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Title:

Problems of Shape and Information in Multiscale Modeling of Transport Phenomena

Abstract approved: _

Brian D. Wood

This work is a compilation of problems that deal with multiscale analysis of transport phenomena in environmental systems. A common feature among the problems studied here is the presence of non-negligible microscale structure in various forms. Each problem is approached from the perspective that a macroscopic observable encodes aspects of the structure on the smaller scales. In some cases, the presence of microscopic structure transforms the macroscopic dynamics in a non-trivial fashion that would be virtually unpredictable without proper upscaling. The different types of microscale structure studied here include stationary morphological information (as would be encountered in porous materials), segregation of mass (as would be seen in a poorly mixed system), molecular-scale structural heterogeneities (i.e. surface roughness), and evolving morphologies (in biofilm growth in porous media). A major focus is porous media systems, and most of the multiscale analyses are performed in the context of the method of volume averaging. [©]Copyright by Sassan Ostvar March 1 2017 All Rights Reserved

Problems of Shape and Information in Multiscale Modeling of Transport Phenomena

by

Sassan Ostvar

A DISSERTATION

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Sassan Ostvar, Author

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CONTRIBUTION OF AUTHORS

The volume-averaged reactive transport model in Chapter 3 was developed by Dr. Brian Wood. Simulations of pore-scale flow reported in Chapter 4 were conducted in close collaboration with Bryan He and Dr. Sourabh Apte of the Computational Flow Physics lab at OSU.

TABLE OF CONTENTS

1	Intro	oduction	1	
	1.1	shape processing in pore-scale diffusion	2	
	1.2	kinetics of mixing-limited reactions	3	
	1.3	pore-scale flow and closure for Darcy's law	4	
	1.4	multiscale adhesion of rough soft interfaces	4	
	1.5	biofilm-induced pressure fluctuations in confined porous media	5	
	1.6	where does (persistent) structure come from?	6	
~	C1		_	
2	Shaj	pe processing in spatially-averaged diffusion through hierarchical porous media	7	
	2.1	Introduction	8	
	2.2	Background	9	
		2.2.1 Setup for spatially-averaged diffusion	9 11	
		2.2.3 Localized closure	$11 \\ 12$	
		2.2.4 Effective diffusivity	14	
		2.2.5 Local effective diffusivity	15	
		2.2.6 Symmetry of \mathbf{D}	16	
	2.3	Methods	17	
	2.4	Results	17	
		2.4.1 isotropic crystalline structures	17	
		2.4.2 anisotropic crystalline structures	18	
	2.5	Discussion	18	
	2.0	2.5.1 Role of shape in transport	20	
	2.6	Conclusions	20	
	2.7	Localization of the closure problem	21	
	2.8	Conservation of \mathbf{b}_{γ}	22	
3	A n	on-scale-invariant form for diffusion-reaction equations	26	
	3.1	Introduction	27	
	3.2	Microscale balance equations	29	
	3.3	Averaging	31	
	3.4	Deviation equations	33	

TABLE OF CONTENTS (Continued)

			Page
		 3.4.1 Localization of the closure problems	34 36 38
	3.5	Closed problem	41
	3.6	Examples of computing the effective parameters	43 49 55 56
	3.7	Summary and Conclusions	57
	3.8	Solution to the diffusion-reaction problem	58 58 61 63
	3.9	Validation of the inequality given by Eq. 3.32	64
4	Con	nputational pore-scale closures for Darcy's law	66
	4.1	Preface	67
	4.2	Goals for this study	69
	4.3	Simulation of fluid flow in porous media	69 70
	4.4	Computation of the permeability tensor	70 70 71 73
		4.4.4 Flow in confined and triply-periodic REVs	74
5	Mul	tiscale Model Describing Bacterial adhesion and Detachment	77
	5.1	Introduction	78
	5.2	Model	81 83 85 86
	5.3	Simulations	87 88

TABLE OF CONTENTS (Continued)

		Page
5.4	Results	90
5.5	Discussion	92
	5.5.1 Adhesion as a multiscale process	92
	5.5.2 Model performance	94
	5.5.3 Surface roughness	95
	5.5.4 The role of roughness in the biology of adhesion $\ldots \ldots \ldots \ldots$	96
5.6	Conclusion	97
ppend	lices	100
.1	Background	102
.2	Flow experiments	103
.3	Time series analysis	104
.4	Conclusions	107
Bibliogi	raphy	108

LIST OF FIGURES

Figure		Page
1.1	Multiscale organization of transport phenomena in natural systems. A river embodies many of the scenarios where structure and transport interact.	3
2.1	Schematic illustrating the setup for the diffusion problem in a hierarchical two-phase medium. Level I, or the <i>microscale</i> , is characterized by the pore length scale L_p , and Level II, or the <i>macroscale</i> , by the length scale L . Averaging is performed over a support scale defined by the length scale L_s . The three length scales satisfy the relationship $L_p \ll L_s \ll L$.	10
2.2	Schematic for the concept of a representative elementary volume (REV). The REV is used to model the spatial fluctuations, $\tilde{\psi}$, around the averaged field $\langle \psi \rangle^{\gamma}$. The REV is defined on the length scale $L_{REV} \gg L_p$. The vectors x and y locate the centroid of the REV and arbitrary points inside the REV, respectively.	11
2.3	Topology of the \mathbf{b}_{γ} field for isotropic unit cells (left to right: monodisperse face-centered cubic (fcc) disk array, bidisperse disk array, and monodisperse simple-cubic ellipse array with orientation bias). In the visualizations, blue dots denote saddles, red dots denote sinks, red curves denote attracting periodic orbits, and black curves denote source boundaries.	18
2.4	Anisotropy, β_D , of the effective diffusivity tensor for a set of 2D and 3D anisotropic unit cells. The ratio is sensitive to the dimensionality and placement of ellipses and ellipsoids. The case of a body-centered fully-oriented ellipse array has been highlighted. The inflection point in the tensor anisotropy curve (marked by a vertical dashed line in A) corresponds to a first-order transition in the topology of \mathbf{b}_{γ} (pre- and post-transition vector fields are depicted in B and C, respectively).	19
3.1	A multiscale representation of the initial condition for a diffusion-reaction system. The two chemical species are denoted by the green (species A) and blue (species B) colors. The system is characterized by two characteristic lengths: the macroscale length, L , and the microscale length ℓ . A third length is defined by the support scale of the averaging volume, r_0 . A separation of length scales is assumed, such that $\ell \ll r_0 \ll L$.	30
3.2	A representation of a mirror-image arrangement of unit cells	37

LIST OF FIGURES (Continued)

Figure		Page
3.3	Cases 1-3. (Left) The configuration of the initial condition. (Center) The (normalized) effective reaction rate and source terms. (Right) Comparison of the upscaled model (blue lines with filled circles), the asymptotic model ($\eta_B = 1, \hat{s}_B = 0$), and direct numerical simulations (DNS) (black solid lines). These results are for $Da = 100$.	48
3.4	Case 4. (Left) The configuration of the initial condition. (Center) The (nor- malized) effective reaction rate and source terms. (Right) Comparison of the upscaled model (blue lines with filled circles), the asymptotic model $(\eta_B = 1, \hat{s}_B = 0)$, and direct numerical simulations (DNS) (black solid lines). These results are for $Da = 100$.	50
3.5	An example segmentation and Voronoi tessellation for cases 1 and 2	52
3.6	The functions η_B and η'_B for Case 3. The parameters $A_{\eta'_B}$, $\bar{t}_{\eta'_B}$, and $\eta'_{B,max}$ are illustrated to aid interpretation.	53
3.7	The correlation between the product $\bar{t}\eta'_{B,max}$ (approximate measure of deviation from classical kinetics) and the normalized characteristic length, ℓ (approximate measure of initial spatial segregation).	55
3.8	Asymptotic behavior of the system for the four initial conditions at $Da = 1, 10$, and 100. Note that in each of the four cases, the late-time reaction rate is exponential with identical constants; this is consistent with classical kinetics. The early-time dynamics of each curve, however, is greatly modified by the initial conditions as Da increases.	56
2.0		

3.9The ratio given in (3.32) as a function of normalized time for the four initial 65

- (A) Drag coefficient (4.11) as a function of solid volume fraction 1ϕ in a 4.1 simple-cubic array of spheres. (B) Comparison of the permeability obtained for the experimental system in [192] (dashed horizontal line), and direct simulations using the fictitious domain method in different REV sizes. Here $\kappa \equiv K_{\xi\xi}$ for flow in the ξ -direction. 71
- 4.2(A) Schematic illustrating the setup for calculating the spatial pressure fluctuations, \tilde{p} . (B) Test of the linearity of pressure drop along the flow direction in a simple cubic array of 3 spheres with periodic side boundaries. 72

LIST OF FIGURES (Continued)

Figure		$\underline{\text{Page}}$
4.3	Streamwise velocity components normalized by their superficial average value for (a) simple-cubic case of [200], (b) a triply periodic monodisperse sphere packing with 8 particles, and (c) a triply periodic monodisperse sphere pack- ing with 40 particles. Note that to improve the visualization, we have allowed the color scheme to vary between the subfigures.	74
4.4	Confined vs periodic vdfs in monodisperse packings of spheres with $\phi = 0.44$. Confinement biases the transverse components of the velocity field in favor of the streamwise component. The transverse vdfs are more symmetric in comparison for the periodic REVs.	76
5.1	Surface roughness on bactera. (A) An SEM image of <i>Burkholderia cepacia</i> showing polymers on the order of 50 nm on the surface. (B) An AFM image of an 0.8 μ m by 0.8 μ m area of a single cell of <i>Escherichia coli</i> JM109 (SF815A) imaged at the nanoscale (data from Amro et al.[6]). (C) Length distribution for the data associated with Figure 1B. (D) A quantile-quantile analysis shows that surface features are approximately normally distributed, but show some evidence of the distribution being short-tailed.	80
5.2	Schematic representation of the two-scale interaction between the cell surface polymers and a substratum (AFM sphere probe) on approach and retraction. The process of adhesion is characterized by highly local short-range forces between the part(s) of polymer molecules that come in contact with the probe, and longer-range forces arising due to the compression or extension of the chains. Figure adapted from Ginn et al.[62]	82
5.3	(A) Geometrical setup of the problem defined by eq 5.6. The polymer base is assumed to be stationary. (B) A force balance for the bead-polymer system in a state of attraction toward the substratum (i.e. chain extension).	84

LIST OF FIGURES (Continued)

Figure

5.4	The landscape for a single polymer molecule. Maximum forces generated by the L-J potential obtained via a parametric sweep of ϵ and σ in eq 5.4 (back- ground contours). Superimposed are the proposed energy scales of inter- molecular hydrogen bonds[78, 83] (inclined hatches), bounds for (experimen- tally obtained) bacterial single-molecule specific forces [25] (dotted region), hydrogen bond strengths statistically inferred from AFM measurements on <i>L. monocytogenes</i> [64] (blue squares) and <i>E. coli</i> [3] (triangle) fitted to eq 5.4, and the parametrization used in the present study (crosses). The labeled con- tour lines mark the upper bound and mean of the measurements complied by Busscher et al.[25].	88
5.5	Sample force-distance profiles for linear (A and B) and nonlinear (C and D) models with different generator distributions for ℓ_{eq} (insets). Bond strengths are tuned to $\epsilon = 5$ kT and $\sigma = 0.5$ nm. Linear chains are constructed with $k_{chain} = 0.01$ N/m, and nonlinear chains with $k_{chain} = 0.0002$ N/m and the values of ℓ_{eq} , ℓ_c , and ℓ_p as reported in Table-5.1. $s_{\ell_{eq}}/\ell_{eq} = 3$, and $N_p = 100$ in all simulations.	91
5.6	Sample adhesion energy profiles for the linear (A) and nonlinear (B) models, describing $N_p = 100$ chains. Linear brushes are constructed using $\epsilon = 5$ kT, $\sigma = 0.5$ nm, and $k_{chain} = 0.01$ N/m. Nonlinear brushes are constructed using the same bond strength, $k_{chain} = 0.002$ N/m, and the values of ℓ_{eq} , ℓ_c , and ℓ_p as reported in Table-5.1. While decreased by heterogeneity in the linear brush, the total adhesion energy stored in a nonlinear brush remains largely unaffected even for large standard deviations in ℓ_{eq} (note the difference in length and energy scales in the two plots).	93
5.7	(a) An example of the force-distance curve for a trimodal brush (parameters are the same as in Figure 5.5). (b) An example of an AFM measurement on <i>S. epidermidis</i> reproduced from Chen et al. [33]. We observe significant qualitative similarities between our modeled results and observations, and	

the role of surface roughness is consistent with the discussion of adhesion properties provided by the authors [33].

Page

94

LIST OF TABLES

<u>Table</u>		Page
3.1	Parameters used in the simulations	47
3.2	Parameters associated with the geometry and reaction properties of the four initial configuration cases.	54
5.1	Ranges of parameters used in the simulations	90
5.2	List of Symbols	99

LIST OF APPENDIX FIGURES

Figure		Page
8	Schematic of the flow experiments (A), and a sample of the imaged biofilm (B). In (B), biofilm=blue, and grains=gray.	104
9	spectral analysis	105
10	(A) Scaling of the power spectral density, $S(f)$, of the pressure drop time series at different loading Reynold's numbers. Pressure fluctuations show a smooth transition from near-Brownian scaling at Re=0.1 to pink noise scaling at Re = 10. (B) Block entropy and entropy rates for the 6 columns - all samples have vanishing entropy rates. (C) Excess entropies associated with (B) as a function of loading Reynolds number	107

$\mathbf{D}_{\mathbf{f}}$

To Maman Parvin, with love.

Chapter 1 – Introduction

HYSICAL reality is manifestly hierarchical. Objects emerging on one spatial scale come together to shape new objects, interactions, and phenomena on larger scales. The task of understanding the nature of a system in terms of the dynamics of its microscopic constituents is a canonical problem in physics and engineering, and serves as a cornerstone in both the top-down program of the 20th century and the bottom-up approach of the 21st century in pursuit of universal physical laws [7]. Multiscale thinking and analysis takes center stage in modern engineering as well, as systems of practical interest grow in size, age, and complexity, and practices of design, prediction, and control, increasingly rely on mathematical modeling and simulation.

A central concept in multiscale analysis is the idea of coarse-graining, where microscopic degrees of freedom are aggregated into *effective* representations to render the dynamics of a system more tractable mathematically and computationaly. The archetypical example for efficient coarse-graining is the ideal gas law that results from modeling $\sim 10^{23}$ microscopic degrees of freedom with the Boltzmann distribution [145]. A marvel of data compression, the ideal gas law allows for heterogeneity in observables (particle positions and momenta), but describes a system that is almost entirely void of microscopic structure. In other words, save for their specific thermodynamic state, instances of the ideal gas are entirely interchangeable. In contrast, spatially extended physical systems can embody microscopic fluctuations due to variations in some structural aspect of their constituents. This work is an exploration of situations where the unique aspects of the structure of microscale fluctuations lead to measurable variation in macroscopic observables or dynamics.

I explore five problems of this sort as they arise in multiscale modeling of transport phenomena in natural and designed environments (Figure 1.1). In each problem I study how (i) a coarse-grained observable carries microscale information, and/or (ii) how the presence of structure affects the nature of coarse-grained dynamics. In Chapters 2 and 4, I study pore-scale transport in porous media, the focus being on understanding and computing the effective diffusivity and permeability tensors from pore-scale information. The microscopic feature of interest here is the morphology of impermeable phase interfaces. In Chapter 3, we explore anomalous reaction kinetics induced by incomplete mixing of reactants. The microscopic structure of interest here is the initial distribution of mass in the system, and the focus is on the rate of relaxation of coarse-grained kinetics to their asymptotic value as a function of the degree of segregation in initial conditions. In Chapter 5, I develop a multiscale model for the adhesion of rough soft interfaces. By treating an adhesive interface as a collection of individual adhesive constituents, I explore how heterogeneities in length and elasticity of these constituents can shape the potential energy function that describes the adhesion of the interface. Finally, in the Appendix, I study the noise in the bulk pressure drop measured across a confined porous medium that is subject to biofilm growth under flow, and its implications for the predictability of biofilm-induced transformation of pore spaces.

