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Heterogeneous hard-sphere interactions for equilibrium transport processes beyond perforated domain formulations

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ABSTRACT

We consider transport of neutral species interacting under a potential of mean force with randomly placed, rigid spherical obstacles. Generally, this kind of transport problems are studied as so-called *perforated domain* problems, where one imposes no-flux or reaction boundary conditions on the pore walls forming the interface between the pore and the solid phase. Here, we advocate a general framework that replaces the perforated domain formulation with interaction energies as well as with *characteristic* and *scale-dependent* randomness of materials. Our framework provides both well-posed effective macroscopic equations for *highly heterogeneous* situations and a full scale description for *weakly heterogeneous* materials for which we present first computational results.

1. Introduction

We study material transport in porous materials characterized systematically by physical interaction energies/potentials. This builds the basis for the reliable, physical description of composites and complex materials relying on van der Waals, Lennard-Jones, and DLVO-type of interactions for heterogeneous and multiphase materials, e.g. transport in biology [1], batteries [2], desalination devices [3], fuel cells [4], interfacial dynamics [5], and ionic solutions [6]. To this end, we propose a general framework for deriving effective equations not relying on the *perforated domain methodology* generally applied in the context of porous materials [7–11] but based on *interaction potentials*, often called *potentials of mean force*, that account for repulsion and attraction such as no penetration properties of solids or other physical, chemical, and biological processes [1]. The here outlined upscaling approach allows for new perspectives of describing and modeling strongly heterogeneous multiphase materials such as complex composites.

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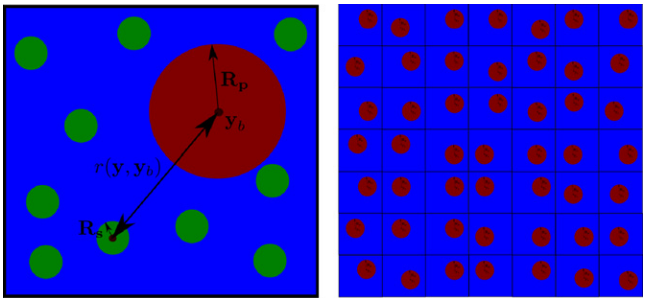

Fig. 1. Left: Reference cell Y containing a single solid hard-sphere obstacle p (red) with barycenter $\mathbf{y}_b$ and radius R_p as well as species s (green) with radius R_s and density c^ϵ. $r(\mathbf{y}, \mathbf{y}_b)$ is the distance of species' barycenter to the obstacle's barycenter. Right: Random medium formed by uniformly distributed hard-sphere particles p. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Our methodology generalizes the description of diffusion, which investigates a single cylindrical channel in [12], towards general diffusion processes in porous materials governed by local hard-sphere interactions between pore walls and diffusing species s of density c^ϵ, i.e.,

$$-\operatorname{div}\left(\hat{\tilde{\mathrm{D}}}\nabla\tilde{c}^\epsilon - \tilde{c}^\epsilon\hat{\tilde{\mathrm{M}}}\nabla\tilde{\psi}^{\theta,\epsilon}_{\mathrm{HS}}\right) = \tilde{f} \quad \text{in } D := [0, L]^d, \tag{1}$$

where $\tilde{f}$ is a steady external source/sink, the heterogeneity $\epsilon := \frac{\ell}{L}$ is defined by the characteristic/average distance ℓ between rigid spherical hard-sphere particles p that are impenetrable for the species s. L is the characteristic length scale of the entire composite comprising the solid particles p and species s, and $d \in \mathbb{N}_{>0}$ is the dimension of space. The identification of a characteristic volume element, which contains the spherical hard-sphere obstacle p surrounded by species s, see Fig. 1, allows us to systematically account for stochasticity induced by the random location of the obstacles' barycenter $\mathbf{y}_b^\epsilon$.

The tensors $\hat{D}$ and $\hat{M}$ in (1) are the diffusion and mobility tensors, respectively. The hard-sphere repulsion[1] in (1) appears in regularized form as follows,

$$\tilde{\psi}^{\theta,\epsilon}_{\mathrm{HS}} := \begin{cases} \delta_\theta(r^\epsilon_{ps} - \sigma) & \text{if } r^\epsilon_{ps} \geq \sigma, \\ \delta_\theta(0) & \text{if } r^\epsilon_{ps} < \sigma, \end{cases} \tag{3}$$

where δ_θ is a Gaussian regularization of the Dirac delta function $\delta(x)$, $x \in \mathbb{R}$, that means, $\delta_\theta(x) := \frac{1}{\theta\sqrt{\pi}}\mathrm{e}^{-\frac{x^2}{\theta^2}}$, and $\sigma := R_p + R_s$ is the hard-sphere radius composed of the solid particle radius R_p and species radius R_s. We note that the parameter θ in (3) can be physically chosen such that repulsive walls of Lennard-Jones-type are obtained. Finally, the variable r^ϵ_{ps} describes the distance between the barycenter of species s and the surface of particle p, i.e., $r^\epsilon_{ps}(\mathbf{x}) := |r(\mathbf{x}/\epsilon, \mathbf{y}^\epsilon_b) - R_p|$, $\mathbf{x} \in D$, where $\mathbf{y}^\epsilon_b$ describes the barycenter of the nearest solid particle p by

$$\mathbf{y}^\epsilon_b(\mathbf{x}; \omega) := \mathbf{y}_b(\tau_{\mathbf{x}/\epsilon}\omega), \tag{4}$$

where $\tau_{\mathbf{x}} : \Omega \to \Omega$ is a *d-dimensional dynamical system* on the probability space $(\Omega, \mathcal{F}, \mathbb{P})$, that is: $\tau_{\mathbf{x}}$ is measure preserving; $\tau_{\mathbf{x}}$ is invertible and the set $\left\{(\mathbf{x}; \omega) \in D \times \Omega \,\middle|\, \tau_{\mathbf{x}}\omega \in \mathcal{F}\right\}$ is $d\mathbf{x} \times d\mathbb{P}$-measurable; and $\tau_{\mathbf{x}}$ satisfies the group property: $\tau_{\mathbf{x}+\mathbf{y}} = \tau_{\mathbf{x}} \circ \tau_{\mathbf{y}}$ where $\tau_{\mathbf{0}}$ denotes the identity map.

The barycenters $\mathbf{y}_b(\omega) \sim \mathcal{U}(\mathcal{Y})$ are uniformly distributed in the domain $D \subset \mathbb{R}^d$ and form an *i.i.d.* random variable with the distribution function $\mathbb{P}_{\mathcal{Y}}(A) := \frac{\mathcal{L}(A)}{(b_u - b_l)^2}$ for the Lebesgue measure $\mathcal{L}$, for all $A \in \mathcal{B}(]b_l, b_u[^2)$

[1] The standard hard-sphere potential avoids the parameter θ, which weights the strength of repulsion in (3), i.e.,

$$\tilde{\psi}^\epsilon_{\mathrm{HS}} := \begin{cases} 0 & \text{if } r_{ps} \geq \sigma, \\ \infty & \text{if } r_{ps} < \sigma. \end{cases} \tag{2}$$