic lattices of inclusions. Their mutual position is generated in a special way so that the radial distribution function is in a good agreement with the solution of the Percus–Yevick equation. This solution was then used to obtain the Pade approximations and higher-order bounds of the effective conductivity, Milton's numbers as well as the sixth- and eighth-order bounds. It was shown that this approach gives better agreement with the Turner's [74] data than Torquato's formulae because more morphological (essentially stochastic) information was involved in the consideration and the rigorous solution of the boundary-value problem.

Effective coefficients, usually thought to be the universal solution to most heterogeneous media problems, are not easily described by a mathematical model like the VAT. The 'heterogeneous' terms in the momentum equation, Eq. (51), yields, by the overall representation of diffusive and 'diffusion-like' terms

$$K_{m,eff}\frac{\partial\tilde{\bar{U}}}{\partial x} = \left(\langle m\rangle\left(\tilde{K}_m + \nu\right)\frac{\partial\tilde{\bar{U}}}{\partial x} + \langle\hat{K}_m\frac{\partial\hat{\bar{u}}}{\partial x}\rangle_f + \langle -\hat{\bar{u}}\,\hat{\bar{u}}\rangle_f\right). \tag{81}$$

Here the variables of velocity and viscosity coefficient are taken in a form suitable for both laminar and turbulent flow regimes. From this expression the effective coefficient $K_{m,eff}$ is not seen to be a constant value, but rather a complex non-linear function explicitly dependent on other functions and variables. The additional friction and drag-resistance terms in Eq. (51) still need to be closed in some way.

For problems with a constant bulk viscosity coefficient (K_m = constant) the second term in this relation vanishes and the whole problem essentially assumes the role of evaluating the influence on the momentum due to dispersion by irregularities of the porous medium. Diffusion–dispersion effects realized through the second derivative terms and relaxation terms in the fluid-phase mass-transport equation, Eq. (54), can be expressed,

$$K_{c,eff}\frac{\partial\tilde{\bar{C}}_f}{\partial x} = \left(\langle m\rangle\left(\tilde{K}_c + D_f\right)\frac{\partial\tilde{\bar{C}}_f}{\partial x} + \langle\hat{K}_c\frac{\partial\hat{\bar{C}}_f}{\partial x}\rangle_f + \right.$$

$$\left. + \langle m\rangle\left\{-\hat{\tilde{c}}_f\hat{\tilde{u}}\right\}_f + \frac{\left(\tilde{K}_c + D_f\right)}{\Delta\Omega}\int_{\partial S_w}\hat{\tilde{c}}_f\vec{ds}\right), \tag{82}$$

where the first and last terms resemble the effective thermal conductivity coefficient for each phase, using constant coefficients, see Nozad et al. [42]. Interpretation of this equation as the equation for effective coefficient calculation means simply adding one more equation to whatever problem was stated at the beginning.

Considering the effective coefficient problem as the cornerstone issue in the heterogeneous media transport, one needs to accommodate the reasoning that the absolute majority of problem stated and studies include the following assumptions: (1) a composite is a two-phase media consisting of a continuous matrix phase and embedded inclusions of disperse phase; (2) phase materials are homogeneous and isotropic, their properties being temperature-independent; (3) the disperse phase consists of the equally-sized spherical particles uniformly distributed within a matrix phase — as a result, the composite is assumed to be macroscopically isotropic; (4) interfaces have the conditions of conventional boundary transport laws, for example, perfect thermal contact is supposed to be maintained; and (5) the external (heat) flux is supposed to be time-independent and macroscopically uniform, etc.

At this time it can be concluded that the two-phase heat conductivity effective coefficient problem for the periodic morphologies is practically resolved (at least in the scientific sense), whereas, for disordered, random morphologies of composites it is far from resolved, even when the above assumptions are appropriate.

4.4. Analysis of pressure-loss experimental data from porous media morphologies based on VAT

Ergum [76] suggested two types of effective bulk friction factors. One of them, the so-called kinetic-energy friction factor, f_{ker}, is similar to the Fanning friction factor, f_f, and is written with the same assumptions,

$$f_f = \frac{f_{ker}}{3} = \frac{d_h}{2_{\rho f}\tilde{\bar{U}}^2}\left(\frac{\Delta P}{L}\right), \tag{83}$$

where d_h is the hydraulic diameter and $\tilde{\bar{U}}$ is the intrinsic averaged velocity including turbulent regime. The problem is what to choose for the hydraulic diameter for a given porous media that properly represents its morphology. Bird et al. [77] used the ratio of the volume available for flow to the cross section available for flow in their derivation of a hydraulic radius, r_{hb}. This assumption led them to

$$r_{hb} = \frac{\langle m \rangle d_p}{6(1 - \langle m \rangle)},$$

where d_p is the particle diameter. A basis for a consistent hydraulic diameter for any systems is

$$d_h = \frac{4\langle m \rangle}{S_w} = \frac{4\langle m \rangle}{a_v(1 - \langle m \rangle)} = \frac{2\langle m \rangle}{3(1 - \langle m \rangle)} d_p = 4r_{hb}, \tag{84}$$

where a_v is the particle specific surface which is equal to the total particle surface divided by the volume of the particle and specific surface $S_w = a_v(1 - \langle m \rangle)$. This expression is justified when an equal or mean particle diameter is $d_p = 6/a_v$, which is exact for spherical particles and often used as a substitute for granular media particles. The value of hydraulic radius given by Bird et al. [77] was chosen by Chhabra [78] and used in his determination of a specific friction factor for capillary models.