The nature of the microscale fluctuations in these different problems varies in significant ways. In Chapters 2 and 4 microscale interfaces are stationary, in the sense that they do not evolve over the timescales that transport takes place in; we are interested in the effects of these structures on transport properties as stationary observables. Similarly in Chapter 5, save for deformations, the makeup of the cell surface is invariant over the time-scales that an adhesion event take place. In contrast, in Chapter 3, the initial distribution of mass dissipates over time. We are interested in how this initial structure affects the macroscopic rates by promoting transience in rate constants and memory terms. In the Appendix, the evolving structure of the pore space (due to biofilm growth) is the generator of noise.

In the remainder of this chapter, I will introduce each problem in greater detail.

1.1 shape processing in pore-scale diffusion

The physics of transport in porous media are deeply influenced by processes at the pore scale. In Chapter 2, I explore the mathematics of how the effective diffusivity tensor of homogeneous porous media encodes the shape of a pore space. When the method of volume averaging is used to derived the coarse-grained diffusion equation, the tensor is defined in terms of a *closure variable*, i.e. an ancillary field variable that maps macroscopic gradient information to microscale spatial fluctuations in the dynamical variable of interest. I discuss a geometric interpretation of this vector field, and provide computations as well as visualizations for a number of crystalline and random arrangements of particles with varying anisotropies. I frame the study as a proposal that the closure variables of the method of



Figure 1.1: Multiscale organization of transport phenomena in natural systems. A river embodies many of the scenarios where structure and transport interact.

volume averaging can be understood as mechanism-specific processors of shape information.

1.2 kinetics of mixing-limited reactions

Chapter 3 deals with anomalous kinetics in a confined mixing-limited system, described by the catalytic reaction $B \xrightarrow{A} C$. Here we are focused on the rate of transformation of B in instances where A and B are initially highly segregated and mix via diffusion. We set up the problem as a special case of a general reactive transport model derived using the method of volume averaging with local closure [125]. If the microscopic reaction is fast enough, incomplete mixing at early times hinders the effective macroscale reaction. We describe the non-classical progression of the reaction as a consequence of both (i) a preasymptotic effective rate of reaction that is relaxing toward the classical value, and (ii) an external source term. The latter indirectly measures the spatial correlations between A and B and represents it as a macroscopic source term for B. We show that for highly segregated initial conditions, this source term is not negligible at early times, and the effective rate of reaction can remain pre-asymptotic over the global reaction timescale.

Our results suggest that the deviation from classical kinetics can be expressed as $\xi \sim Da^{\delta} \ell^{\alpha}$, where ℓ is an appropriate microscopic diffusive length scale, and the Damköhler number, Da, measures the relative timescales of diffusion and reaction. We estimate ℓ to be on the order of a the mean equivalent diameter of coherent subdomains that are exclusively occupied by one reactant at t = 0. Large clusters and fast reactions lead to the most deviation from classical rates. We also observe that a local closure for the theory is valid for bi-symmetric initial conditions. Configurations that induce persistent macroscopic fluxes can cause instabilities in the local model and require a nonlocal treatment.

1.3 pore-scale flow and closure for Darcy's law

Chapter 4 serves as the second half of a forthcoming monograph on upscaling the Stokes equations to obtain Darcy's law. The work is a reinterpretation of the application of volume averaging to Darcy flow via the Stokeslet. The material presented in this chapter is the computational component of the work that provides closure for Darcy's law by resolving the pore-scale velocity and pressure fields via high-fidelity direct numerical simulations. The analysis is constructed around a representative elementary volume analysis for an experimental dataset. We use periodically disorderd packings of monodisperse spheres as models of the pore space, and study the structure of the velocity and pressure fields. We also compute the permeability tensor for these structures, and compare the results to the ones obtained for the experimental system. We discuss how the flow field varies for sample of different sizes, and in response to confinement.

1.4 multiscale adhesion of rough soft interfaces

Chapter 5 deals with the adhesion of bacteria to mineral or synthetic surfaces. Cell surfaces are *soft* because they are deformable, and are rough because they are made up of diverse constituents with different molecular structures and average lengths. The motion of bacteria in fluid environments is affected by adhesion, especially in porous media where cells are likely to encounter interfaces and surfaces frequently. In multiscale approaches to modeling motion, bacteria are often thought of as individual particles that form an effective macroscopic bond with surfaces. To represent this bond, it has been common to borrow

chapter	macroscale observable	microscale (structural) fluctuations
2	effective diffusivity	morphology of phase interfaces
3	bulk kinetics	initial distribution of mass
4	permeability	morphology of phase interfaces
5	potential energy function of adhesion	polymer lengths and elasticities
appendix	bulk pressure drop	morphology of biofilm-fluid interfaces

potential energy functions originally developed to describe the motion of particulate matter like suspended colloids.

Instead I explore constructing the potential energy function out of the smaller-scale micromechanics of surface polymers, the idea being that for complex surfaces adhesion can be a consequence of a finite number of bonds between exposed macromolecules and mineral surfaces. In this setting, heterogeneities in length (roughness) and in the mechanical properties of surface macromolecules can be encoded into the net potential energy function of the surface. Our results show that length heterogeneities lead to the emergence of metastable states in the potential function. We also find that nonlinear elasticity combined with length heterogeneities can create a scenario where roughness is advantages for a cell that benefits from being surface-bound.

1.5 biofilm-induced pressure fluctuations in confined porous media

The Appendix originated from a 3D imaging study of biofilm growth under flow in model bead pack columns [77] conducted in Dr. Dorthe Wildenschild's lab. Biofilm was grown in model porous media in these experiments over a span of ~ 2 weeks, after which they were interrupted and the columns imaged using a synchrotron-based x-ray microtomography method. Continuous transducer readings of bulk pressure drop across these columns are noisy and fluctuate on multiple timescales. We can understand this noise originating in the coupled dynamics of flow and biofilm growth. I study the information content of these signals in an attempt to answer (i) whether or not the point at which the experiment was terminated was representative, and (ii) if biofilm-altered flow in porous media can access states that are stochastic but still (macroscale) predictive in a meaningful way.

1.6 where does (persistent) structure come from?

The antecedent processes that generate the structures studied in this work are irrelevant, but it behoves the discussion to briefly discuss some of them. Shapes and patterns in nature generally have dynamical origins [172], and these dynamics are often transport-related [131], but the dynamics that generate the shapes studied in this work can be ad hoc. The morphological information discussed in Chapters 2 and 4 could be geological (as in sand, rock, etc.), biological (as in fibrous materials) or even synthesized (as in topology-optimized 3D printed media).

For the purposes of this work, these structures are quenched or 'frozen in'. This assumption preserves the linearity of the diffusion and Stokes equations. Conversely, the morphological information in the Appendix originates in the ongoing interaction of flow and cell growth, making it an inherently nonlinear (feedback-driven) process.

The structure of bacterial surfaces in Chapter 5 is believed to emerge out of the an intricate dynamical system involved in the determination of polymer lengths. The problem of O-antigen chain length control in gram-negative bacteria is particularly well-known and currently studied in biophysics [90]. In this case, structure is an output of an adjacent dynamical system. For the purposes of our study, we are assuming that the timescales associated with the structural evolution of these surfaces are much longer than those of adhesion events.

Finally the origins of structure can be arbitrary or even ad hoc. For instance, the segregated initial distributions discussed in Chapter 3 could represent the accidental dump of contaminants into a stagnant environment.

Chapter 2 – Shape processing in spatially-averaged diffusion through hierarchical porous media

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Abstract

We study the relationship between the morphology of impermeable phase interfaces and the effective diffusivity of porous media in the context of volume averaging. We show that the effective diffusivity tensor is defined in terms of a microscale vector field that encodes purely morphological information. We show that the vector field is globally shape-aware and provide visualizations of its structure in a variety of 2D and 3D periodic models for two-phase porous materials.

2.1 Introduction

A defining characteristic of transport in porous materials is the prevalence of phase interfaces and the constraints that they impose on motion. The relationship between the information contained in phase interfaces and effective transport properties of porous media has been of theoretical and applied interest across the board. The transient inverse problem for passive diffusion is particularly well-known [85] and fundamental to imaging applications [108]. The forward problem for diffusion with or without forced convection appears in design of materials (e.g. for energy applications), and multiscale analysis of environmental systems among others.

In the Fickian regime, diffusion through porous media is characterized by an effective diffusivity, based on the notion that a coarse-grained (effective) flux, \mathbf{J}^* , can be constructed that describes the evolution of an associated coarse-grained scalar field, Ψ^* , as $\mathbf{J}^* = \mathbf{D} \cdot \nabla \Psi^*$, where the tensor \mathbf{D} carries the influence of microstructure.

The earliest computation of **D** for porous media is Maxwell's solution for a periodic regular array of circular inclusions near infinite dilution [106], at the limit where one phase is impermeable. Maxwell's solution is now understood to be the Hashin-Shtrikman bound for this particular problem [69]. Subsequent work on other geometries has shown that porosity is a fairly accurate predictor of the diagonal components of **D** in ordered isotropic structures, but higher-order quantifiers of shape or spatial correlations are needed to describe anisotropic or disordered media (e.g. [122]).

In this letter, we study **D** in a context where J^* and Ψ^* are interpreted as spatial averages of microscale information. The tensor **D** is shown to be defined in terms of the gradient of a microscale vector field that naturally arises in the theory and encodes morphological information. We study the topology of this vector field for a variety of structures. We propose that the structure of this field (and its counterparts for other transport problems) provides a natural approach to understanding how the morphology of the impermeable phase affects the effective diffusivity of the conductive phase. We are particularly interested in how this approach can be used in conjunction with recent work using global morphology [107, 144].

2.2 Background

In this section we will briefly revisit the theoretical framework for developing the spatially averaged diffusion equation, and derive the effective diffusivity tensor. The analysis is based on the Neumann problem for the diffusion of a tracer in a percolating medium with reflecting interfaces. For simplicity, we will restrict the analysis to two levels or operational scales, but the study can be trivially extended to multi-level systems [30].

2.2.1 Setup for spatially-averaged diffusion

Consider the domain \mathcal{V} enclosed by boundary $\partial \mathcal{V}$ that is defined as the union of impermeable phase κ and conductive phase γ

$$\mathcal{V} := \mathcal{V}_{\gamma} \cup \mathcal{V}_{\kappa},\tag{2.1}$$

where the two phases are separated by the boundary $\mathcal{A}_{\gamma\kappa} \approx \partial \mathcal{V}_{\gamma}$). And consider the piece-wise smooth scalar field ψ undergoing diffusion in \mathcal{V}_{γ} as described by

$$\frac{\partial \psi}{\partial t} = \nabla \cdot (\mathcal{D}_{\gamma} \nabla \psi)
- \mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{\gamma} \nabla \psi = 0 \quad \forall \mathbf{r} \in \mathcal{A}_{\gamma\kappa}$$
(2.2)

with arbitrary initial conditions and Dirichlet or Neumann conditions on $\partial \mathcal{V}$. Diffusion takes place in the γ -phase (i.e. *pore* space) over the length scale L_p on time scale T_{ψ}^* (figure 2.1). Next, consider a spatial averaging operator defined using a weight function, w, with compact support on \mathcal{V}_{γ} and applied to ψ :



Figure 2.1: Schematic illustrating the setup for the diffusion problem in a hierarchical twophase medium. Level I, or the *microscale*, is characterized by the pore length scale L_p , and Level II, or the *macroscale*, by the length scale L. Averaging is performed over a support scale defined by the length scale L_s . The three length scales satisfy the relationship $L_p \ll L_s \ll L$.

$$\langle \psi \rangle |_{(\mathbf{x},t)} = \int_{\mathbf{r} \in \mathcal{V}_{\gamma}(\mathbf{x})} w(\mathbf{x} - \mathbf{r}) \psi(\mathbf{r}, t) \, dV(\mathbf{r}).$$
 (2.3)

The weight function is supported on the length scale L_s , chosen such that $L_p \ll L_s$ to ensure that averaging is performed on volumes that filter out small-scale fluctuations on the order of L_p [134]. For simplicity, we will adopt the function $w = 1/\mathcal{V}_{\gamma}$.

The action of (2.3) results in the coarse-grained field $\langle \psi \rangle^{\gamma}$, where the superscript implies averaging over the conductive phase.



Figure 2.2: Schematic for the concept of a representative elementary volume (REV). The REV is used to model the spatial fluctuations, $\tilde{\psi}$, around the averaged field $\langle \psi \rangle^{\gamma}$. The REV is defined on the length scale $L_{REV} \gg L_p$. The vectors **x** and **y** locate the centroid of the REV and arbitrary points inside the REV, respectively.

2.2.2 Perturbation analysis

Next we are interested in reformulating (2.2) in terms of an averaged scalar field and spatial fluctuations around it. This involves implementing the following spatial decomposition [66]:

$$\psi(\mathbf{x},t) = \langle \psi \rangle^{\gamma} |_{(\mathbf{x},t)} + \tilde{\psi}(\mathbf{x},t), \qquad (2.4)$$

that is, at each point $\mathbf{x} \in \mathcal{V}$, the point-wise and averaged scalar fields are related via a spatial fluctuation field $\tilde{\psi}$ also defined on \mathcal{V}_{γ} .

Averaging of the Fickian diffusion problem using (2.3) has been outlined extensively in the literature [185, 110, 195]. After the application of (2.4) and the interfacial boundary conditions, the most general averaged form of (2.2) is

$$\frac{\partial \langle \psi \rangle^{\gamma}}{\partial t} = \nabla \cdot \left(\mathbf{J}_{\langle \psi \rangle^{\gamma}} + \mathbf{J}_{\phi} + \mathcal{N} \langle \psi \rangle^{\gamma} + \mathcal{N} \tilde{\psi} \right), \qquad (2.5)$$

where the nonlocal operator \mathcal{N} acting on a scalar field φ is defined as:

$$\mathcal{N}\varphi = \frac{\mathcal{D}_{\gamma}}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \varphi \, dA.$$
(2.6)

The contribution of the impermeable phase appears as two nonlocal surface fluxes and

a convective flux. $\mathcal{N}\langle\psi\rangle^{\gamma}$ and $\mathcal{N}\tilde{\psi}$ constitute/represent nonlocal diffusive fluxes for the average and fluctuation fields, $\mathbf{J}_{\phi} = (\mathcal{D}_{\gamma}\nabla\phi)\langle\psi\rangle^{\gamma}$ is a *geometric* convective flux that responds to macroscopic porosity gradients, and $\mathbf{J}_{\langle\psi\rangle\gamma} = \mathcal{D}_{\gamma}\langle\psi\rangle^{\gamma}$ a local diffusive flux. Nonlocal (or macro-) diffusion characterizes memory-driven systems, e.g. media with (strong) long-range disorder. Despite being representative, nonlocal models can be challenging to implement in practice. It is also unclear if a coarse-grained model like (2.5) is optimal in the sense of [189].

We are interested in problems where the evolution of $\langle \psi \rangle^{\gamma}$ is more or less driven by local information. We can show that this is the case for media with negligible macroscopic inhomogeneities. We can define this class of materials more precisely in terms of a series of spatial quasi-stationarity conditions that can be shown to imply that the macrodiffusive term $\mathcal{N}\langle\psi\rangle^{\gamma}$ is zero [185, 194].

One could argue that the term \mathbf{J}_{ϕ} is likely to vanish too for media that are reasonably homogeneous on the macroscale and averaged on a proper support scale. We will assume this is the case. Since this term does not require closure, the structure of the forthcoming analysis would not change should one decide to keep it. Homogenized models of transport in macroscopic porosity gradients is the subject of ongoing research [24] and have found interesting applications, for instance in maximizing the lifespan of materials that evolve toward a non-percolating state [38, 39].

We are also interested in situations where a subset of \mathcal{V} , or a so-called representative elementary volume (REV), exists such that spatial fluctuations everywhere in \mathcal{V} are very similar and therefore interchangeable with those in this volume. An REV, when valid, significantly reduces the number of causal microscale degrees of freedom in the problem by (i) making smaller the domain over which a microscale solution is saught, and (ii) eliminating the dependence of the microscale problem on external boundary conditions. The latter are usually replaced with periodic boundary conditions (figure 2.2).

2.2.3 Localized closure

When these approximations are valid, the homogenized equation simplifies to [195, 185, 194]:

$$\frac{\partial \langle \psi \rangle^{\gamma}}{\partial t} = \nabla \cdot \left[\mathcal{D}_{\gamma} \left(\nabla \langle \psi \rangle^{\gamma} + \frac{1}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \,\tilde{\psi} \, dA \right) \right]$$
(2.7)

At this point, (2.7) requires closure for the nonlocal term $\mathcal{N}\tilde{\psi}$. The functional form of the spatial fluctuation field is a solution to the evolution equation that is found by subtracting (2.7) from (2.2)

$$\frac{\partial \tilde{\psi}}{\partial t} + \nabla \cdot \left[\frac{\mathcal{D}_{\gamma}}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \; \tilde{\psi} \; dA \right] = \nabla \cdot \left(\mathcal{D}_{\gamma} \nabla \tilde{\psi} \right) \tag{2.8}$$

and the associated boundary conditions:

$$-\mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{\gamma} \nabla \tilde{\psi} = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{\gamma} \nabla \langle \psi \rangle^{\gamma}}_{\text{interfacial source}} \quad \mathbf{x} \in \mathcal{A}_{\gamma\kappa}$$
(2.9)

$$\tilde{\psi}(\mathbf{r}+\ell_i) = \tilde{\psi}(\mathbf{r}) \quad i = 1, 2, 3 \tag{2.10}$$

$$\langle \tilde{\psi} \rangle^{\gamma} = 0 \tag{2.11}$$

Note that (2.8) allows for time-dependent fluctuations. Often, on short time scales when the initial conditions still dominate the problem, the time evolution of the fluctuations cannot be neglected. Once the initial conditions have smoothed out sufficiently, we can consider a temporal regime where $\langle \psi \rangle^{\gamma}$ evolves much more slowly than $\tilde{\psi}$, i.e. $\mathcal{O}(T^*_{\tilde{\psi}}/T^*_{\langle \psi \rangle^{\gamma}}) \ll 1$. When this approximation is valid, the two scales are temporally separable, and the problem for $\tilde{\psi}$ essentially stationary from the perspective of the evolution of $\langle \psi \rangle^{\gamma}$. Passive diffusion in homogeneous media has been shown to relax its initial state fairly quickly [110]. Transient closure problems are often essential to the macroscale behavior of problems where the initial conditions can persist beyond early times, e.g. in mixing-limited reactive systems [125].

It is equally desirable to justify the elimination of the nonlocal term in (2.8), however the arguments for this are generally more or less intuition-based. Briefly, we can argue that local evolution is likely much more strongly influenced by derivative than integral information.

The problem for $\tilde{\psi}$ has the following general solution in terms of the Green's function

G [195]:

$$\tilde{\psi}(\mathbf{y}) = -\int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} \left[\mathbf{n}_{\gamma\kappa}(\mathbf{z})G(\mathbf{y};\mathbf{z})\cdot\mathcal{D}_{\gamma}\nabla_{z}\langle\psi\rangle^{\gamma}|_{\mathbf{z}}\right] dA(\mathbf{z}).$$
(2.12)

The spatial convolution of the interfacial source in (2.12) implies very close coupling between the average and fluctuations, since $\nabla \langle \psi \rangle^{\gamma}$ has to be evaluated at every point in the REV. Closure of (2.7) using (2.12) therefore results in a nonlocal equation. In the original work on spatial averaging, the spatial fluctuations were posited to be linearly proportional to the gradient source term (2.9)

$$\tilde{\psi}(\mathbf{y}) = -\mathbf{b}_{\gamma}(\mathbf{y}) \cdot \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}}, \qquad (2.13)$$

where \mathbf{b}_{γ} is an auxiliary vector field commonly referred to as a *closure* variable [185], and $\nabla \langle \psi \rangle^{\gamma}$ evaluated at the centroid of the averaging volume. In appendix 2.7 we show that (2.13) is the leading order approximation to a series expansion of (2.12) around \mathbf{x} , and \mathbf{b}_{γ} is defined as

$$\mathbf{b}_{\gamma}(\mathbf{y}) = \int_{\mathbf{z} \in \mathcal{A}_{\gamma\kappa}(\mathbf{y})} \mathbf{n}_{\gamma\kappa}(\mathbf{z}) \ G(\mathbf{y}; \mathbf{z}) \ dA(\mathbf{z}).$$
(2.14)

Simplification of (2.12) to (2.13) is commonly referred to as the localization of the spatial fluctuation field. In appendix 2.7, we show that (2.12) can be truncated after higher-order terms, and that each term will have a corresponding closure variable. An example of truncating (2.12) after two terms and the resulting 4th order homogenized diffusion equation is given in [195].

2.2.4 Effective diffusivity

By combining (2.13) and (2.7), we can now show that the effective diffusivity tensor is indirectly defined in terms of the microscale propagator, G, via the vector field \mathbf{b}_{γ} as

$$\mathbf{D} = \mathcal{D}_{\gamma} \left(\mathbf{I} + \frac{1}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{y}) \otimes \mathbf{b}_{\gamma}(\mathbf{x} + \mathbf{y}) \, dA(\mathbf{y}) \right), \tag{2.15}$$

where \mathbf{b}_{γ} is the solution to the following problem:

$$\nabla^2 \mathbf{b}_{\gamma} = 0 \tag{2.16}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \mathbf{b}_{\gamma} = \mathbf{n}_{\gamma\kappa} \quad \mathbf{x} \in \mathcal{A}_{\gamma\kappa} \tag{2.17}$$

$$\mathbf{b}_{\gamma}(\mathbf{r}+\ell_i) = \mathbf{b}_{\gamma}(\mathbf{r}) \quad \mathbf{x} \in \mathcal{A}_{\gamma e} \tag{2.18}$$

$$\langle \mathbf{b}_{\gamma} \rangle^{\gamma} = \mathbf{0}. \tag{2.19}$$

Since the problem for \mathbf{b}_{γ} is stationary, (2.15) describes the asymptotic effective diffusivity ($\mathbf{D} \equiv \mathbf{D}^{\infty}$). Recent results for dual-permeable systems (where both the γ and κ phases are conductive) show that the rate of relaxation of the effective diffusivity to \mathbf{D}^{∞} is particularly sensitive to the type of disorder present in the medium [121]. When computable, the rate of relaxation of \mathbf{D} to \mathbf{D}^{∞} is a reliable indicator of whether or not the separation of time scales assumption that was discussed above is valid.

The problem for \mathbf{b}_{γ} given by (2.16)-(2.19) has a very compelling structure. It describes a manifold with zero constant curvature throughout \mathcal{V}_{γ} and carries the unit normal vector field that defines the γ - κ interface as a boundary source. In very simple terms, it describes the assimilation of shape information from the interface into the domain \mathcal{V}_{γ} as would take place in a classical diffusive process. In this sense, we can think of the asymptotic effective diffusivity tensor as carrying the lasting influence of microscale morphology on macroscale diffusion.

2.2.5 Local effective diffusivity

Like the permeability tensor, the effective diffusivity tensor is constructed as a boundary integral. In periodic REVs, we can obtain a definition for **D** in terms of a volume average of \mathbf{b}_{γ} , by observing that

$$\frac{1}{V_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{\gamma} \, dA \equiv \frac{1}{V_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa} \cup \mathcal{A}_{\gamma e}} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{\gamma} \, dA, \qquad (2.20)$$

and applying the divergence theorem to (2.20) to rewrite (2.15) as

$$\mathbf{D} = \mathcal{D}_{\gamma} \left\langle \mathbf{I} + \nabla \otimes \mathbf{b}_{\gamma} \right\rangle^{\gamma}.$$
(2.21)

We can interpret the kernel of the averaging operator in (2.21) as a *local* (pointwise) effective diffusivity tensor

$$\mathbf{D}_{loc} = \mathcal{D}_{\gamma} \left(\mathbf{I} + \nabla \otimes \mathbf{b}_{\gamma} \right). \tag{2.22}$$

2.2.6 Symmetry of **D**

The diffusion tensor for periodic systems must be symmetric. To demonstrate this, we show in Appendix B that \mathbf{b}_{γ} is a Laplacian vector field; therefore, it is the gradient of a scalar potential field, φ , such that $\mathbf{b}_{\gamma} = \nabla \varphi$. Substituting this into Eq. (2.22), we find

$$\mathbf{D}_{loc} = \mathcal{D}_{\gamma} \left(\mathbf{I} + \nabla \otimes \nabla \varphi \right) \tag{2.23}$$

Here, $\nabla\otimes\nabla\varphi$ is the Hessian of φ

$$\mathbf{H}(\varphi) = \nabla \otimes \nabla \varphi = \begin{pmatrix} \frac{\partial^2 \varphi}{\partial x^2} & \frac{\partial^2 \varphi}{\partial x \partial y} & \frac{\partial^2 \varphi}{\partial x \partial z} \\ \frac{\partial^2 \varphi}{\partial y \partial x} & \frac{\partial^2 \varphi}{\partial y^2} & \frac{\partial^2 \varphi}{\partial y \partial z} \\ \frac{\partial^2 \varphi}{\partial z \partial x} & \frac{\partial^2 \varphi}{\partial z \partial y} & \frac{\partial^2 \varphi}{\partial z^2} \end{pmatrix}$$
(2.24)

Because φ is a harmonic function, $Tr(\mathbf{H}(\varphi)) = 0$.

Noting that φ is an smooth field with derivatives of all orders, then the order of derivation in the mixed derivatives is commutable, and this matrix is symmetric. The idemfactor is identically symmetric, so Eqs. (2.21) and (2.22) represent symmetric tensors.

2.3 Methods

A number of unit cell geometries were studied, including crystalline arrangements of grains with various shapes and aspect ratios, and random spatial placement of particles (aka the Boolean model). System (2.16-2.19) was solved for each unit cell using a finite elements method in the commercial package COMSOL Multiphysics[®] 5.0. The solution was used to compute the effective diffusivity tensor according to (2.15). Numerical convergence was found to be sensitive to the spatial uniformity of the unit cells, so instances of the Boolean model were chosen carefully to satisfy a baseline of symmetry. Convergence was studied and ensured using the symmetry of the tensor as a guideline, and using standard grid convergence analysis. Mesh refinement was implemented on the source boundaries to improve convergence.

2.4 Results

2.4.1 isotropic crystalline structures

Figure 2.3 shows visualizations of the \mathbf{b}_{γ} vector field for isotropic 2D periodic unit cells. Several aspects of the topology of this field are noteworthy: (i) for simple particle placements (e.g. fcc, bcc, and sc), three types of fixed points are observed: sinks, saddles, and source boundaries (sinks and saddles are distinguished by Poincaré indices of +1, and -1, respectively). The presence of the latter is a direct consequence of the $\gamma - \kappa$ boundary condition in the problem for \mathbf{b}_{γ} ; (ii) in more complex cells (bidisperse arrays), often more esoteric features are observed including regular periodic orbits; the radii of periodic orbits in this case appear to be sensitive to the ratio of the radii of the particles. In the structure studied here, saddles tend to occur on (or near) maximally constricted loci, and sinks on (or near) minimally constricted loci. We can intuitively understand these points as either *redirecting* and *attracting* the flow of shape information from the source boundaries. The exact locations of these points tend to be strongly affected by polydispersity. The topology of $\mathbf{b}_{\gamma\kappa}$ appears to be invariant at different porosities for axisymmetric isotropic structures.



Figure 2.3: Topology of the \mathbf{b}_{γ} field for isotropic unit cells (left to right: monodisperse face-centered cubic (fcc) disk array, bidisperse disk array, and monodisperse simple-cubic ellipse array with orientation bias). In the visualizations, blue dots denote saddles, red dots denote sinks, red curves denote attracting periodic orbits, and black curves denote source boundaries.

2.4.2 anisotropic crystalline structures

In Figure 2.4A we have reproduced computations of the anisotropy ratio of the effective diffusivity tensor in crystalline cells with grain anisotropy. The ratio, β_D , is defined as the ratio of the smallest to the largest eigenvalue:

$$\beta_D = \frac{max \ eig(\mathbf{D})}{min \ eig(\mathbf{D})} \tag{2.25}$$

In contrast with the isotropic cases, the topology of \mathbf{b}_{γ} varies at different porosities for crystalline unit cells with grain anisotropy. Figure 2.4 shows an example where a sink transforms into a saddle and two sinks via a first-order transition at an aspect-ratio-dependent critical porosity. Interesting, this point corresponds to the inflection point in the anisotropy index curve for this geometry. We observed the same feature in other instances of the model with different grain aspect ratios and different crystalline placements.

2.5 Discussion

We can view pore-scale transport in porous media as a special case of a class of problems where out-of-equilibrium dynamical systems exchange information. In the particular case of two-phase media with time-invariant phase boundaries we can consider two dynamical systems, one of which is in a deep quench state. The information instantiated by this



Figure 2.4: Anisotropy, β_D , of the effective diffusivity tensor for a set of 2D and 3D anisotropic unit cells. The ratio is sensitive to the dimensionality and placement of ellipses and ellipsoids. The case of a body-centered fully-oriented ellipse array has been highlighted. The inflection point in the tensor anisotropy curve (marked by a vertical dashed line in A) corresponds to a first-order transition in the topology of \mathbf{b}_{γ} (pre- and post-transition vector fields are depicted in B and C, respectively).

quench state is stored in and represented by the morphology the phase boundaries. This interpretation is partially supported for diffusion by recent results that diffusion in porous media can be thought of as a special case of size-excluded diffusion in a binary mixture at the limit where the diffusivity of one phase vanishes [23].

As such approaches to describing the effective diffusivity and permeability of porous materials using tools from mathematical morphology show great promise [107, 144]. Much like the vector field \mathbf{b}_{γ} , integral shape quantifiers (e.g. Minkowski functionals) encode morphological information in a global fashion, by taking into account information from all orders and therefore circumvent the limitations of truncated order correlation functions [107]. Integral shape quantifiers also provide a more natural setting to study porous media near the percolation threshold, than more simplistic statistical measures.

Closure variables of spatially-averaged transport equations can be considered as complimentary to this program, a they embody how exactly the transfer of shape information from the interfaces to the conductive phase takes place. The closure variable for diffusion is a globally shape-aware vector field with units of length, that is shown to be conserved. We have shown that the topology of this field is sensitive to the shape of the phase boundaries, and that certain features of effective diffusivity tensor can be explained by navigating the topological features of this field and their transitions at different porosities.
2.5.1 Role of shape in transport

The preceding provides a platform for understanding and comparing how different transport mechanisms in porous media process the morphology of the pore space. Thinking in terms of Kac's inverse spectral problem for \mathbf{b}_{γ} , we can anticipate morphologies that produce more or less the same **D**. The same morphologies might generate different values for another transport tensor **T** that is constructed using a different operator with a different spectrum. One way to compare the relative sensitivities of **D** and **T** to morphological information might be to study the eigenfunction spaces of the closure problems associated with each transport mechanism.

2.6 Conclusions

In future work, the analysis presented here will be expanded to other transport phenomena, particular creeping flow. We will also explore potential algorithmic analogs of the closure variables that might be used to generate distance maps that mirror these field variables.

Appendix

2.7 Localization of the closure problem

In order to simplify the solution given in (2.12), we can replace the gradient term in (2.12) with its expansion around the centroid of an averaging window and carry the resulting derivatives out of the integral [195]:

$$\nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}+\mathbf{z}} = \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} + \mathbf{z} \cdot \nabla \otimes \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} + \frac{1}{2!} \mathbf{z} \otimes \mathbf{z} : \nabla \otimes \nabla \otimes \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} + \dots$$
(2.1)

Here it is assumed that the order of operations requires that outer products be completed before contractions [1].