The particle diameter, d_p, is often used as a characteristic length when a particulate medium is of primary interest, as is done by Chhabra [78]. The friction factor used in his book is written in the form

$$f_{cb} = \frac{d_p}{\langle m \rangle^2 \rho_f \tilde{\bar{U}}^2} \frac{\Delta p}{L}.$$

This friction factor, f_b [given by Bird et al. [77] for a packed bed, see Equation (6.4-1)], the Fanning friction, f_f, and the Ergun's kinetic energy friction factor, f_{ker}, are related by the following

$$f_{cb} = 2f_b = \left(\frac{1 - \langle m \rangle}{\langle m \rangle^3} \right) f_{ker} = 3 \left(\frac{1 - \langle m \rangle}{\langle m \rangle^3} \right) f_f. \tag{85}$$

All these models use different length scales. It is not clear from evaluation of experimental data which is the most appropriate. To address this, the momentum equation for turbulent flow of an incompressible fluid in a porous media based on a simplified VAT (SVAT) and *K*-theory, Eq. (51), will be used to develop a consistent set of morphological properties and a characteristic length. The one-dimensional form of the momentum equation, Eq. (51), can be simplified for a regular morphology medium with constant porosity to the form of Eq. (65) which is written

$$-\frac{d\tilde{\bar{p}}}{dx} = \left(c_f + c_{dp} \frac{S_{wp}}{S_w} \right) \left(\frac{S_w}{\langle m \rangle} \right) \frac{\rho_f \tilde{\bar{U}}^2}{2} = c_d \left(\frac{S_w}{\langle m \rangle} \right) \frac{\rho_f \tilde{\bar{U}}^2}{2}, \tag{86}$$

where c_f is the friction factor and c_{dp} is the form drag (S_{wp} is actually the cross flow form specific surface). The drag terms are combined into a single total drag

coefficient

$$c_d = \left(c_f + c_{dp} \frac{S_{wp}}{S_w} \right), \tag{87}$$

to model the flow-resistence terms in the general simplified momentum VAT equation. The drag resistance can be evaluated for a homogeneous porous media from measurements of pressure drop,

$$-\frac{d\tilde{\bar{p}}}{dx} = f_f \left(\frac{S_w}{\langle m \rangle} \right) \frac{\rho_f \tilde{\bar{U}}^2}{2}. \tag{88}$$

It was shown by Travkin and Catton [17] that a good approximation for such media is

$$c_d \cong f_f,$$

where a bulk value of the pressure-loss coefficient, f_f, can be obtained from experimental correlations. There are a few reasons why these quantities are not identical. One of them is the neglect of media inflow, outflow and other pressure losses which are usually incorporated into the correlations for f_f. Another reason is the loss of geometric characteristics represented partially by the ratio of S_{wp}/S_w.

Some details of a media composed of globular morphologies can also be described in terms of specific surface S_w, porosity $\langle m \rangle$ and particle diameter d_p. For a spherical particle medium when

$$S_w = \frac{6(1 - \langle m \rangle)}{d_p}, \quad d_h = \frac{2}{3} \frac{\langle m \rangle}{(1 - \langle m \rangle)} d_p,$$

which in turn yields the same relationship between the equivalent pore diameter and their parameters, as found for a one-diameter capillary morphology, and leads to

$$S_w = \frac{6(1 - \langle m \rangle)}{d_p} = \frac{6(1 - \langle m \rangle)}{\left(\frac{3}{2} \frac{(1 - \langle m \rangle)}{\langle m \rangle} d_h \right)} = \frac{4\langle m \rangle}{d_h}. \tag{89}$$

This leads to a relationship for d_h that takes the form

$$d_h = \frac{4\langle m \rangle}{S_w}. \tag{90}$$

This form is consistent with two major morphologies, both capillary and globular,

and incorporates two properties of the media, both void fraction and specific surface area. It has a solid theoretical basis at least for two types of canonical porous-media morphology (straight-capillary parallel-pore morphology, SPPM, and one-diameter sphere globular morphology) and was arrived at with different theoretical reasonings by others in previous years like Kays and London [79].

There are a number of analysis and experimental studies of different porous-media morphology leading to the use of a porous-media Reynolds number of the form

$$Re_{por} = \frac{4\tilde{\bar{U}}\langle m\rangle}{\nu S_w}. \tag{91}$$

Although various porous-media pressure-resistance models are described by others [77,78,80], the above description for d_h and Re_{por} allows the transformation and comparison of correlation equations and experimental results obtained for diverse morphology media and the use of various scaling. Also, it allows experimentally-determined characteristics of the media to be related to the closure relationship derived from the VAT analysis.

It was shown by Travkin and Catton [4,17] that a straight equal-diameter tube morphology model yielding the morphology functions $S_w/\langle m\rangle$ and d_h is obtained from the above expression. A c_d for such a capillary morphology with its corresponding skin-friction coefficient is given by Travkin and Catton [17],

$$c_d = \tilde{c}_d \cong \frac{f_D}{4}, \tag{92}$$

which relates the Darcy pressure loss coefficient, f_D, to the SVAT model for some capillary morphologies. The generalized two-term quadratic Reynolds–Forchheimer equation,

$$\frac{\Delta P}{L} = \alpha\mu\tilde{\bar{U}}\langle m\rangle + \beta\rho_f\tilde{\bar{U}}^2\langle m\rangle^2, \alpha = \frac{1}{k_D}\left[\frac{1}{m^2}\right], \quad \beta = \beta\left[\frac{1}{m}\right]. \tag{93}$$

needs to be compared to the SVAT momentum equation with constant morphological characteristics and flow field properties using the only resistance coefficient, c_d, described above

$$\frac{\Delta P}{L} = c_d\left(\frac{S_w}{\langle m\rangle}\right)\frac{\rho_f\tilde{\bar{U}}^2}{2}, \quad \left[\frac{Pa}{m}\right]. \tag{94}$$