Combining Eq. (2.1) with Eq. (2.12) yields the following result (here, truncating at second-order derivatives in ψ)

$$\begin{split} \tilde{\psi}(\mathbf{y}) &= \\ &- \mathcal{D}_{\gamma} \int_{\mathbf{z} \in \mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y}; \mathbf{z}) \, \mathbf{n}_{\gamma\kappa}(\mathbf{z}) \cdot \nabla \left\langle \psi \right\rangle^{\gamma} |_{\mathbf{x}} \, dA(\mathbf{z}) \\ &- \mathcal{D}_{\gamma} \int_{\mathbf{z} \in \mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y}; \mathbf{z}) \mathbf{n}_{\gamma\kappa}(\mathbf{z}) \cdot (\mathbf{z} \cdot \nabla \otimes \nabla \left\langle \psi \right\rangle^{\gamma} |_{\mathbf{x}}) \, dA(\mathbf{z}) \end{split}$$

The expansion allows us to rewrite (2.7) as follows where all quantities are conditioned on the centroid **x**:

$$\frac{\partial \langle \psi \rangle^{\gamma} |_{\mathbf{x}}}{\partial t} = \nabla \cdot \left(\mathcal{D}_{\gamma} \mathbf{I} \cdot \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} \right) + \nabla \left\{ \left[\left(\frac{\mathcal{D}_{\gamma}}{V_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{\gamma} \, dA \right) \cdot \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} \right] + \nabla \cdot \left[\left(\frac{\mathcal{D}_{\gamma}}{V_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{B}_{\gamma} \, dA \right) : \nabla \nabla \langle \psi \rangle^{\gamma} |_{\mathbf{x}} \right] + \dots \qquad (2.2)$$

The terms \mathbf{D}_0 , \mathbf{D}_1 , and \mathbf{D}_2 in (2.2) are the n-th order effective diffusivity tensors, and the *closure variables* \mathbf{b}_{γ} , and \mathbf{B}_{γ} are defined by

$$\mathbf{b}_{\gamma}(\mathbf{y}) = \int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z})\mathbf{n}_{\gamma\kappa}(\mathbf{z}) \, dA(\mathbf{z})$$
$$\mathbf{B}_{\gamma}(\mathbf{y}) = \int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z})\mathbf{n}_{\gamma\kappa}(\mathbf{z}) \otimes \mathbf{z} \, dA(\mathbf{z})$$
(2.3)

Assuming that the average concentration is a C^{∞} smooth field, the only choices that maintain a positive-definite operator are (i) all terms of the expansion are kept, or (ii) only terms leading to second-order derivatives in average concentration are kept. Thus, the conventional parabolic coarse-grained diffusion equation is an approximation that results from first-order localization of (2.7). In the following we will adopt the second of these two options.

2.8 Conservation of b_{γ}

In this appendix, the proof that the vector field **b** is conservative is developed. Note that, by definition, **b** is harmonic everywhere in the domain $\mathbf{x} \in V_{\gamma}$; thus, it possesses derivatives of all orders.

To start, we note that a vector field is conservative if it can be expressed in the form

 $\mathbf{b}_{\gamma} = \nabla \varphi$ (the choice to put a negative sign in front of the gradient is inconsistently applied; here, we have adopted the conventional approach without the negative sign). Clearly φ has derivatives of all orders. We consider \mathbf{b}_{γ} to be a known field, determined uniquely by solving Eqs. (2.16)-(2.19). From this definition, we can make the following statements

$$-\mathbf{n} \cdot \nabla \varphi = -\mathbf{n} \cdot \mathbf{b}_{\gamma} \tag{2.1}$$

$$\nabla^2 \varphi = \nabla \cdot \mathbf{b}_{\gamma} \tag{2.2}$$

In combination with the periodic boundary conditions and averaging constraint adopted for the \mathbf{b}_{γ} , the necessary potential φ can apparently be constructed by solving the following set of equations

$$\nabla^2 \varphi = \nabla \cdot \mathbf{b}_{\gamma}, \text{ in } \mathcal{V}_{\gamma} \tag{2.3}$$

$$-\mathbf{n} \cdot \nabla \varphi = -\mathbf{n} \cdot \mathbf{b}_{\gamma}, \text{ at } \mathcal{A}_{\gamma \kappa}$$
(2.4)

$$\nabla \varphi(\mathbf{x} + \ell_i) = \nabla \varphi(\mathbf{x} + \ell_i) \tag{2.5}$$

$$\langle \nabla \varphi \rangle^{\gamma} = \mathbf{0} \tag{2.6}$$

The set of equations given by Eqs. (2.19)-(2.22) are linear, and provide sufficient information to determine φ within an arbitrary constant. Thus, these equations define the function ϕ , such that $\mathbf{b}_{\gamma} = \nabla \varphi$. This means that, by definition, \mathbf{b}_{γ} is a conservative vector field. All conservative vector fields are irrotational; this is easily proved by noting

$$\nabla \times \mathbf{b}_{\gamma} = \nabla \times \nabla \varphi = 0 \tag{2.7}$$

where $\nabla \times \nabla \varphi = 0$ is an identity of vector calculus.

Now we show that, no only must \mathbf{b}_{γ} be a conservative field, but it must also be a *Laplacian* vector field. A Laplacian vector field is defined as a vector field that is both irrotational and divergence free. Although \mathbf{b}_{γ} must be irrotational, it has not been established that it must also be divergence free. To prove this, we start by noting the vector identity

$$\nabla^2 \mathbf{b} = \nabla (\nabla \cdot \mathbf{b}_{\gamma}) - \nabla \times (\nabla \times \mathbf{b})$$
(2.8)

Noting that the field \mathbf{b}_{γ} is curl-free, and that $\nabla^2 \mathbf{b}_{\gamma} = \mathbf{0}$, we have

$$\nabla(\nabla \cdot \mathbf{b}_{\gamma}) = \mathbf{0} \tag{2.9}$$

The only solution to this equation is

$$\nabla \cdot \mathbf{b}_{\gamma} = c_0 \tag{2.10}$$

where c_0 is a constant. Integrating both sides of this, we find

$$\int_{V_{\gamma}} \nabla \cdot \mathbf{b}_{\gamma} dV = \int_{V_{\gamma}} c_0 dV \tag{2.11}$$

$$\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \mathbf{b}_{\gamma} dV = c_0 V_{\gamma} \tag{2.12}$$

Now noting that from the first boundary condition in Eqs. (2.19)-(2.22), we can write

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{\gamma} \cdot \mathbf{b}_{\gamma} = \mathbf{n}_{\gamma\kappa} \cdot \mathbf{b}_{\gamma}, \text{ at } A_{\gamma\kappa}$$

$$(2.13)$$

The left-hand side of this can be manipulated as follows

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{\gamma} \cdot \mathbf{b}_{\gamma} = -\mathbf{n}_{\gamma\kappa} \cdot \nabla(\mathbf{b}_{\gamma} \cdot \mathbf{b}_{\gamma})$$
$$= -2\mathbf{n}_{\gamma\kappa} \cdot \nabla(b_x + b_y + b_z)$$
(2.14)

Thus, the boundary condition now reads

$$-2\mathbf{n}_{\gamma\kappa} \cdot \nabla(b_x + b_y + b_z) = \mathbf{n}_{\gamma\kappa} \cdot \mathbf{b}_{\gamma}, \text{ at } A_{\gamma\kappa}$$
(2.15)

Integrating both sides of this equation over the area $A_{\gamma\kappa}$ yields

$$-2\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\cdot\nabla(b_x+b_y+b_z)dA = \int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\cdot\mathbf{b}_{\gamma}dA \qquad (2.16)$$

Use of the divergence theorem (and accounting for the periodic conditions on \mathbf{b}_{γ} on $A_{\gamma e}$) yields

$$-2\int_{A_{\gamma\kappa}}\nabla^2(b_x+b_y+b_z)dA = \int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\cdot\mathbf{b}_{\gamma}dA \qquad (2.17)$$

The right-hand side of this expression is identically zero, yielding

$$\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \mathbf{b}_{\gamma} dA = 0 \tag{2.18}$$

Finally, comparing this result with the result given in Eq. (2.12), we find $c_0 = 0$. Thus, from Eq. ((2.10), we have that $\nabla \cdot \mathbf{b}_{\gamma} = 0$. Because \mathbf{b}_{γ} is both divergence-free and irrotational, then it must be Laplacian. Finally, we note then, that the potential function for \mathbf{b}_{γ} is now given explicitly by

$$\nabla^2 \varphi = 0, \text{ in } \mathcal{V}_{\gamma} \tag{2.19}$$

$$-\mathbf{n} \cdot \nabla \varphi = -\mathbf{n} \cdot \mathbf{b}_{\gamma}, \text{ at } \mathcal{A}_{\gamma \kappa}$$
(2.20)

$$\nabla \varphi(\mathbf{x} + \ell_i) = \nabla \varphi(\mathbf{x} + \ell_i) \tag{2.21}$$

$$\langle \nabla \varphi \rangle^{\gamma} = \mathbf{0} \tag{2.22}$$

Chapter 3 – A non-scale-invariant form for diffusion-reaction equations

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Abstract

The process of mixing and reaction is a challenging problem to understand mathematically. Although there have been successes in describing the effective properties of mixing and reaction under a number of regimes, process descriptions for early times have been challenging for cases where the structure of the initial conditions are highly segregated. In this paper, we use the method of volume averaging to develop a rigorous theory for diffusive mixing with reactions from initial to asymptotic times under highly segregated initial conditions in a bounded domain. One key feature that arises in this development is that the functional form of the averaged differential mass balance equations is not, in general, scale invariant. Upon upscaling, an additional source term arises that helps to account for the initial configuration of the reacting chemical species. In this development, we derive the the macroscopic parameters (a macroscale source term and an effectiveness factor modifying the reaction rate) defined in the macroscale diffusion-reaction equation, and provide example applications for several initial configurations.

3.1 Introduction

The study of diffusion-reaction equations has a long history that spans several disciplines; early works on the topic have been published in physics[157, 178, 160, 31], chemistry[173, 35], engineering[20, 41, 42, 40, 166, 74], and biology [137, 138, 171]. The literature for diffusionreaction equations is large, especially for the case of nonlinear diffusion and reactions[36, 92]. Most of the recent literature has been focused on the understanding of anomalous kinetics in bi-molecular reactions. Kinetics are considered anomalous when, because of transport limitations, the apparent rate of reaction depends upon time[93]. The primary effort to date has been focused on the search for scaling laws (usually power law functions of time) in unbounded domains, and these efforts have uncovered several interesting regimes as the systems evolve toward their asymptotic limits[126, 167, 86, 149, 94, 201, 16, 44]. The initial conditions for much of this work has, historically, been specified by uncorrelated random fields, in part because such conditions lead to more anomalous behavior[103]. Initial conditions in which there are spatial correlations (but still specified as random fields) have also been investigated[47, 129, 142]. A handful of studies have examined, either purposefully or because of computational limits, the influence of bounded (including periodically-bounded) systems. These studies have illustrated that bounded systems behave differently from unbounded ones, and the effects of the boundaries as system-specific, although ultimately such systems decay according to classical (non-anomalous) kinetics[142].

It has been well recognized that no single exponent on time will describe the concentration (density) decay in diffusion-reaction equations for all time [5, 142]. Early time behavior has been particularly difficult to elucidate. The results that do exist for early time behavior are primarily focused on the motion and width of the front when reactants are separated at a discrete interface [59, 70, 95, 99, 161, 162, 163, 168]. In the engineering literature on diffusion-reaction equations, anomalous kinetics are characterized by the *effectiveness* factor, which is defined as the ratio of the observed reaction rate to the the classical (i.e., non-transport-limited) reaction rate [166]. Although this parameter provides no information about the exponents for scaling in time, it is nevertheless a useful concept to describe the effective rate of reaction in the regimes where no simple scaling law is expected to exist.

In this paper, we develop a time- and space- local effective theory of diffusive mixing for the general class of second-order catalytic reactions of the form $B \xrightarrow{A} C$, via the method of volume averaging with closure. We are interested in how the initial condition configuration influences the evolution of the effective rate of reaction. Thus, we specifically examine initial conditions where the characteristic dimensions of the initial cluster sizes of the reactants is a large fraction of the domain size (rather than, for example, random uncorrelated, or fractal initial conditions^[142]). The resulting macroscale model incorporates an effective reaction rate, and a memory term that accounts for pre-asymptotic mixing effects by inhibiting the reaction at early times. Both parameters arise naturally in the localized theory, and are unambiguously linked to the smaller scales via a set of transient closure problems. The most striking feature of our model is that it shows that the functional form of the coarse-grained diffusion-reaction equation is not, in general, scale invariant. A new source term arises in the upscaled equation that represents the influence of the initial condition. This term is exponentially decaying in time, but the rate of this decay is strongly dependent upon the configuration of the initial condition. Scale invariance has conventionally been assumed to hold for reaction-diffusion systems [94]; thus, the development of a non-scale-invariant macroscale equation is a novel feature of our work.

3.2 Microscale balance equations

Our starting point is a set of mass balances for the two species. In this model, species A is a conservative catalyst; species B is transformed in the presence of species A to a product, i.e., $B \xrightarrow{A} C$ (species C is not tracked in this work). Note, this system is similar to the conventional nonlinear $A + B \rightarrow C$ reaction after appropriate transformation[142].

We particularly focus on a system that represents chemical species distributed in either a single fluid phase or a homogeneous porous medium (i.e. one where the pore scale has been coarsened so that no internal boundaries are resolved). In either case, the subscript γ indicates the fluid phase. The system is multiscale; thus, we think of the system as being characterized by a macroscale length, L (in this case, representing the domain size), and a microscale length (in this case, a measure of the diffusion length of the system). Specific metrics for the microscale length will be discussed in additional detail in the material that follows; intuitively, one can think of this length as being the average separation between species A and B in the initial configuration (Fig. 3.1).

For a domain \mathscr{V}^0 with external boundary $\mathscr{A}^0_{\gamma e}$ (Fig. 3.1), the reactive transport equations for species A and B can be written as (in terms of molar concentrations)

Species A

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) \text{ for } \mathbf{x} \in \text{ in } \mathscr{V}^0$$
(3.1)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) = F_A(\mathbf{x}, t) \text{ for } \mathbf{x} \in \mathscr{A}_{\gamma e}^0$$
(3.2)

$$c_{A\gamma}(\mathbf{x},0) = \varphi_A(\mathbf{x}) \quad \text{for } \mathbf{x} \in \text{in } \mathscr{V}^0 \tag{3.3}$$

Species B

$$\frac{\partial c_{B\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{B\gamma} \cdot \nabla c_{B\gamma}) \tag{3.4}$$

$$-k_{B\gamma}^0 c_{A\gamma} c_{B\gamma}$$
 for $\mathbf{x} \in \text{in } \mathscr{V}^0$

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla c_{B\gamma}) = F_B(\mathbf{x}, t) \text{ for } \mathbf{x} \in \mathscr{A}_{\gamma e}^0$$
(3.5)

$$c_{A\gamma}(\mathbf{x},0) = \varphi_B(\mathbf{x}) \text{ for } \mathbf{x} \in \text{ in } \mathscr{V}^0$$

$$(3.6)$$



Figure 3.1: A multiscale representation of the initial condition for a diffusion-reaction system. The two chemical species are denoted by the green (species A) and blue (species B) colors. The system is characterized by two characteristic lengths: the macroscale length, L, and the microscale length ℓ . A third length is defined by the support scale of the averaging volume, r_0 . A separation of length scales is assumed, such that $\ell \ll r_0 \ll L$.

Note that here there is a factor of the porosity, ε_{γ} embedded in the reaction rate such that $k_{B\gamma}^{0} = k'_{B\gamma}/\varepsilon_{\gamma}$, where $k'_{B\gamma}$ is the intrinsic reaction rate. When there is no solid phase present, then $k_{B\gamma}^{0} = k'_{B\gamma}$. Although in principle, a balance equation for chemical species C could also be written, because the net rate of generation of this species is the same as the reduction of species B we have chosen not to explicitly track species C. If one were interested in the particular spatial distribution of chemical species C, a set of balance equations like those above would have to be specified.

Although the flux at the external boundaries $(F_A \text{ and } F_B)$ may be non-zero, maintaining these non-zero boundary conditions adds significant complexity to the analysis without adding much in the way of additional insight. Although these terms can certainly be maintained in the analysis, we have chosen here to set the boundary flux terms to zero $(F_A = F_B = 0)$ for the remainder of the analysis. For determinism, we will also impose the condition that the macroscale fluxes, i.e., $\langle F_A \rangle^{\gamma} = \langle F_B \rangle^{\gamma} = 0$, are also zero. This represents the case where either (1) the boundaries are sufficiently distant from the initial condition that no significant mass fluxes are occur at the boundary for the time scale of interest, or (2) the boundaries are impermeable. The first of these approximations is made frequently in regard to chemical transport in porous media. The case where the boundary fluxes are non-zero are easily accommodated in an obvious way.

One advantage to this particular reaction-diffusion system is that it is linear, and an explicit analytical solution is possible. The solution to Eqs. (3.1)-(3.6) with, $F_A = F_B = 0$ and with box car type initial conditions is developed in Appendix 3.8.

3.3 Averaging

A (linear) multiscale system is defined as one where there exist hierarchical structure containing disorganized complexity [153, 181]. Such systems are complex from the perspective that an enormous amount of information is required to perfectly describe the microscale state of the system. However, much of this information is redundant, and can be eliminated by taking the appropriate statistics of the system. As an example, the system illustrated in Fig. 3.1 is multiscale. Although in principle it may be possible to solve the diffusion-reaction equations at the microscale everywhere within the domain \mathscr{V}^0 , generally this computation is impractical. Even if the computation were possible, the result would contain more information than is conventinally desired; in other words, some sort of aggregation would have to be conducted to make the result useful.

In this paper, we use volume averages to *coarse-grain* (or *upscale* or *aggregate*) the system behavior. The underlying assumption in this approach is that there exists volumes that are sufficiently large compared to the microscale characteristic length, ℓ that the fluctuations within these volumes can be well represented by a statistical description; in other words, the volumes are in some sense *representative* (or, frequently, a *representative elementary volume*, abbreviated by REV; we will adopt this acronym in the material below). For any such volume, the intrinsic volume average for a scalar field property ψ_{γ} is defined over the region $\mathscr{V}(\mathbf{x})$ by

$$\langle \psi_{\gamma} \rangle^{\gamma} |_{(\mathbf{x},t)} = \int_{\mathbf{r} \in \mathscr{V}(\mathbf{x})} w(\mathbf{x} - \mathbf{r}) \psi_{\gamma}(\mathbf{r}, t) dV(\mathbf{r})$$
(3.7)

Here, w is a weighting function that is compact in \mathscr{V} . For the remainder of this work, we take w to be a boxcar-type weighting function, although none of the results depend on this particular choice. Upon averaging the microscale mass balance equations, the result is

Species A

$$\frac{\partial \langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)}}{\partial t} = \nabla \cdot \left(\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)} \right) \quad \text{for } \mathbf{x} \in \text{in } \mathscr{V}^{0}$$
(3.8)

$$-\mathbf{n}_{\gamma\kappa}(\mathbf{x}) \cdot \left(\mathbf{D}_{A\gamma} \cdot \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma} \right|_{(\mathbf{x},t)} \right) = 0 \quad \text{for } \mathbf{x} \in \text{in } \mathscr{A}_{\gamma e}^{0}$$
(3.9)

$$\langle c_{A\gamma} \rangle^{\gamma} |_{(\mathbf{x},0)} = \langle \varphi_A \rangle^{\gamma} |_{\mathbf{x}} \text{ for } \mathbf{x} \in \text{in } \mathscr{V}^0$$
 (3.10)

Species B

$$\frac{\partial \langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)}}{\partial t} = \nabla \cdot \left(\mathbf{D}_{B\gamma} \cdot \nabla \langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)} \right)
- k_{B\gamma}^{0} \langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)} \langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)}
- k_{B\gamma}^{0} \langle \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)} \text{ for } \mathbf{x} \in \text{ in } \mathscr{V}^{0}$$
(3.11)

$$-\mathbf{n}_{\gamma\kappa}(\mathbf{x}) \cdot \left(\mathbf{D}_{B\gamma} \cdot \nabla \left\langle c_{B\gamma} \right\rangle^{\gamma} |_{(\mathbf{x},t)} \right) = 0 \text{ for } \mathbf{x} \in \text{ in } \mathscr{A}_{\gamma e}^{0}$$
(3.13)

$$\langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)} = \langle \varphi_B \rangle^{\gamma}|_{\mathbf{x}} \text{ for } \mathbf{x} \in \text{in } \mathscr{V}^0$$

$$(3.14)$$

Note that the average equation for species A requires no closure; the averaged equation has no unclosed deviations. For development of the balance equation for species B, we have used the spatial decompositions [65]

$$c_{A\gamma}(\mathbf{x},t) = \left. \left\langle c_{A\gamma} \right\rangle^{\gamma} \right|_{(\mathbf{x},t)} + \tilde{c}_{A\gamma}(\mathbf{x},t) \tag{3.15}$$

$$c_{B\gamma}(\mathbf{x},t) = \langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},t)} + \tilde{c}_{B\gamma}(\mathbf{x},t)$$
(3.16)

In subsequent presentation, the explicit functional dependence of such quantities will be dropped unless it is needed for clarity.

In Eq. (3.11), there are two terms requiring closure: $\tilde{c}_{A\gamma}$, and $\tilde{c}_{B\gamma}$. In the averaging process, we have removed averages from within averages. This approximation can be justified by the length-scale constraint[184] $r_0 \ll L$. We have also made the explicit assumption that $\langle \tilde{c}_{A\gamma} \rangle^{\gamma} \ll \langle c_{A\gamma} \rangle^{\gamma}$ and $\langle \tilde{c}_{B\gamma} \rangle^{\gamma} \ll \langle c_{B\gamma} \rangle^{\gamma}$, so that these terms may be neglected in the average balance. This restriction will generally be valid; it is true identically when the averaging volume can be treated as having no-flux boundaries (as in the examples presented in §3.6).

3.4 Deviation equations

To complete the upscaling processes we need a set of ancillary problems to model the microscale deviation terms in the 'unclosed' model given by Eq. (3.11). We start by subtracting the averaged equations from the point equations [Eqs. (3.1)-(3.6)] Species A

$$\frac{\partial \tilde{c}_{A\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma})$$

for $\mathbf{x} \in \text{ in } \mathscr{V}^0$ (3.17)

$$-\mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_{A\gamma}\cdot\nabla\tilde{c}_{A\gamma})=\mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_{A\gamma}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma})$$

for
$$\mathbf{x} \in \text{in } \mathscr{A}^0_{\gamma e}$$
 (3.18)

$$\tilde{c}_{A\gamma} = \underbrace{\tilde{\varphi}_A}_{source} \quad \text{for } \mathbf{x} \in \text{in } \mathscr{V}^0 \tag{3.19}$$

Species B

$$\frac{\partial \tilde{c}_{B\gamma}}{\partial t} - \nabla \cdot (\mathbf{D}_{B\gamma} \cdot \nabla \tilde{c}_{B\gamma}) \\
+ k_{B\gamma}^{0} \tilde{c}_{B\gamma} \langle c_{A\gamma} \rangle^{\gamma} + k_{B\gamma}^{0} \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} \\
- k_{B\gamma}^{0} \langle \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} \rangle^{\gamma} \\
= -\underbrace{k_{B\gamma}^{0} \tilde{c}_{A\gamma} \langle c_{B\gamma} \rangle^{\gamma}}_{source} \\
\text{for } \mathbf{x} \in \text{ in } \mathscr{V}^{0}$$
(3.20)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla \tilde{c}_{B\gamma}) = \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla \langle c_{B\gamma} \rangle^{\gamma})$$

for $\mathbf{x} \in \text{in } \mathscr{A}_{\gamma e}^{0}$ (3.21)

$$\tilde{c}_{B\gamma} = \underbrace{\tilde{\varphi}_B}_{source} \quad \text{for } \mathbf{x} \in \text{in } \mathscr{V}^0$$
(3.22)

Here, we have adopted the following notation: $\tilde{\varphi}_A(\mathbf{x}) = \varphi_A - \langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)}$, and $\tilde{\varphi}_B(\mathbf{x}) = \varphi_B(\mathbf{x}) - \langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)}$.

3.4.1 Localization of the closure problems

The closure problems above are linear but nonlocal (in space) diffusion-reaction equations. The solutions and properties of such problems is an active area of research [9]. However, it can be shown that solutions exist, that the solutions depend continuously on the initial conditions, and that the nonlocal equations converge to the local ones as the nonlocal terms become small enough [32, 60, 76, 8]. Much less information is available about the properties

of even linear nonlocal equations in the presence of boundaries, although they are frequently solved numerically [55]. Fortunately, for this particular set of equations, we can make some very compelling arguments indicating that the integral terms are negligible for the purposes of the closure problems.

To make these arguments, we start by developing some estimates for the order-ofmagnitude of various terms in the equations. First, we define the following statistical measure for the concentration deviation fields

$$\langle \tilde{c}_{A\gamma} \tilde{c}_{A\gamma} \rangle^{\gamma} = \sigma_A^2 (\tilde{c}_{A\gamma}) \tag{3.23}$$

$$\langle \tilde{c}_{B\gamma} \tilde{c}_{B\gamma} \rangle^{\gamma} = \sigma_B^2(\tilde{c}_{B\gamma}) \tag{3.24}$$

$$\langle \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} \rangle^{\gamma} = cov_{AB} (\tilde{c}_{A\gamma} \tilde{c}_{B\gamma}) \tag{3.25}$$

where σ_A^2 and σ_B^2 are the concentration variances, and cov_{AB} is the concentration covariance. Then, we make the following estimates for the concentration averages and deviations appearing in the balance equations

$$\|\tilde{c}_{A\gamma}\| = \sigma_A \tag{3.26}$$

$$|\tilde{c}_{B\gamma}\| = \sigma_B \tag{3.27}$$

$$\|\tilde{c}_{A\gamma}\tilde{c}_{B\gamma}\| = cov_{AB} \tag{3.28}$$

$$\|\langle c_{A\gamma} \rangle^{\gamma}\| \sim \mathbf{O}(\|\tilde{c}_{A\gamma}\|) = \sigma_A \tag{3.29}$$

$$\|\langle c_{B\gamma} \rangle^{\gamma}\| \sim \mathbf{O}(\|\tilde{c}_{B\gamma}\|) = \sigma_B \tag{3.30}$$

For the purposes of the closure problem only, we would like to assume

$$k_{B\gamma}^0 \langle \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} \rangle^{\gamma} \ll k_{B\gamma}^0 \langle c_{B\gamma} \rangle^{\gamma} \tilde{c}_{A\gamma} + k_{B\gamma}^0 \langle c_{A\gamma} \rangle^{\gamma} \tilde{c}_{B\gamma}$$
(3.31)

Using the order-of-magnitude estimates above, this requires

$$\frac{cov_{AB}}{\sigma_A^2 + \sigma_B^2} \ll 1 \tag{3.32}$$

Because initially we assume that the two species are unmixed, this inequality must be true at early times. However, one expects the cross variance to increase in time, so it is unclear if this restriction is met for all time. One can develop an evolution equation for the product $\tilde{c}_{A\gamma}\tilde{c}_{B\gamma}$, which is frequently done [46, 87, 101]. Although this shows that the evolution of $\tilde{c}_{A\gamma}\tilde{c}_{B\gamma}$ depends upon the scalar dissipation rate, this in itself is not entirely helpful because one does not know the scalar dissipation rate a priori either. Additionally, the expression for $\tilde{c}_{A\gamma}\tilde{c}_{B\gamma}$ exhibits the typical hierarchy problem for nonlinear equations; thus, it is not technically possible to close and expression for this product without significant approximations. In order to validate the inequality given by (3.32), we compute σ_A , σ_B , and cov_{AB} from direct numerical simulation. This computation is reported in Appendix 3.9; the results suggest that the approximation is a reasonable one.

3.4.2 Treatment of boundary terms

Although the initial-boundary-value problem defined by Eqs. (3.17)-(3.22) apply everywhere in the fluid phase of the domain \mathscr{V}^0 , as discussed above, we hope to solve these closures over a much smaller domain that we consider to be *representative* in a statistical sense. The idea of the existence of a statistically representative volume is central to almost all approaches for coarse-graining[104, 13, 113, 184, 190].

One of the most significant questions about closure for a representative region is what conditions one should impose at the boundary of any such REV. Referring back to Fig. (3.1), it is apparent that the boundary $\mathscr{A}_{\gamma e}$ is embedded in the large domain \mathscr{V}^0 . In principle, if we knew the value of $\langle c_{A\gamma} \rangle^{\gamma}$ everywhere on $\mathscr{A}_{\gamma e}$, then we would be able to solve the balance equations for the deviations, given by Eq. (3.17)-(3.22), exactly. This, however, would require that the macroscale problem be coupled to the microscale problem; in addition, one would potentially have to solve a different microscale problem for each patch, $\mathscr{V}(\mathbf{x})$, that is required to fully tesselate the domain \mathscr{V}^0 . This process, although providing a method to decompose the solution of the domain \mathscr{V}^0 into a sequence of smaller (but coupled) problems, would not reduce the amount of information required to specify the problem.

Typically, for problems of this type, the the approach is to solve the problem for *only* the REV (the domain $\mathscr{V}(\mathbf{x})$); when referring to the closure process, the REV is often referred to as a *unit cell*. To do so dramatically reduces the size of the problem that needs to be solved. However, it requires that something sensible is done to approximate the bound-



Figure 3.2: A representation of a mirror-image arrangement of unit cells.

ary conditions at the boundary, $\mathscr{A}_{\gamma e}(\mathbf{x})$. Usually, the approach is to replace the original boundary conditions with some form of periodic condition. The implications for adopting such conditions has been extensively discussed elsewhere[113, 191, 195]. In this particular case, we adopt the approach of using mirror-image periodic cells [113] (Fig. 3.2). For the diffusion operator, such an organization of the unit cells results in zero flux boundaries due to the symmetry of the resulting problem. Adopting this set of approximations yields the following set of *localized* closure problems.

Species A (localized)

$$\frac{\partial \tilde{c}_{A\gamma}}{\partial t} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla_r \tilde{c}_{A\gamma}) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
(3.33)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla_r \tilde{c}_{A\gamma}) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.34)

$$\tilde{c}_{A\gamma} = \underbrace{\tilde{\varphi}_A(\mathbf{r})}_{source} \quad \text{for } \mathbf{r} \in \text{ in } \mathscr{V}(\mathbf{x}) \tag{3.35}$$

Species B (localized)

$$\frac{\partial \tilde{c}_{B\gamma}}{\partial t} - \nabla \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r \tilde{c}_{B\gamma}) + k_{B\gamma}^0 \tilde{c}_{B\gamma} \langle c_{A\gamma} \rangle^{\gamma} + k_{B\gamma}^0 \tilde{c}_{A\gamma} \tilde{c}_{B\gamma} = -\underbrace{k_{B\gamma}^0 \tilde{c}_{A\gamma} \langle c_{B\gamma} \rangle^{\gamma}}_{source}$$
for $\mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$ (3.36)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r \tilde{c}_{B\gamma}) = 0 \quad \text{for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.37)

$$\tilde{c}_{B\gamma} = \underbrace{\tilde{\varphi}_B(\mathbf{r})}_{source} \quad \text{for } \mathbf{r} \in \text{ in } \mathscr{V}(\mathbf{x}) \tag{3.38}$$

Note that here we have adopted \mathbf{r} to be the independent spatial variable in these equations (Fig. 3.2); hence, the symbol ∇_r is the gradient with respect to the independent variable \mathbf{r} . The variable \mathbf{x} locates the centroid of the unit cell $\mathscr{V}(\mathbf{x})$, and the variable \mathbf{w} is a variable of integration.