To make the transition between the both equations one can rewrite the first equation in terms of the second one

$$\left[\frac{2\alpha\mu\langle m\rangle}{\rho_f\bar{\bar{U}}} + 2\beta\langle m\rangle^2\right]\frac{\rho_f\bar{\bar{U}}^2}{2} = \left[\frac{2\alpha\mu\langle m\rangle}{\rho_f\bar{\bar{U}}}\left(\frac{\langle m\rangle}{S_w}\right) + 2\beta\langle m\rangle^2\left(\frac{\langle m\rangle}{S_w}\right)\right]$$

$$\left(\frac{S_w}{\langle m\rangle}\right)\frac{\rho_f\bar{\bar{U}}^2}{2}.$$

Observing the right-hand side of this expression, it is obvious that the Fanning friction factor which is thought for the equation of one-dimensional SVAT momentum flow, is

$$c_d = f_f = \left[\frac{\alpha\mu}{\rho_f\bar{\bar{U}}} + \beta\langle m\rangle\right]\left(\frac{2\langle m\rangle^2}{S_w}\right). \tag{95}$$

This equation should be used to correlate experimental data on friction factor for highly-porous media written in terms of a generalized two-term quadratic Reynolds–Forchheimer equation. In this case the equation for Fanning friction factor, f_f, following from above, can be written in the form

$$c_d = f_f = \frac{A}{Re_{por}} + B, \tag{96}$$

where

$$Re_{por} = \frac{4\bar{\bar{U}}\langle m\rangle}{\nu S_w}, A = \frac{8\alpha\langle m\rangle^3}{S_w^2}, \quad B = 2\beta\frac{\langle m\rangle^3}{S_w}. \tag{97}$$

If Ergun's correlation is taken in the following generally-used notation

$$\frac{\Delta p}{L} = \left(150\frac{(1-\langle m\rangle)^2}{d_p^2\langle m\rangle^3}\right)\mu\langle m\rangle\bar{\bar{U}} + \left(1.75\frac{(1-\langle m\rangle)}{d_p\langle m\rangle^3}\right)\varrho_f\langle m\rangle^2\bar{\bar{U}}^2, \tag{98}$$

with some additional algebra it can be transformed to

$$\frac{\Delta p}{L} = \left[300\frac{(1-\langle m\rangle)^2}{d_p^2\langle m\rangle^2}\frac{\nu}{\bar{\bar{U}}} + 3.5\frac{(-\langle m\rangle)}{d_p\langle m\rangle}\right]\left(\frac{\varrho_f\bar{\bar{U}}^2}{2}\right)$$

$$= \left[\left(\frac{50(1-\langle m\rangle)}{\langle m\rangle}\right)\frac{1}{Re_p} + \frac{3.5}{6}\right]\left(\frac{S_w}{\langle m\rangle}\right)\frac{\varrho_f\bar{\bar{U}}^2}{2},$$

where the specific surface, S_w, and particle Reynolds number, Re_p, are used as

$$S_w = \frac{6(1 - \langle m \rangle)}{d_p}, \quad Re_p = \frac{\tilde{\bar{U}} d_p}{\nu}.$$

From this formula, the following will result as an expression for the Ergun drag resistance coefficient in terms of simplified VAT

$$f_{er} = \frac{A_p^*}{Re_p} + B_p^*, \quad A_p^* = \left(\frac{50(1 - \langle m \rangle)}{\langle m \rangle} \right), \quad B_p^* = \frac{3.5}{6} = 0.583. \tag{99}$$

The same formulation can be written in terms of the hydraulic diameter Reynolds number, Re_{ch}, by noting that

$$Re_p = \frac{\tilde{\bar{U}} d_p}{\nu} = \frac{\tilde{\bar{U}}}{\nu} \left[\frac{3(1 - \langle m \rangle)}{2\langle m \rangle} \right] d_h = Re_{ch} \left[\frac{3(1 - \langle m \rangle)}{2\langle m \rangle} \right],$$

$$Re_{ch} = \frac{\tilde{\bar{U}} d_h}{\nu} = \frac{2}{3} \frac{\langle m \rangle}{3(1 - \langle m \rangle)} \frac{\tilde{\bar{U}} d_p}{\nu}, \tag{100}$$

which leads to

$$f_{er} = \frac{A_{ch}^*}{Re_{ch}} + B_{ch}^*, \quad A_{ch}^* = \frac{100}{3} = 33.33, \quad B_{ch}^* = B_p^* = 0.583. \tag{101}$$

These parameters are very close to those of the Klenov and Matros [81] correlation with $A = 36.3$ and $B = 0.45$ for spherical particles and $A = 37.6$ and $B = 0.585$ for cylindrical particles. The correlation for the same 'Ergun's' SVAT drag-resistance coefficient based on Re_{por} was derived above in Eq. (96) while known coefficients are α, β, as well as porosity $\langle m \rangle$ and specific surface S_w. The former can be assessed using

$$\alpha = 150 \frac{(1 - \langle m \rangle)^2}{d_p^2 \langle m \rangle^3}, \quad \beta = 1.75 \frac{(1 - \langle m \rangle)}{d_p \langle m \rangle^3}. \tag{102}$$

A large amount of data exists that demonstrates the insufficiencies of the Ergun drag resistance correlation, Eq. (98). Because it was developed for specific morphology, in particular, globular 'granular' media, an application of the Ergun correlation to arbitrary selected or at least with arbitrary chosen relationships between porosity, $\langle m \rangle$, specific surface, S_w, and pore (particle) diameter, d_h, can be quite unsatisfactory.