3.4.3 Integral solutions to the closure problem

The two simplified closure problems above are local and linear parabolic equations. The solution to the problem for species A is completely independent from that for species B, and is a classical solution that can be represented in integral form by (cf. Polyanin [133, $\S 0.8.1$])

$$\tilde{c}_{A\gamma}(\mathbf{r},t) = \underbrace{\int_{\mathbf{w}\in\mathscr{A}_{\gamma\kappa}(\mathbf{x})} G_A(\mathbf{r},\mathbf{w},t,0) \,\tilde{\varphi}_A(\mathbf{w}) \, dV(\mathbf{w})}_{initial \ condition \ source}$$
(3.39)

where $G_A(\mathbf{r}, \mathbf{w}, t, \tau)$ is the Greens function for this problem. For species A, the solution for the deviation equations is a function of only the initial condition, and it takes the form[184, 195, 193]

$$\tilde{c}_{A\gamma}(\mathbf{r},t) = \Phi_A(\mathbf{r},t) \tag{3.40}$$

where

$$\Phi_{A\gamma}(\mathbf{r},t) = \int_{\mathbf{w}\in\mathscr{A}_{\gamma\kappa}(\mathbf{x})} G_A(\mathbf{r},\mathbf{w},t,0) \,\tilde{\varphi}_A(\mathbf{w}) \, dV(\mathbf{w}) \tag{3.41}$$

Note that Φ_A is an exponentially-decaying function of time (this can be easily seen by attempting a conventional separation of variables solutions for $\tilde{c}_{A\gamma}$). At early times, the magnitude of this function can be significant. In the macroscale equation, it and can create (apparent) deviations from Fickian behavior (especially in the second moment), even though the spreading process is a Fickian one.

The solution for species B is somewhat more complicated, but substituting the solution for $\tilde{c}_{A\gamma}$ helps simplify things a little.

$$\frac{\partial \tilde{c}_{B\gamma}}{\partial t} - \nabla_r \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r \tilde{c}_{B\gamma}) + k_{B\gamma}^0 \langle c_{A\gamma} \rangle^{\gamma} \tilde{c}_{B\gamma} + k_{B\gamma}^0 \Phi_{A\gamma} \tilde{c}_{B\gamma} \\
= -\underbrace{k_{B\gamma}^0 \Phi_{A\gamma} \langle c_{B\gamma} \rangle^{\gamma}}_{source} \\
\text{for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.42)

$$-\mathbf{n}_{\gamma\kappa}\cdot\mathbf{D}_{B\gamma}\cdot\nabla_{r}\tilde{c}_{B\gamma}=0$$

for
$$\mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
 (3.43)

$$\tilde{c}_{B\gamma} = \underbrace{\tilde{\varphi}_B(\mathbf{r})}_{source} \quad \text{for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x}) \tag{3.44}$$

This problem is, as before, linear (in $\tilde{c}_{B\gamma}$) with well-defined source terms. In terms of the macroscopic variables, the sources are proportional to $\langle c_{B\gamma} \rangle^{\gamma}$, and $\tilde{\varphi}_B$. The integral solution is given by

$$\widetilde{c}_{B\gamma}(\mathbf{r},t) = -\int_{\tau=0}^{\tau=t} \int_{\mathbf{w}\in\mathscr{V}(\mathbf{x})} k_{B\gamma}^{0} \Phi_{A\gamma}(\mathbf{w},\tau) \times G_{B}(\mathbf{r},\mathbf{w},t,\tau) \langle c_{B\gamma}\rangle^{\gamma}|_{(\mathbf{y},\tau)} dA(\mathbf{w})d\tau + \underbrace{\int_{\mathbf{w}\in\mathscr{A}_{\gamma\kappa}(\mathbf{r})} G_{B}(\mathbf{r},\mathbf{w},t,0) \,\widetilde{\varphi}_{B}(\mathbf{w}) \, dV(\mathbf{w})}_{initial \ condition \ source}$$
(3.45)

We have already imposed the length-scale constraints $\ell/L \ll 1$, which allows us to remove average quantities from spatial integrals. At this juncture, we also impose the condition that our solution be time-local. In short, this assumption requires that the characteristic time for changes in the averaged concentration, $\langle c_{B\gamma} \rangle^{\gamma}$ are much longer than those for the remaining terms in the first integral on the right-hand side of Eq. (3.45), so that it can be removed from under the integral. This approximation is a version of the *quasi-steady* approximation, and it is described in additional detail in Wood [193] and Wood and Valdés-Parada [195]. If we adopt this assumption, then we can define a localized solution of the form

$$\tilde{c}_{B\gamma}(\mathbf{r},t) = f_{B\gamma}(\mathbf{r},t) \left\langle c_{B\gamma} \right\rangle^{\gamma}|_{(\mathbf{r},\mathbf{t})} + \Phi_B(\mathbf{r},t)$$
(3.46)

where

$$f_{B\gamma}(\mathbf{r},t) = -\int_{\tau=0}^{\tau=t} \int_{\mathbf{w}\in\mathscr{V}(\mathbf{x})} k_{B\gamma}^0 \,\Phi_{A\gamma}(\mathbf{w},\tau) \\ \times G_B(\mathbf{r},\mathbf{w},t,\tau) \,\,dA(\mathbf{w}) \,d\tau$$
(3.47)

$$\Phi_{B\gamma} = \int_{\mathbf{w} \in \mathscr{A}_{\gamma\kappa}(\mathbf{r})} G_B(\mathbf{r}, \mathbf{w}, t, 0) \,\tilde{\varphi}_B(\mathbf{w}) \, dV(\mathbf{w}) \tag{3.48}$$

Examining Eq. (3.45) shows that the problem for $\tilde{c}_{B\gamma}$ is coupled to that for $\tilde{c}_{A\gamma}$ through $\Phi_{A\gamma}$. Thus, any initial configurations that force the solution for species A to have long characteristic time scales (compared to the characteristic time scale for $\langle c_{B\gamma} \rangle^{\gamma}$) will invalidate the assumption of time local behavior.

It is difficult to determine under exactly what conditions the time-local approximation will be valid. Because the assumption involves the details of a convolution, conventional order-of-magnitude estimates are likely to be far too severe to be useful [183]. We propose using constraints based on the spatial moments of the quantities involved. As a rough constraint, we require that the first three spatial moments of species A (the zeroth, first, and second) should at least be quasi-stationary in time (i.e., they relax much faster than the characteristic time for $\langle c_{B\gamma} \rangle^{\gamma}$). To meet this requirement, we impose that the initial conditions must be such that: (1) the center of mass of $\tilde{c}_{A\gamma}$ does not move significantly during the evolution, and (2) the principle axes of the second spatial moment for $\tilde{c}_{A\gamma}$ do not rotate during the evolution. If either of these two conditions were to occur, it would suggest that the characteristic times were not separated, and no localized form would be possible. Together, these requirements are met by initial conditions that are (approximately) bisymmetric. In the remainder of the analysis, we will impose this condition.

3.5 Closed problem

With the formal solution for the concentration deviations given above, we can return to the averaged equations to close them by eliminating the deviation quantities. For species A, no closure is required, so the upscaled result is

Species A

$$\frac{\partial \langle c_{A\gamma} \rangle^{\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma})$$

for $\mathbf{x} \in \text{in } \mathscr{V}^{0}$
$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma}) = 0 \text{ for } \mathbf{x} \in \text{in } \mathscr{A}_{\gamma e}^{0} \qquad (3.49)$$

$$\langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)} = \langle \varphi_{A} \rangle^{\gamma} \text{ for } \mathbf{x} \in \text{in } \mathscr{A}_{\gamma e}^{0} \qquad (3.50)$$

The development of the closed form of the balance equation for species B is reasonably straight forward. Substituting Eqs. (3.40)-(3.46) into Eq. (3.20), we find

Species B

$$\frac{\partial \langle c_{B\gamma} \rangle^{\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{B}^{*} \cdot \nabla \langle c_{B\gamma} \rangle^{\gamma}) - k_{B}^{*} \langle c_{A\gamma} \rangle^{\gamma} \langle c_{B\gamma} \rangle^{\gamma} - s_{B}^{*} \text{for } \mathbf{x} \in \text{ in } \mathscr{V}^{0}$$
(3.51)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla \langle c_{B\gamma} \rangle^{\gamma}) = 0 \quad \text{for } \mathbf{x} \in \text{in } \mathscr{A}_{\gamma e}^{0}$$
(3.52)

$$\langle c_{B\gamma} \rangle^{\gamma} |_{(\mathbf{x},0)} = \langle \varphi_B \rangle^{\gamma} \text{ for } \mathbf{x} \in \text{ in } \mathscr{V}^0$$
 (3.53)

Here, the effective parameters are given by

$$k_B^*(\mathbf{x},t) = k_{B\gamma}^0 \left(1 + \frac{\langle f_{B\gamma} \Phi_{A\gamma} \rangle^{\gamma}}{\langle c_{A\gamma} \rangle^{\gamma}} \right)$$
(3.54)

$$s_B^*(\mathbf{x},t) = k_{B\gamma}^0 \langle \Phi_{A\gamma} \Phi_{B\gamma} \rangle^\gamma \tag{3.55}$$

In these expressions, k_B^* is the effective rate of reaction that applies to the averaged diffusion-reaction equations, and s_B^* is a source term that represents the influence of the initial configuration on the dynamics of the averaged diffusion-reaction equations. Because the term s_B^* is not present in the microscale diffusion-reaction equations, this term creates an upscaled diffusion-reaction equation that has a mathematical form that is inherently different from the microscale equation (i.e., it makes the macroscale diffusion-reaction equation non-scale-invariant).

The expression for k_B^* can also be used to define the classical effectiveness factor

$$\eta_B(\mathbf{x},t) = \frac{k_B^*}{k_B^0} = \left(1 + \frac{\langle f_{B\gamma} \Phi_{A\gamma} \rangle^{\gamma}}{\langle c_{A\gamma} \rangle^{\gamma}}\right)$$
(3.56)

With this definition, the balance equation for species B can be put in a form that is closer to the traditional form used in chemical engineering

$$\frac{\partial \langle c_{B\gamma} \rangle^{\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{B}^{*} \cdot \nabla \langle c_{B\gamma} \rangle^{\gamma}) - \eta_{B} k_{B}^{0} \langle c_{A\gamma} \rangle^{\gamma} \langle c_{B\gamma} \rangle^{\gamma} - s_{B}^{*}$$
(3.57)

Note that, unlike the case for species A, the averaged mass balance of species B is not scale invariant. The upscaled balance equation takes a different mathematical form than does the microscale mass balance (i.e., there is no term equivalent to s_B^* in Eq. (3.5)). This is a source term that accounts for the initial microscale configuration of the two species, and this term should be important at early times for some configurations of initial conditions. This term is an exponentially decreasing function of time, so the scale invariance disappears asymptotically. However, the time required for the source term to decay (and return the equation to its scale invariant form) depends strongly upon the structure of the initial condition.

The development of the closed forms for the equations is now complete. However, in practice the effective parameters k_B^* and s_B^* must also be predicted by solving the microscale closure problems. Although in principle, these effective parameters can be found by finding the appropriate Green's functions (an example of this is provided in Appendix 3.8), it is generally simpler to find the solutions to the closure problems numerically. This is described in the next section through the development of an example application.

3.6 Examples of computing the effective parameters

If we consider a problem for a closed domain, where we average over the entire domain, we achieve a situation where there are no macroscopic gradients. The resulting problem takes a particularly simple form that makes the effect of the initial conditions particularly easy to examine.

The macroscale balance equations for this problem are

$$\frac{\partial \langle c_{A\gamma} \rangle^{\gamma}}{\partial t} = 0 \tag{3.58}$$

I.C. 2
$$\langle c_{A\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)} = \langle \varphi_A \rangle^{\gamma}$$
 (3.59)

Species A is a conserved catalyst; hence, in a closed system, it starts with a particular average concentration, and it stays at that concentration. Hence, the solution can be obtained by direct integration of Eq. (3.59), and the result is

$$\langle c_{A\gamma} \rangle^{\gamma} |_{(\mathbf{x},t)} = \langle \varphi_A \rangle^{\gamma} \tag{3.60}$$

The balance equation for species B is also simplified, but it does still contain effective parameters for which ancillary closure problems need to be solved. The simplified problem for species B is Species B

$$\frac{\partial \langle c_{B\gamma} \rangle^{\gamma}}{\partial t} = -k_B^* \langle c_{A\gamma} \rangle^{\gamma} \langle c_{B\gamma} \rangle^{\gamma} - s_B^* \tag{3.61}$$

I.C. 2
$$\langle c_{B\gamma} \rangle^{\gamma}|_{(\mathbf{x},0)} = \langle \varphi_B \rangle^{\gamma}$$
 (3.62)

Although the *macroscopic* spatial information has been averaged out of this equation, there is still microscopic spatial information encoded in the effective parameters k_B^* and s_B^* . These effective parameters are defined by

$$k_B^* = k_{B\gamma}^0 \left(1 + \frac{\langle f_{B\gamma} \Phi_{A\gamma} \rangle^{\gamma}}{\langle c_{A\gamma} \rangle^{\gamma}} \right)$$
(3.63)

$$s_B^* = k_{B\gamma}^0 \langle \Phi_{A\gamma} \Phi_{B\gamma} \rangle^\gamma \tag{3.64}$$

For this particular problem, the average value of species A is known; for this example, we will assume explicitly that $\langle c_{A\gamma} \rangle^{\gamma} = 1$. Thus, we need only to solve closure problems for the functions $\Phi_{A\gamma}$, $\Phi_{B\gamma}$, and $f_{B\gamma}$. As mentioned in the previous section, the easiest way to do this is not necessarily to solve for the Green's functions (although this can be done for some cases, as illustrated in Appendix 3.8), but actually to solve the closure problems numerically. To do this, we substitute Eqs. (3.40) and (3.46) into the balance equations for $\tilde{c}_{A\gamma}$ and $\tilde{c}_{A\gamma}$. The result is a set of three linearly independent closure problems (one from the balance for $\tilde{c}_{A\gamma}$, and two for the balance for $\tilde{c}_{B\gamma}$. These three closure problems is given by

Species A closure for $\Phi_{A\gamma}$

$$\frac{\partial \Phi_{A\gamma}}{\partial t} - \nabla_r \cdot (\mathbf{D}_{A\gamma} \cdot \nabla_r \Phi_{A\gamma}) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
(3.65)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla_r \Phi_{A\gamma}) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.66)

$$\Phi_{A\gamma} = \tilde{\varphi}_A \quad \text{for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x}) \tag{3.67}$$

Species B closure for $\Phi_{B\gamma}$ (assuming $\langle c_{A\gamma} \rangle^{\gamma} = 1$)

$$\frac{\partial \Phi_{B\gamma}}{\partial t} - \nabla_r \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r \Phi_{B\gamma})
+ k_{B\gamma}^0 \Phi_{A\gamma} \Phi_{B\gamma} + k_{B\gamma}^0 \cdot 1 \cdot \Phi_{B\gamma}
= 0 \text{ for } \mathbf{r} \in \text{ in } \mathscr{V}(\mathbf{x})$$
(3.68)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r \Phi_{B\gamma}) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.69)

$$\Phi_{B\gamma}(\mathbf{x},0) = \tilde{\varphi}_B(\mathbf{x}) \text{ for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
(3.70)

Species B closure for $f_{B\gamma}$ (assuming $\langle c_{A\gamma} \rangle^{\gamma} = 1$)

$$\frac{\partial f_{B\gamma}}{\partial t} - \nabla_r \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r f_{B\gamma})
+ k_{B\gamma}^0 \Phi_{A\gamma} f_{B\gamma} + k_{B\gamma}^0 \cdot 1 \cdot f_{B\gamma}
= -\underbrace{k_{B\gamma}^0 \Phi_{A\gamma}}_{source} \quad \text{for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
(3.71)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r f_{B\gamma}) = 0 \quad \text{for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.72)

$$f_{B\gamma}(\mathbf{x},0) = 0 \text{ for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x})$$
 (3.73)

To compute the effective parameters k_B^* and s_B^* , we solved the system of coupled partial differential equations defined by equations (3.65) through (3.73) for different instances of initial distributions of species A and B on a square (2-dimensional) domain. Note that, even though this set of equations is coupled, they are separable, so that the coupling can be handled by solving the equations in sequence in one pass (i.e., no iteration among the equations is necessary). The resulting concentration histories computed via the upscaled model (3.61) were then compared with direct numerical simulations of the original microscale problem (Eqs 3.1 through 3.6). We assumed isotropic diffusivity tensors ($\mathbf{D}_{A\gamma} = \mathscr{D}_{A\gamma} \mathbf{I}, \mathbf{D}_{B\gamma} = \mathscr{D}_{B\gamma} \mathbf{I}$) for all species. Here we solve the diffusion-reaction equations directly [142] rather than as a lattice gas as is often done in diffusion-reaction studies.

For plotting purposes, we have defined the following dimensionless variables

$$\langle c_{B\gamma} \rangle^* = \langle c_{B\gamma} \rangle^{\gamma} / c_{B0} \tag{3.74}$$

$$\tau_A = \ell_{REV}^2 / \mathscr{D}_{A\gamma} \tag{3.75}$$

$$\tau_B = \ell_{REV}^2 / \mathscr{D}_{B\gamma} \tag{3.76}$$

$$\tau = \frac{1}{2}(\tau_A + \tau_B) \tag{3.77}$$

$$\tau_R = 1/(k_{B\gamma}^0 \langle c_{A\gamma} \rangle^\gamma) \tag{3.78}$$

$$t^* = t/\tau \tag{3.79}$$

$$Da = \tau_B / \tau_R = k_{B\gamma}^0 \ell_{REV}^2 \langle c_{A\gamma} \rangle^{\gamma} / \mathscr{D}_{B\gamma}$$
(3.80)

$$\hat{s}_B = s_B^* / k_{B\gamma}^0 \tag{3.81}$$

$$\eta_B = k_B^* / k_{B\gamma}^0 \tag{3.82}$$

where $\langle c_{B\gamma} \rangle^*$ is the dimensionless averaged concentration for species B, τ is the characteristic diffusion time, t^* is the dimensionless time, Da is the Damköhler number measuring the ratio of the diffusion time scale to the reaction time scale, \hat{s}_B is the nondimensional source term, and η_B is the nondimensional effective reaction rate term (the effectiveness factor).

Four different cases were examined. For three of these cases, the structure of the initial condition was changed to create increasingly segregated systems (Fig. 3.3, left column). For the fourth case (Fig. 3.4, left side), the initial condition was both highly segregated and the reacting species were separated by regions that contain zero concentration of either A or B. For this case, we expect to see some delay in the reaction while the two chemical species diffuse through the zero concentration regions to create contact. In all cases, the characteristic size associated with the initial condition is within an order of magnitude of the domain size, so we we expect none of the nonclassical time scalings (such as Ovchinnikov-Zeldovich behavior[126]) observed for large, random systems[11]. We do, however, expect to see substantial deviations from classical kinetics for early times.

The physical parameters for the simulations are specified in Table 3.1. Note that although for these simulations the diffusion coefficient for species A and B are equal, this is not a requirement of the approach. The characteristic length adopted was the side length of the unit cell, ℓ_{REV} . Ideally, this length should perhaps be related to the characteristic length for diffusion; however, convenient metrics for such a length are generally not known, even for cases where the initial condition is specified. We will investigate the characteristic

Table 3.1: Parameters used in the simulations

Parameter	Value	Definition
ℓ_{REV}	0.01 m	$=2r_0$, Length of a unit cell side
Δ_x	$1\times 10^{-5}~{\rm m}$	Grid spacing, x -direction
Δ_y	$1\times 10^{-5}~{\rm m}$	Grid spacing, $y-$ direction
c_{A0}	1 mol/m^3	Initial concentration of species A
c_{B0}	$\frac{1}{2}$ mol/m ³	Initial concentration of species B
$\mathscr{D}_{A\gamma}$	$5\times 10^{-10}~\mathrm{m^2/s}$	Molecular diffusivity, species ${\cal A}$
$\mathscr{D}_{B\gamma}$	$5\times 10^{-10}~\mathrm{m^2/s}$	Molecular diffusivity, species ${\cal B}$
$k^0_{B\gamma}$	$5 \times 10^{-6} \text{ m}^3/(\text{s}\cdot\text{mol})$	Intrinsic reaction rate, $Da = 1$
$k^0_{B\gamma}$	$5 \times 10^{-5} \text{ m}^3/(\text{s}\cdot\text{mol})$	Intrinsic reaction rate, $Da = 10$
$k^0_{B\gamma}$	$5\times 10^{-4}~{\rm m^3/(s{\cdot}mol)}$	Intrinsic reaction rate, $Da = 100$

diffusion length further in §3.6.1. For now, we simply note that the characteristic length ℓ_{REV} , although conventional, is larger than a diffusion length based on the configuration of the system might be. Thus, the characteristic time for diffusion, τ , is potentially somewhat smaller than what a more physically-based length scale would predict.

To ensure that convergence was reached in the numerical computations, a grid refinement study was performed for Case 3 at the highest Damköhler number. Spatial grid resolutions in the set $\Delta x/\ell_{REV} = \{0.1, 0.05, 0.033, 0.02\}$, and temporal grid resolutions in the set $\Delta t/\tau = \{5 \times 10^{-5}, 1.0 \times 10^{-4}, 1.5 \times 10^{-4}\}$ were studied. The finest resolution $(\Delta x/\ell_{REV} =$ 0.02 and $\Delta t/\tau = 5.0 \times 10^{-5})$ was used as the base case, compared with which the coupled PDE solver showed first-order convergence for $\Delta t/\tau < 1.5 \times 10^{-4}$. The maximum point-wise percent relative errors (i.e. L_{∞} norms of percent relative errors) converged toward values < 2%, for the concentration of species B. All the numerical results reported in this study were obtained using this base case resolution. All computations were performed using the finite elements package COMSOL Multiphysics 4.4.



Figure 3.3: Cases 1-3. (Left) The configuration of the initial condition. (Center) The (normalized) effective reaction rate and source terms. (Right) Comparison of the upscaled model (blue lines with filled circles), the asymptotic model ($\eta_B = 1, \hat{s}_B = 0$), and direct numerical simulations (DNS) (black solid lines). These results are for Da = 100.

Results and Discussion

Our focus has been on the influence of the initial configuration on the effective rate of reaction for a set of diffusion-reaction equations in a bounded domain. Equations (3.49)-(3.55) represent the coarse-grained balance equations and associated effective parameters for the system. As previously pointed out by Sancho et al. [142], the bounded case is fundamentally different from the unbounded one in that no additional segregation of species occur as the system evolves. Such spontaneous segregation has been seen in unbounded nonlinear reaction-diffusion systems with random (including correlated) initial conditions [102, 126].

One of the more interesting features of our analysis is that the upscaled diffusion-reaction equation is not scale invariant. The upscaled equation contains a source term (s_B^*) that does not have a corresponding term in the microscale equations. Although this term decreases exponentially with time, at early times it can be important in the behavior of the system. We are aware of no other results to date for which this particular kind of scale invariance–arising strictly from the initial condition–has been reported in the literature.

3.6.1 Influence of the initial condition structure

In the center column of Figs. 3.3 and 3.4, the effectiveness factor, η_B , and the source term, \hat{s}_B , are plotted as a function of the nondimensional time. In each of Cases 1-3, half of the region is initially filled with species A, and the other half with species B; thus, the total volumes filled with species A and B are equal (although the total mass of species A is twice that of B). However, as can be observed in the plots for the effective parameters \hat{s}_B and η_B , the particular configuration of the initial condition dramatically changes the dynamic behavior of the system as it evolves in time. This is perhaps best illustrated through examination of the plots for the effectiveness factor (a number between zero and one), which modulates the effective rate of reaction. In all cases, the effectiveness factor starts at a value near unity, decreases to a minimum at around $\tau = 0.02$, and then recovers asymptotically to unity again. Similar behavior for the effective rate of reaction has been observed for the classical (nonlinear) bi-molecular reaction case with initially separated reactants [163].

It is difficult to generate a universal characteristic length that might optimally represent



Figure 3.4: Case 4. (Left) The configuration of the initial condition. (Center) The (normalized) effective reaction rate and source terms. (Right) Comparison of the upscaled model (blue lines with filled circles), the asymptotic model ($\eta_B = 1, \hat{s}_B = 0$), and direct numerical simulations (DNS) (black solid lines). These results are for Da = 100.

the influence of the initial condition on the diffusion process. For isotropic systems, a length that measures the characteristic "cluster" size of each of the reactants (and spaces devoid of reactants for Case 4) is a reasonable one that has physical content. To give some indication of the average cluster size for each chemical species in each initial configuration, we performed the following sequence to segment the image.

- 1. First, the structure of the initial condition was segmented into circular clusters (using ImageJ[143]) representing the local size of contiguous chemical species. The result of this process was a collection of N_e circles. Because species A and B are initially completely segregated, the radius of each circle provides in this segmentation provide information about how far the species have to diffuse before they are completely mixed. Note that this algorithm sequentially segments the *largest* circles that are completely contained in the contiguous domain (as opposed to, for example, the *smallest* circles that completely contain the contiguous domain). Thus, the algorithm will sometimes segment a single contiguous region into a large circular region, plus several small circular regions near the boundary (e.g., as in Case 2 in Fig. 3.6). Such a segmentation is still consistent with the physics of diffusion in an isotropic medium.
- 2. The circular segmentation provides information about the local *size* of clusters, but it is not space filling. Thus, as a second step, we created a Voronoi tessellation of the circles into N_e polygons (using the C++ library Voro++), with area given by

 A_n , $(n = 1 \dots N_e)$; examples of the tessellations are illustrated in Fig. 3.6. The result of this step was that the image was broken into regions, where the sum of the areas of each region was equal to the original area of the unit cell. This step was important to achieve a consistent scheme for weighting when determining the average diffusion distance (discussed below). It was also important as a method to consistently associate an area for systems where the the initial condition of species A and B do not fill the domain (e.g., as in Case 2 in Fig. 3.6).

3. An average length, Λ_n was associated with the clusters by assuming that they were nearly circular. Thus the length was specified by

$$\Lambda_n = \left| \sqrt{\frac{A_n}{\pi}} \right| \tag{3.83}$$

Note: This result did not always provide the radius of the original cluster. Where there were clusters separated by zero-concentration regions (e.g., Case 4 illustrated in Fig. 3.6(b), the resulting value provided a more accurate distance of how far individual species would have to diffuse before being mixed.

4. For the final step, the characteristic microscale diffusion length, ℓ , was then determined by taking the arithmetic average.

$$\ell = \frac{1}{N_e} \sum_{n=1}^{N_e} \Lambda_n \tag{3.84}$$

This value gives a measure of the average diffusion distance for a particular initial configuration.

The characteristic length for each initial condition is given above the figures in the lefthand column of Figs. 3.3 and 3.4. It is interesting to note that this metric does correlate with the increasing time scale of the transient effects observed in the center column of Fig. 3.3. This matches our intuition about the diffusion and mixing processes. Structures that have characteristic lengths that are large compared to the domain size will take a substantial fraction of the diffusive time scale to become mixed. For the particular initial conditions examined here, the average cluster size appears to correlate well with the increasing transience in the system.



Figure 3.5: An example segmentation and Voronoi tessellation for cases 1 and 2.

To push this analysis a little farther, one might hope that a relationship between the characteristic lengths, ℓ , and the effectiveness factor could be found. In preparation for this, we propose that the effectiveness factor curves be characterized by the complimentary function

$$\eta'_B(\eta_B, t) = 1 - \eta_B(t) \tag{3.85}$$

This function is a curve that starts at zero, becomes strictly positive (and less than unity) to some maximum, and then decreases asymptotically back to zero. To provide a measure of the characteristic time for this function, we chose the zeroth and first moments

$$A_{\eta'_B} = \int_{\tau=0}^{\tau \to \infty} [1 - \eta_B(\tau)] d\tau$$
 (3.86)

$$\bar{t}_{\eta'_B} = \frac{1}{A_{\eta'_B}} \int_{\tau=0}^{\tau \to \infty} \tau [1 - \eta_B(\tau)] d\tau$$
(3.87)

Note that with these definitions, $\bar{t}_{\eta'_B}$ provides a characteristic time scale for the transient part of the process as influenced by the initial configuration. Although the characteristic time of η'_B is an important metric, it does not provide any information about the magnitude of the effectiveness factor (i.e., two curves with very different magnitudes in η'_B may still have the same value of $\bar{t}_{\eta'_B}$). To characterize this, we picked the L_{∞} norm



Figure 3.6: The functions η_B and η'_B for Case 3. The parameters $A_{\eta'_B}$, $\bar{t}_{\eta'_B}$, and $\eta'_{B,max}$ are illustrated to aid interpretation.

$$\eta'_{B,max} = \max(\eta'_B) \tag{3.88}$$

Thus, a metric representing both the magnitude, $\eta'_{B,max}$ and characteristic time, $\bar{t}_{\eta'_B}$ for a particular curve $\eta'_B(t)$ is given by the product $\bar{t}_{\eta'_B}\eta'_{B,max}$. One can think of the product $\bar{t}_{\eta'_B}\eta'_{B,max}$ as a measure of how important the effectiveness factor is in the upscaled diffusion-reaction equation. A summary of the data for $A_{\eta'_B}$, $\bar{t}_{\eta'_B}$, $\eta'_{B,max}$, and ℓ are provided in Table 3.2.

In Fig. 3.7 we have plotted $\bar{t}_{\eta'_B}\eta'_{B,max}$ versus the normalized cluster size for each of the four cases and at Da = 1, 10, and 100 on a log-log scale. The figure does show that there is a relationship between these variables, and that generally increasing the cluster size also increases the product $\bar{t}\eta'_{B,max}$. For these data, we fit (heuristically) a power law of the form

$$\bar{t}_{\eta'_B}\eta'_{B,max} = \beta Da^{\delta} \left(\frac{\ell}{\ell_{REV}}\right)^{\alpha}$$
(3.89)

to the data, while requiring that the value of α and β be the identical for all three values of Da. The best-fit results ($r^2 = 0.76$) suggested that a single power-law exponent, $\alpha = 1.72$, and scale factor given by βDa^{δ} with $\beta = 0.00127$ and $\delta = 0.67136$. Although the total number of data used to generate this figure is somewhat limited, it does suggest that cluster size and the product $\bar{t}_{\eta'_B} \eta'_{B,max}$ may be useful variables for predicting a priori the behavior

Case	Da	$A_{\eta'_B}$ (s)	\bar{t} (s)	$\eta'_{B,max}$	<i>l</i> (m)
1	1	4 40	10990	0.0266	0.0010
1	1	4.40	10220	0.0200	0.0010
	10	35.80	8880	0.0029	
	100	136.48	4720	0.0266	
2	1	21.03	5700	0.0029	0.0017
	10	187.31	5220	0.0277	
	100	1000.00	3820	0.1958	
3	1	75.52	8320	0.0061	0.0050
	10	640.00	7880	0.0551	
	100	3040.00	6080	0.3478	
4	1	35.61	3980	0.0068	0.0033
	10	300.00	3800	0.0630	
	100	1480.00	2296	0.3856	

Table 3.2: Parameters associated with the geometry and reaction properties of the four initial configuration cases.

of systems for which the clusters are nearly isotropic. For this relationship to be useful, one should solve the closure problem for at least once for the initial configuration of interest (as described above) at a particular value of Da. Then, these data can be rescaled to represent the results for other values of Da by using the heuristic relationship specified above. Note that, at this point these results are quite heuristic, and only allow constraining the product of $\bar{t}_{\eta'_B}\eta'_{B,max}$, i.e., we do not know these values independently. However, even this constraint is potentially a useful one. Additional research will have to be conducted to determine if such a power law holds for a wider array of initial configurations and Damköhler numbers.



Figure 3.7: The correlation between the product $\bar{t}\eta'_{B,max}$ (approximate measure of deviation from classical kinetics) and the normalized characteristic length, ℓ (approximate measure of initial spatial segregation).