The formula for drag resistance of a spherical particle bed derived from Watanabe [82] results in a drag-resistance coefficient that corresponds to the present notation

$$f_w = c_{sph}\frac{25(1-\langle m\rangle)}{12} = c_{d,w}, \tag{103}$$

where c_{sph} is the drag-resistance coefficient of a single isolated bead of diameter, d_p. The drag-resistance coefficient derived from the correlations of Fand and Thinakaran [83], for a large range of Reynolds numbers

$$10^{-5}\langle Re_p = \frac{\tilde{\bar{U}}d_p}{\nu}\rangle \approx 0(10^3),$$

is

$$c_{d,ft} = f_{ft} = \frac{2A_{ft}}{(9Re_{por})} + \frac{B_{ft}}{3}, \tag{104}$$

where A_{ft} and B_{ft} are given by Fand and Thinakaran [83].

The widely used and cited Koseny–Carman pressure-loss equation can be written in few forms depending on the length scale taken and on the friction factor chosen. A form which incorporates morphological parameter is

$$\frac{\Delta p}{L} = k_{kc}\,\mu\left(\frac{S_w^2}{\langle m\rangle^2}\right)\tilde{\bar{U}}, \tag{105}$$

where the coefficient k_{kc} (Koseny–Carman coefficient) has been found for some media to be between 4.5 and 5. There are studies arguing such a narrow range [80]. Permeability in the Darcy sense following this equation can be written as

$$k_D = \frac{\langle m\rangle^3}{k_{kc}S_w^2}. \tag{106}$$

When the particle diameter serves as the length scale, then the Kozeny–Carman dependency is

$$\frac{\Delta p}{L} = \mu\left(\frac{180}{d_p^2}\right)\tilde{\bar{U}}\left(\frac{(1-\langle m\rangle)^2}{\langle m\rangle^2}\right), \tag{107}$$

which is distinguished from the Blake–Kozeny equation only by factor 180 instead of 150 in the last equation. With the hydraulic diameter length scale d_h this equation looks much simpler

$$\frac{\Delta p}{L} = \left[\mu/\left(\frac{d_h^2}{80}\right)\right]\tilde{\bar{U}}, \tag{108}$$

with the Darcy permeability value estimated as

$$k_D = \left[\frac{d_h^2}{80} \langle m \rangle \right]. \tag{109}$$

The Fanning friction factor based on the Kozeny–Carman drag-resistance model has the simple equation

$$f_{f,kc}(Re_{por}) = \frac{40}{Re_{por}}, \quad Re_{por} = \frac{4\tilde{\bar{U}}\langle m \rangle}{\nu S_w}. \tag{110}$$

Meanwhile, another well-known high flow regime drag-resistance coefficient of Burke–Plummer [77,78] has the very plain equation if written in the form of a Fanning friction factor using d_h, as the scale length (valid naturally and for the SVAT pressure loss equation, Eq. (86))

$$f_{f,bp} = \frac{1.75}{3} = 0.5833.... \tag{111}$$

The Burke–Plummer friction loss model written in general d_p terms of the length scale d_p (Equation (6.4-11) in Bird et al. [77], which was written rather intuitively as analogous to the more strict definition of capillary pressure loss model) is

$$\frac{\Delta p}{L} = f_{f,bp} \left(\frac{6}{d_p} \frac{(1 - \langle m \rangle)}{\langle m \rangle} \right) \left(\frac{\varrho_f \tilde{\bar{U}}^2}{2} \right). \tag{112}$$

Note, that this is exactly the SVAT drag resistance model, Eq. (86), written in terms of globular (granular) media where it can usually be assumed that

$$\frac{S_w}{\langle m \rangle} = \frac{6}{d_p} \frac{(1 - \langle m \rangle)}{\langle m \rangle}.$$

From Eq. (112), it follows that the friction factor is

$$f_{f,bp} = \frac{d_p}{\varrho_f \tilde{\bar{U}}^2} \left(\frac{\langle m \rangle}{3(1 - \langle m \rangle)} \right) \frac{\Delta p}{L}, \tag{113}$$

which is just the Fanning friction factor written for the globular length scale, d_p. The various friction factors are related by

$$f_{f,bp} = \frac{f_{ker}}{3} = f_f.$$

Bird et al. [77] states that the Burke–Plummer friction factor coefficient is

$$f_{f,bp} = \frac{3.5}{6},$$

which is equal to the value given by Eq. (111) found for the capillary Fanning friction factor pressure loss model. The same scaling approach applied to the Darcy pressure loss model shows that the drag-resistance coefficient for spherical particles is

$$c_{d,Dar} = f_{f,D} = \frac{8k_{kc}}{Re_{por}}, \tag{114}$$

or, if following the finding by Fand et al. [80] that the Koseny–Carman coefficient is $k_{kc} = 5.34$ then

$$f_{f,D} = \frac{42.72}{Re_{por}}, \tag{115}$$

as pointed out by Travkin and Catton [17]. Discussions of a number of porous media pressure resistance models can be found in analysis by different authors, see, for example, Bird et al. [77], Fand et al. [80], Chhabra [78], etc.

The reason for the current description is that it shows how the transformation and comparison of correlation equations and results obtained for diverse-morphology media and written with various coordinates and scaling units can be provided on the basis of a unified VAT approach. First introduced before WWII in the transport in porous media literature, the general porous media length scale $l_{por} = 4\langle m\rangle/S_w$ is still rarely used in various engineering circles.

Based on the above, one can make the conclusion that most experimental correlations can be reformulated for use in the SVAT based bulk one-dimensional momentum equation,

$$\frac{\Delta P}{L} = f_f(Re_{por})\left(\frac{S_w}{\langle m\rangle}\right)\frac{\rho_f \tilde{\bar{U}}^2}{2}. \tag{116}$$

With this expression, any Fanning friction factor correlation can be easily compared and analyzed after reformulating the corresponding expressions in terms of Re_{por} as shown in Fig. 5. The correlations presented in Fig. 5 are for experiments carried out by the following:

(1) the Gortyshov et al. [84] correlations were experimentally derived for the Reynolds–Forchheimer momentum equation (porous medium resistance equation) in the form

$$\alpha = 6.61 \cdot 10^7 \left(\bar{d}_h\right)^{-1.98} \langle m\rangle^{(-4.75)},$$
$$\beta = 5.16 \cdot 10^2 \left(\bar{d}_h\right)^{-1.07} \langle m\rangle^{(-11.16)}, \tag{117}$$

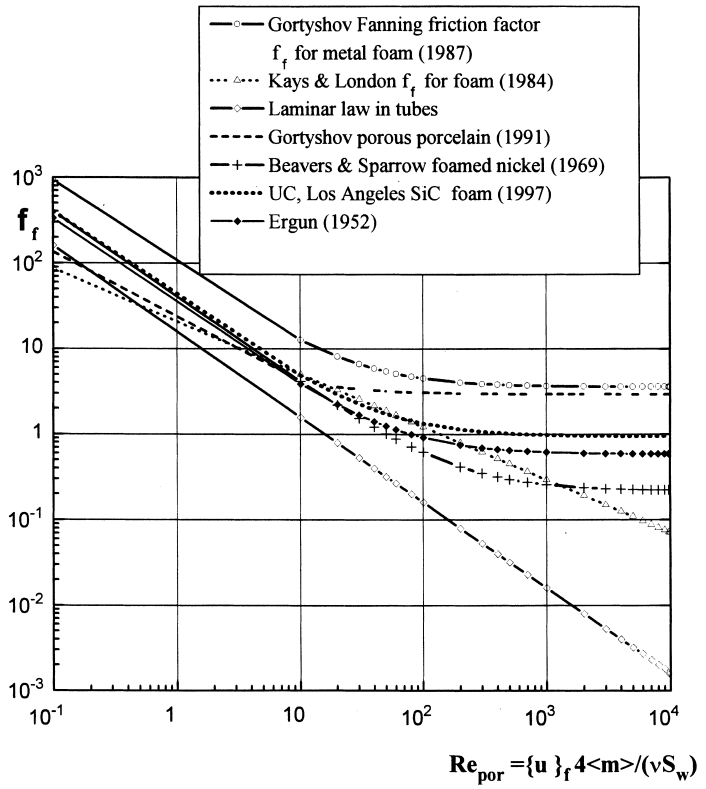

Fig. 5. Comparison of porous media pressure loss models using Fanning friction factor.

when the hydraulic diameter, $\bar{d}_h$, is taken in millimeters. These correlations are for highly porous ($\langle m\rangle = 0.87 \div 0.97$) foamy metallic media.

(2) A Darcy type of friction factor obtained by Gortyshov et al. [85] for very low-conductivity porous porcelain with high porosity is

$$f_D(Re_h) = \frac{40}{Re_h}\left(1 + 2.5\cdot 10^{-2}\langle m\rangle^{-8.8} Re_h\right), \quad \langle m\rangle = 0.83 \div 0.92, \tag{118}$$

where

$$Re_h = \frac{\tilde{\bar{U}} d_h \langle m\rangle}{\nu}.$$

To modify this equation to the SVAT momentum equation form, one needs to replace Re_h with Re_{por} and divide by four to obtain the Fanning friction factor

$$f_f(Re_{por}) = \frac{1}{4}\left[\frac{40}{Re_{por}\langle m\rangle}\left(1 + 2.5\cdot 10^{-2}\langle m\rangle^{-8.8} Re_{por}\langle m\rangle\right)\right],$$
$$\langle m\rangle = 0.83 \div 0.92, \tag{119}$$

to

$$Re_h \cong Re_{por}\langle m\rangle.$$

(3) The correlation derived by Beavers and Sparrow [86] for foam morphologies is

$$f_{bs}(R_w) = \frac{1}{R_w} + 0.074, \tag{120}$$

with the Reynolds number suggested by Ward [87] given by

$$R_w = \frac{\tilde{\bar{U}}\langle m\rangle\sqrt{k_D}}{\nu},$$

is just another problem if the permeability, k_D, is not known. After some algebra performed to relate this equation to the SVAT general form of pressure loss, the Fanning friction factor, f_f, written for the Beavers and Sparrow [86] pressure-loss coefficient finally is

$$f_{f,bs}(Re_{por}) = \left[\frac{1}{Re_{por}}\left(\frac{4\sqrt{\alpha}}{S_w}\right) + 0.074\right]\left(\frac{2\sqrt{\alpha}\,\langle m\rangle^3}{S_w}\right), \tag{121}$$

where

$$\alpha = \frac{1}{k_D}.$$

One of experimental curves in Fig. 5 is given on the basis of the pressure loss data obtained at the University of California for the SiC foam (Fig. 6) highly regarded as one of the prospective porous media for high-technology applications [88].

4.5. The mass transport issues in porous media with VAT modeling

Several issues important in the VAT-based treatment of the processes governing mass transport in different scale porous media with chemical exchange is considered in this section. Great attention to particular deviations from the assumption of regularity and homogeneity of interacting media of packed-bed reactors was paid in the work by Cybulski et al. [89]. The issues of porosity and flow distributions inside the tubes and over the intertubular space were discussed and some recom-

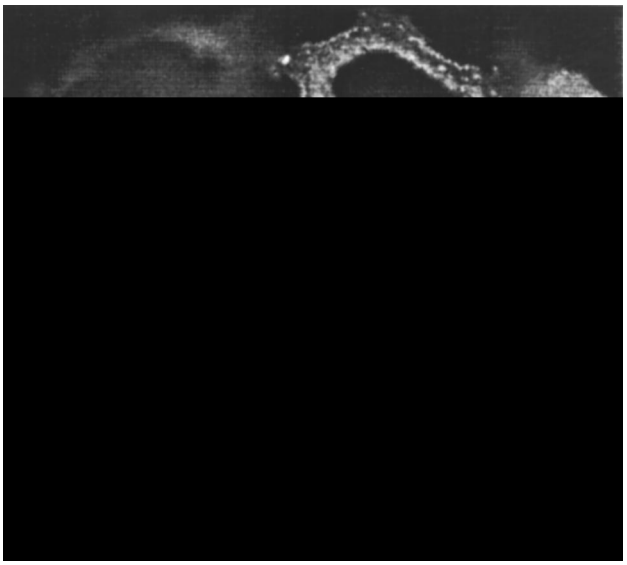

Fig. 6. Ceramic SiC open-cell high-porosity foam.

mendations suggested. Also, the idea of treatment of the reactor's media and design objectives as components of special heterogeneous porous multiscale constructs was surfaced. Meanwhile, it is obvious that in this direction at the present time the development lacks in understanding and availability of tools.

Churchill and co-workers recently [90–92] introduced a thoroughly-evaluated approach to model the turbulent transport using integral formulations of the momentum and energy balances near the interface surface. The method's general equations, developed for specific problems, allowed new integral correlations for the friction factor, Nusselt number and most of algebraic analogies. As noticed by Churchill [92], 'neglect or misrepresentation of the variation of the heat (or mass) flux density within the fluid and the misrepresentation of the molecular and turbulent transport near the wall, in the turbulent core, or in both regions are the principal sources of error in the analogies. These deficiencies are not generally identified or emphasized in our current textbooks'.

These findings are in general agreement with derivations supported by VAT, such as in terms of importance of interfacial and near-interface phenomena as well as regarding dependencies between bulk overall quantities (field functions) and interface shear stress and heat (mass) flux densities. The VAT-based approach goes steps further and formulates exact general differential equations for bulk (averaged) field quantities using local function values which are thought or found throughout the spatial area of the problem.

For example, when the linear equation of mass transport in the fluid phase of a porous media (in reactors, adsorbers, etc.)

$$\frac{\partial C_f}{\partial t} + V \cdot \nabla C_f = D_f \nabla^2 C_f + S_{C_f}, \tag{122}$$

and the solid-phase diffusion equation

$$\frac{\partial C_s}{\partial t} = D_s \nabla^2 C_s + S_{C_s}, \tag{123}$$

can be averaged in the same way as non-linear Eq. (54), while preserving the interface surface fluxes in an equation form with the only fluctuation dependent diffusivity-like terms

$$\langle m \rangle \frac{\partial \tilde{C}_f}{\partial t} + \langle m \rangle \tilde{U}_i \nabla \tilde{C}_f - \frac{\tilde{C}_f}{\Delta \Omega} \int_{\partial S_w} U_i \cdot \vec{ds} + \nabla \langle \hat{C}_f \hat{U}_i \rangle_f + \frac{1}{\Delta \Omega} \int_{\partial S_w} C_f U_i \cdot \vec{ds}$$
$$= D_f \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{C}_f \vec{ds} \right] + \frac{D_f}{\Delta \Omega} \int_{\partial S_w} \nabla \hat{C}_f \cdot \vec{ds} + \langle m \rangle S_{C_f}, \tag{124}$$

or when there is no interfacial flux

$$\langle m \rangle \frac{\partial \tilde{C}_f}{\partial t} + \langle m \rangle \tilde{U}_i \nabla \tilde{C}_f = - \nabla \langle \hat{C}_f \hat{U}_i \rangle_f + D_f \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} \hat{C}_f \vec{ds} \right]$$
$$+ \frac{D_f}{\Delta \Omega} \int_{\partial S_w} \nabla \hat{C}_f \cdot \vec{ds} + \langle m \rangle S_{C_f}, \tag{125}$$

the full-averaged concentration integral term equation yields

$$\langle m \rangle \frac{\partial \tilde{C}_f}{\partial t} + \langle m \rangle \tilde{U}_i \nabla \tilde{C}_f - \frac{\tilde{C}_f}{\Delta \Omega} \int_{\partial S_w} U_i \cdot \vec{ds} + \nabla \langle \hat{C}_f \hat{U}_i \rangle_f + \frac{1}{\Delta \Omega} \int_{\partial S_w} C_f U_i \cdot \vec{ds}$$
$$= D_f \nabla \cdot \left(\nabla \langle m \rangle \tilde{C}_f \right) + D_f \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} C_f \vec{ds} \right]$$
$$+ \frac{D_f}{\Delta \Omega} \int_{\partial S_w} \nabla C_f \vec{d} s + \langle m \rangle S_{C_f}, \tag{126}$$

while the shortened version with an impermeable interface is

$$\langle m \rangle \frac{\partial \tilde{C}_f}{\partial t} + \langle m \rangle \tilde{U}_i \nabla \tilde{C}_f = - \nabla \langle \hat{C}_f \hat{U}_i \rangle_f$$
$$+ D_f \nabla \cdot \left(\nabla \langle m \rangle \tilde{C}_f \right) + D_f \nabla \cdot \left[\frac{1}{\Delta \Omega} \int_{\partial S_w} C_f \vec{ds} \right]$$
$$+ \frac{D_f}{\Delta \Omega} \int_{\partial S_w} \nabla C_f \cdot \vec{ds} + \langle m \rangle S_{C_f}. \tag{127}$$

Similarly, in the solid phase, two form-governing equations are

$$\langle s\rangle \frac{\partial \tilde{C}_s}{\partial t} = D_s \nabla \cdot \left[\frac{1}{\Delta\Omega} \int_{\partial S_w} \hat{C}_s \vec{ds}_1 \right] + \frac{D_s}{\Delta\Omega} \int_{\partial S_w} \nabla \hat{C}_s \cdot \vec{ds}_1 + \langle s\rangle S_{C_s}, \tag{128}$$

and the second form when the full-averaged concentration function under the integral is the following:

$$\langle s\rangle \frac{\partial \tilde{C}_s}{\partial t} = D_s \nabla \cdot \left(\nabla \langle s\rangle \tilde{C}_s \right) + D_s \nabla \cdot \left[\frac{1}{\Delta\Omega} \int_{\partial S_w} C_s \vec{ds}_1 \right] + \frac{D_s}{\Delta\Omega} \int_{\partial S_w} \nabla C_s \cdot \vec{ds}_1 + \langle s\rangle S_{C_s}. \tag{129}$$

It could be observed that the above equations present and give important roles to those terms which bear significant responsibilities for the interfacial transport.

What is to be considered as significant tool for closure of the certain VAT equations is the network modeling approach. Considerable improvement of network models appeared recently when authors ([93,94], for example) started to address the transport phenomena in networks, including adsorbtion, as written in each separate pore in the network using continuum equations of an adopted form. In this way, the transport of momentum and species between the nodes in the network is no longer described by simple algebraic dependencies (as is usually done), but with differential equations of mathematical physics. The next step in this direction would be when addressing the complex transport phenomena in nodes (sites) of network will be thought also through the employment of continuum models.

When porous material morphological characteristics are changing in space as, for example, unidirectionally along of one axis (name it x), equations of homogeneous medium transport are no longer valid. This seriously diminishes the value of a theoretical effort (including modeling) if not properly addressed. An example of the problem is a capillary medium with pore sizes changing in space. Among other techniques which are worth to mention in this field is the pore modification technique-deploying the supercritical solution fluid (SCF) infiltration, see Lin [95], Lin and Burggraaf [96] and Wang et al. [97]. Ceramic membranes treated with SCF can change their pore sizes and have modified pore-size distribution (PDS), at least, along of one axis.

In experimental work by Huang et al. [98], the PSD of the modified membrane evidenced as much as 300-fold general reduction in gas permeance compared to data for non-modified initial membrane, which is the great difference. Meanwhile, no specifics regarding the type and morphology of pore coating were given.

One-dimensional momentum equation for such a media should have one of the VAT forms as described above, for example

$$\varrho_f\left(\langle m\rangle\frac{\partial\tilde{V}}{\partial t} + \langle m\rangle\tilde{V}\cdot\nabla\tilde{V} + \nabla\langle\hat{v}\hat{v}\rangle_f\right) = -\nabla(\langle m\rangle\tilde{p}) - \frac{1}{\Delta\Omega}\int_{\partial S_w} p\vec{ds}$$
$$+\mu\nabla\cdot\nabla(\langle m\rangle\tilde{V}) + \mu\nabla\cdot\left[\frac{1}{\Delta\Omega}\int_{\partial S_w} V\cdot\vec{ds}\right] + \frac{\mu}{\Delta\Omega}\int_{\partial S_w}\nabla V\cdot\vec{ds}$$
$$+\langle m\rangle\varrho_f\vec{g}. \tag{130}$$

Using for the modified adsorbing ceramic membrane the modeling SVAT equation

$$-\frac{d\tilde{\bar{p}}}{dx} = c_d\left(\frac{S_w}{\langle m\rangle}\right)\frac{\rho_f\tilde{\bar{U}}^2}{2}, \tag{131}$$

undermines the value of analysis pertinent to this particular problem. The same needs to be said regarding the mass-transport models typically found in the literature. An example of a widespread mass-transport modeling equation in gaseous phase of porous adsorber presented in the work by Silva and Rodrigues [99]

$$\langle m\rangle\frac{\partial\varrho_f\{C\}_f}{\partial t} + (1-\langle m\rangle)\varrho_s\frac{\partial\{C\}_s}{\partial t} + \frac{\partial\varrho_f\{U\}_f\{C\}_f}{\partial x}$$
$$= \langle m\rangle D_L\frac{\partial}{\partial x}\left(\varrho_f\frac{\partial\{C\}_f}{\partial x}\right), \tag{132}$$

where $\{C\}_s$ is the mole fraction of the average adsorbed concentration and D_L is the effective longitudinal dispersivity. This equation should be compared to the VAT-based equations shown above.

Nano- and microporous membranes at present time are of sufficient interest due to many of their applications. The modeling techniques used for some of them, gas mixture separation and adsorption techniques in particular (for example [98,100]), will be discussed. Also a valuable issue to address in the nanosize adsorbing membrane technology is the phenomena description for the two-or-more layer membranes. There are usual structures when the thin layer membrane is supported by a thicker layer of porous support with distinctly larger pore sizes. This two-layer structure has at least three sublayers (or imaginable surfaces) which divide and change the transport characteristics in membrane and support layers with up to approximately three orders of magnitude in pore size difference.

This issue could be rather naturally addressed using the VAT procedures. As was shown in the previous section the most vital and substantial swing of data on friction factor in porous medium momentum transport observed in the low-flow rate. Given this note it is clear how important and economically significant and influential might be improvement in the process modeling. Thus, Huang et al. [98] gave, for example, an estimation of needed membrane area for recovery of acetone from nitrogen based on the balance flow rate equation of type

$$\frac{\Delta p}{L} = \frac{1}{\pi'} J, \tag{133}$$

where J is the molar flux [kmol/m^2] and π' is the gas permeability written in terms of [kmol/(m · s · Pa)]. As soon as the permeability values assessed through the Darcy type of momentum transport model can have different orders of magnitude, then the same swing would apply for the need of such expensive material as ceramic nanopore membranes, zeolite consisting adsorbers, etc. If one can write Eq. (2) by Acharya et al. [101] as an equation with mass flow rate written in terms of velocity

$$\varrho \langle m \rangle \tilde{U} = J M_g = \left(\frac{\pi'}{L} \Delta p \right) M_g, \tag{134}$$

or

$$\frac{\Delta p}{L} = \left(\frac{\varrho}{\pi' M_g} \right) \langle m \rangle \tilde{U}, \tag{135}$$

where M_g is the gas molecular weight. This equation is exactly the type of Darcy equation with all deficiencies peculiar to this equation (meaning that only an experiment actually establishes a correlation for permeability). Rewriting Eq. (135) with the following notations of the Darcy law (in terms of the Darcy permeability, k_D), or

$$\frac{\mu}{k_D} = \frac{\varrho}{\pi' M_g},$$

from which the Darcy permeability can be found to be

$$k_D = \nu M_g \pi', \quad [m^2]. \tag{136}$$

While resolving equation of mass balance for membrane gas permeation written in form [101]

$$\frac{dp_2}{dt} = \frac{A R_s T}{V_2} \left[\pi' \frac{(p_1 - p_2)}{L} \right] M_g, \tag{137}$$

and the final equation for the pressure transient increasing in the permeation volume V_2 is found to be

$$p_2(t) = p_1 - \frac{p_1}{\exp\left(\pi' \dfrac{t}{Lb} \right)}, \quad b = \frac{V_2}{A R_s T}. \tag{138}$$

Here A is the membrane input–output surface area, R_s is the specific gas constant, L is the membrane thickness, V_2 is the down side permeate volume, p_1 is

the feed stream pressure ($p_1 > p_2$). At the same time the permeability transient function can be found from the above expression as

$$\pi'(p_2, L, t) = \ln\left(\frac{p_1}{p_1 - p_2}\right)\frac{bL}{t}, \tag{139}$$

with an experimentally-determined permeate pressure, p_2. The permeability value π' (also the Darcy permeability) is obtained above through the balance reasonings explicitly dependent on the sample thickness, media physical characteristics and time of experiment. No internal peculiarities of the membrane itself are present in this formulation, meaning that the permeate pressure, p_2, curve implicitly includes all necessary information.

At the current time, a strong interest attracts the problems concerning zeolite sorbents technology. The proper methodology to approach the various modeling issues as well as design of adsorbers for this particular media has not even been addressed in full detail. Meanwhile, practical approaches developed up to now include the range of models from three equations [102], to four equations (by Silva and Rodrigues [99] and to the eight-equation model by Mohamad et al. [103] for zeolite-based adsorbers). Not one of these mentioned works used correctly-formulated averaging models as their basis.

As long as specifics of zeolite industrial sorbents reveal the three different scales of the medium-zeolite crystals with nanoscale size pores, zeolite pellets with the μm size porous scale and adsorber bed medium with pores of 10^{-3} m and up, the peculiarities of each scale demanding different mathematical description, primarily due to different physico-chemistry of phenomena. To those three distinctly different spacial scales of VAT formulations, one needs to add an initial scale of the smallest pore characteristics (10^{-9}–10^{-10} m) and a scale of adsorber's working volume, which results in an up to five-scale medium consideration.

Averaging at scales of approx. 10^{-9}, 10^{-6} and 10^{-3} m to formulate of mathematical models at each level is not the only challenge. Complications arise when interscale transition physics need to be outlined and mathematically formulated. The problem of such enormous complexity that it has not been undertaken as yet. Most known approaches are based on heuristic reasoning and judgement.

It seems that the only working details of multiscale porous media were dealt with in the study by Plump and Whitaker [25,26] where in the three scale-averaging medium were formulated the mathematical statements along with the analysis of the situation in general. Of those three scale problems the first scale task was formulated as a diffusion one-equation mass-transfer problem. The second scale statement consisted of the two-media (solid–liquid) diffusion–convection linear system of mathematical equations which later, after great simplifications, is reduced to the single-variable diffusion–convection equation. The third level averaging problem is based on a two-equation linear diffusion–convection statement. A reader of that work can observe an enormous amount of general integro-differential equations, as well as suggested methods of their closure. Analysis of these results and the attempts of others during the past 30 or 40 years gives the

impression that the proper development of a mathematical theory is difficult and very complex and that results achieved to date differ greatly from one to another. In spite of the complexity, a VAT-based approach to the study of multiscale heterogeneous media is the only practical method available. Furthermore, it points the way to the development of meaningful models.

5. Conclusions

Numerous studies of transport processes in porous media of different morphologies were analyzed and critiqued using the advantages of volume-averaging theory (VAT). Among those considered with the help of this powerful tool, porous media transport applications, are those with laminar, non-linear and turbulent regimes. Meanwhile, dilute morphologies frequently give an advantage of capillary or globular 'cell' models which are treatable even analytically. There are a few excellent studies of such problems (mainly globular regular morphologies) with the results directly applicable for transport equations closure in regular and sometimes random arrangements of porous medium elements. Selected averaged VAT-based momentum and heat-transport equations suitable for direct analytical or semi-analytical closure are derived in the present work.

Care must be taken when the problem statement is formulated that the equations contain all the necessary closure terms resulting from the averaging process. It was shown by comparison of a DNM solution with a VAT-based solution that several terms usually ignored are of the same order as those usually kept. There are many terms that appear as a result of flow which are ignored and their importance is yet to be determined.

A VAT-based approach to modeling transport phenomena in porous media has been developed and demonstrated by experimental data analysis, reduction and modeling using one-dimensional equations resulting from SVAT. It has been shown that many canonical morphologies can naturally be treated with VAT-based modeling and that data from a wide variety of geometrically different morphologies can be normalized with a general porous-medium length scale.

Acknowledgements

The authors wish to acknowledge the help and collaboration of V.I. Kushch. This work was sponsored by the US Department of Energy, Office of Basic Energy Sciences under the Grant DE-FG03-89ER14033 A002.

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