3.6.2 Reaction delay case

As mentioned above, Case 4 encapsulates slightly different physics than the first three cases. Here, because there are regions of zero concentration initially, an early-time regime forms where diffusion is the sole microscale process. Mixing and reaction take place only after some initial spreading, and when the concentration fronts make contact. This delay is evident in Fig. 3.4, and is properly incorporated in the upscaled model for species B (3.61) via the memory term s_B^* .

To understand why this behavior exists, we can recall that s_B^* is the covariance of $\Phi_{A\gamma}$ and $\Phi_{B\gamma}$; these two variables encode the influence of the initial configurations the deviation quantities $\tilde{c}_{A\gamma}$ and $\tilde{c}_{B\gamma}$. In Case 4, these quantities are maximally correlated initially– in part, because much of the domain initially contains neither species A nor B, so $\tilde{c}_{A\gamma} = 2\tilde{c}_{B\gamma}$ there. The two species deviations co-vary at least until the sharp distributions of species A and B relax into larger clusters. This effect leads to a large value of s_B^* and strong inhibition of reaction at early times.


Figure 3.8: Asymptotic behavior of the system for the four initial conditions at Da = 1, 10, and 100. Note that in each of the four cases, the late-time reaction rate is exponential with identical constants; this is consistent with classical kinetics. The early-time dynamics of each curve, however, is greatly modified by the initial conditions as Da increases.

3.6.3 Long time behavior

In Fig. 3.8, we have plotted the concentration versus time histories for each value of Da and for all four initial conditions. These results show some interesting behavior that can be summarized as follows. First, the degree of deviation from non-classical rate behavior is greater with increasing values of Da.

Secondly, it appears that at large enough times, the effective reaction rate becomes identical regardless of the initial condition structure. We show in Appendix 3.8 that the concentration must decay exponentially at long times. Such a return to classical kinetic behavior at long times for bounded systems has been noted previously[142].

Finally, we note that as the value of Da increases, the configuration of the initial condition has a larger impact on the complete time history of the averaged concentration. Thus in Fig. 3.8 at Da = 100, even though each system converges to the same effective reaction rate, the time history for each average concentration can be distinctly different. The curves continue to be non-overlapping, even down to concentrations as low as 1 part in 1000). This means that, for any fixed time interval, the total concentration of species B transformed is dependent strongly upon its initial configuration.

3.7 Summary and Conclusions

In this work we have studied a set of coupled diffusion-reaction equations in a finite domain subject to highly segregated initial conditions. Our primary focus has been on elucidating the early-time kinetics of mixing-limited systems. Our main findings are that (1) early-time reaction kinetics are highly dependent upon the initial configurations of the reactants in a non-trivial fashion, and (2) the spatially-averaged evolution laws for the decaying species is not scale-invariant.

We find that the deviations from classical kinetics (as measured by the effectiveness factor) are directly proportional to the degree of segregation in the initial conditions (as measured by a mean cluster size or an effective diffusion length). Generally, the larger the cluster size of the initial conditions are, the larger the early-time deviations from classical kinetics become.

A predicted in previous studies for bounded systems [142], we observe a return to classical kinetics at late times. Interestingly, for high Damköhler numbers, the concentration histories for different initial conditions may have very different time trajectories. This deviation suggests that, although the influence of initial conditions over the effective rates of reaction relaxes, the trajectories of the system for different initial conditions can remain separated. The 'crossover' from early-time (anomalous) to late-time (classical) kinetics is naturally accounted for in the present framework as both regimes are described by the same coarse-grained evolution laws.

Appendix

3.8 Solution to the diffusion-reaction problem

3.8.1 Solution

The solution for the problem for species A is given by

$$c_{A\gamma}(x,y,t) = \int_{\xi=0}^{\xi=L} \int_{\eta=0}^{\eta=L} \varphi_A(\xi,\eta) \ G_A(x,y,\xi,\eta,t) \ d\eta \ d\xi$$
(3.90)

where the Green's function, G_A , for the problem is well known [27, 133]

$$G_{A}(x, y, \xi, \eta, t) = \frac{1}{L_{x}} \left[1 + 2\sum_{n=1}^{\infty} \exp\left(-\frac{\pi^{2}n^{2}Dt}{L_{x}^{2}}\right) \cos\left(\frac{n\pi x}{L_{x}}\right) \cos\left(\frac{n\pi\xi}{L_{x}}\right) \right] \\ \times \frac{1}{L_{y}} \left[1 + 2\sum_{m=1}^{\infty} \exp\left(-\frac{\pi^{2}m^{2}Dt}{L_{y}^{2}}\right) \cos\left(\frac{m\pi y}{L_{y}}\right) \cos\left(\frac{m\pi\eta}{L_{y}}\right) \right]$$
(3.91)

For the case of a 2-dimensional boxcar initial distribution (similar to Case 3 with side lengths Δ_{Ax} and Δ_{Ay}), the initial condition is

$$\varphi_A(x,y) = c_{A0}B(x, x_{A0}, \Delta_{Ax})B(y, y_{A0}, \Delta_{Ay})$$
(3.92)

where

$$B(\xi,\xi_0,\Delta) = H[\xi-\xi_0] - H[\xi-\xi_0-\Delta]$$
(3.93)

and H is the Heaviside distribution.

The integrations are straightforward. The result is

$$c_{A\gamma}(x, y, t) = c_{A0}$$

$$\times \left[\frac{\Delta_{Ax}}{L_x} + 2\sum_{n=1}^{\infty} \exp\left(-\frac{\pi^2 n^2 D t}{L_x^2}\right) \Gamma_{An} \cos\left(\frac{n\pi x}{L_x}\right) \right]$$

$$\times \left[\frac{\Delta_{Ay}}{L_y} + 2\sum_{m=1}^{\infty} \exp\left(-\frac{\pi^2 m^2 D t}{L_y^2}\right) \Gamma_{Am} \cos\left(\frac{m\pi y}{L_y}\right) \right]$$
(3.94)

where the Fourier coefficients for the boxcar distribution are given by

$$\Gamma_{An} = \frac{1}{n\pi} \left(\sin\left[\frac{n\pi(x_{A0} + \Delta_{Ax})}{L_x}\right] - \sin\left[\frac{n\pi x_{A0}}{L_x}\right] \right)$$
(3.95)

$$\Gamma_{Am} = \frac{1}{m\pi} \left(\sin\left[\frac{m\pi(y_{A0} + \Delta_{Ay})}{L_y}\right] - \sin\left[\frac{m\pi y_{A0}}{L_y}\right] \right)$$
(3.96)

The solution for species B is somewhat more difficult to obtain, but the solution is helped by the transformation

$$c_{B\gamma}(x,y,t) = w(x,y,t)exp\left(-\int_{\tau=0}^{\tau=t} k_B^0 c_{A\gamma}(x,y,\tau) \,d\tau\right)$$
(3.97)

Substituting this into Eqs. (3.5)-(3.6) yields the simplified set of equations (for $F_B = 0$)

$$\frac{\partial w}{\partial t} = \nabla_r \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r w) \text{ for } \mathbf{r} \in \text{ in } \mathscr{V}(\mathbf{x})$$
(3.98)

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{B\gamma} \cdot \nabla_r c_{B\gamma}) = 0 \quad \text{for } \mathbf{r} \in \text{in } \mathscr{A}_{\gamma e}(\mathbf{x})$$
(3.99)

$$w(\mathbf{x},0) = \varphi_B(\mathbf{x}) \quad \text{for } \mathbf{r} \in \text{in } \mathscr{V}(\mathbf{x}) \tag{3.100}$$

The solution for w, then, is of exactly the same form as the solution for species A.

$$w(x,y,t) = \int_{\xi=0}^{\xi=L} \int_{\eta=0}^{\eta=L} \varphi_B(\xi,\eta) \ G_B(x,y,\xi,\eta,t) \ d\eta \ d\xi \tag{3.101}$$

or, upon inverting the transformation

$$c_{B\gamma}(x,y,t) = \exp\left(-\int_{\tau=0}^{\tau=t} k_B^0 c_{A\gamma}(x,y,\tau) d\tau\right)$$
$$\int_{\xi=0}^{\xi=L} \int_{\eta=0}^{\eta=L} \varphi_B(\xi,\eta) G_B(x,y,\xi,\eta,t) d\eta d\xi$$
(3.102)

Assuming a second 2-dimensional boxcar function as initial condition for species ${\cal B}$ of the form

$$\varphi_B(x, y) = c_{B0}B(x, x_{B0}, \Delta_{Bx})B(y, y_{B0}, \Delta_{By}) \tag{3.103}$$

then the final solution can be written

$$c_{B\gamma}(x, y, t) = c_{B0}$$

$$\times \left[\frac{\Delta_{Bx}}{L_x} + 2\sum_{n=1}^{\infty} \exp\left(-\frac{\pi^2 n^2 D t}{L_x^2}\right) \Gamma_{Bn} \cos\left(\frac{n\pi x}{L_x}\right) \right]$$

$$\times \left[\frac{\Delta_{By}}{L_y} + 2\sum_{m=1}^{\infty} \exp\left(-\frac{\pi^2 m^2 D t}{L_y^2}\right) \Gamma_{Bm} \cos\left(\frac{m\pi y}{L_y}\right) \right]$$

$$\times \exp\left[-k_B^0 \Phi_A(x, y, t; x_{A0}, y_{A0})\right]$$
(3.104)

Here, Γ_{Bn} , Γ_{Bm} , and Φ_A are given by

$$\Gamma_{Bn} = \frac{1}{n\pi} \left(\sin\left[\frac{n\pi(x_{B0} + \Delta_{Bx})}{L_x}\right] - \sin\left[\frac{n\pi x_{B0}}{L_x}\right] \right)$$
(3.105)

$$\Gamma_{Bm} = \frac{1}{m\pi} \left(\sin\left[\frac{m\pi(y_{B0} + \Delta_{By})}{L_y}\right] - \sin\left[\frac{m\pi y_{B0}}{L_y}\right] \right)$$
(3.106)

$$\Phi_{A}(x, y, t; x_{0}, y_{0}) = c_{A0} \frac{\Delta_{Ax} \Delta_{Ay} t}{L_{x} L_{y}}$$

$$+ \frac{2c_{A0} \Delta_{Ax}}{L_{x}} \sum_{m=1}^{\infty} \frac{L_{y}^{2}}{\pi^{2} m^{2} D} \left[1 - exp \left(-\frac{\pi^{2} m^{2} D t}{L_{y}^{2}} \right) \right]$$

$$\times \Gamma_{Am} \cos \left(\frac{m \pi y}{L_{y}} \right)$$

$$+ \frac{2c_{A0} \Delta_{Ay}}{L_{y}} \sum_{n=1}^{\infty} \frac{L_{x}^{2}}{\pi^{2} n^{2} D} \left[1 - exp \left(-\frac{\pi^{2} n^{2} D t}{L_{x}^{2}} \right) \right]$$

$$\times \Gamma_{An} \cos \left(\frac{n \pi x}{L_{x}} \right)$$

$$+ 4c_{A0} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\pi^{2} D \left[\frac{n^{2}}{L_{x}^{2}} + \frac{m^{2}}{L_{y}^{2}} \right]}$$

$$\times \left[1 - exp \left(-\pi^{2} D t \left[\frac{n^{2}}{L_{x}^{2}} + \frac{m^{2}}{L_{y}^{2}} \right] \right) \right]$$

$$\times \Gamma_{An} \cos \left(\frac{n \pi x}{L_{x}} \right) \Gamma_{Am} \cos \left(\frac{m \pi y}{L_{y}} \right)$$
(3.107)

The averaged concentration for species B can then be found by a double quadrature

$$\langle c_{B\gamma} \rangle^{\gamma} = \frac{1}{L_x L_y} \int_{x=0}^{x=L_x} \int_{y=0}^{x=L_y} c_{B\gamma}(x, y, t) \, dy \, dx$$
 (3.108)

Although it may be possible to determine this integral analytically using term-by-term integration, the effort required to do this would be substantial because of the numbers of terms involved. Alternatively, one could compute the integration using a numerical quadrature scheme; we have adopted this latter approach.

3.8.2 Early-time behavior

Determining the early-time behavior of the spatially-averaged diffusion-reaction equations is a challenging task. For this work, we have the advantage of an analytical solution, which makes further analysis less difficult. To start, we first develop an estimate for the solution for species A that is more amenable to analysis of time behavior. Using a Jacobi-type method of images identity (c.f., Dym and McKean [52], p. 68), one can show

$$c_{A\gamma} = \int_{0}^{L_{x}} \int_{0}^{L_{y}} \left[\frac{1}{2} \vartheta_{3} \left(-\frac{1}{2Lx} \pi(x-\xi), Exp\left[\frac{-\pi^{2}Dt}{Lx^{2}}\right] \right) \right]$$

+
$$\frac{1}{2} \vartheta_{3} \left(-\frac{1}{2Lx} \pi(x+\xi), Exp\left[\frac{-\pi^{2}Dt}{Lx^{2}}\right] \right) \right]$$

×
$$\left[\frac{1}{2} \vartheta_{3} \left(-\frac{1}{2Ly} \pi(y-\eta), Exp\left[\frac{-\pi^{2}Dt}{Ly^{2}}\right] \right) \right]$$

+
$$\frac{1}{2} \vartheta_{3} \left(-\frac{1}{2Ly} \pi(y+\eta), Exp\left[\frac{-\pi^{2}Dt}{Ly^{2}}\right] \right) \right]$$

×
$$c_{B0}B(x, x_{B0}, \Delta_{Bx})B(y, y_{B0}, \Delta_{By}) d\eta d\xi \qquad (3.109)$$

where ϑ_3 is the Jacobi theta function of type 3. Carrying out this integration, the solution can be put in the form

$$c_{A\gamma}(x, y, t) = c_{A0}\Psi(x, t; x_{A0}, \Delta_{Ax}, L_x)\Psi(y, t; y_{A0}, \Delta_{Ay}, L_y)$$
(3.110)

where

$$\Psi(w,t;w_{A0},\Delta_{Aw},L_{w}) = \sum_{n=-\infty}^{\infty} -\frac{2L_{w}n - w + w_{A0}}{2|2L_{w}n - w + w_{A0}|} \\ \times \operatorname{erf}\left(\frac{|2L_{w}n - w + w_{A0}|}{\sqrt{4Dt}}\right) \\ +\frac{1}{2}\operatorname{erf}\left(\frac{2L_{w}n - w + w_{A0} + \Delta_{Aw}}{\sqrt{4Dt}}\right) \\ -\frac{1}{2}\operatorname{erf}\left(\frac{2L_{w}n - w - (w_{A0} + \Delta_{Aw})}{\sqrt{4Dt}}\right) \\ +\frac{1}{2}\operatorname{erf}\left(\frac{2L_{w}n - w - w_{A0}}{\sqrt{4Dt}}\right)$$
(3.111)

This solution is a function whose functional dependence on time goes as the error function of $t^{-\frac{1}{2}}$. Recalling that

$$\operatorname{erf}\left(t^{-\frac{1}{2}}\right) = \frac{2}{\sqrt{\pi}}\left(t^{-\frac{1}{2}} - \frac{1}{3}t^{-\frac{3}{2}} + \dots\right)$$
(3.112)

it is clear that the solution for species A involves no simple powers of time for small t. From Eq. (3.104), it is easy to find the following relationship

$$\langle c_{B\gamma} \exp\left[k_B^0 \Phi_A(x, y, t; x_{A0}, y_{A0})\right] \rangle^{\gamma} = c_{B0} \frac{\Delta_{Bx}}{L_x} \frac{\Delta_{By}}{L_y}$$
(3.113)

Because the right-hand side of this expression is a constant, we must have that the time component of the behavior of $c_{B\gamma}$ is proportional to

$$c_{B\gamma} \propto \exp\left[-k_B^0 \Phi_A(x, y, t; x_{A0}, y_{A0})\right]$$
 (3.114)

In other words, the time dependence of species B is an exponential function of the time integral of species A. It must have multiple time scales, then, each proportional to $t^{-n\frac{1}{2}}$ (where n is an odd integer greater than 1). Thus, there is no simple power law time exponent for the spatially averaged concentration $\langle c_{B\gamma} \rangle^{\gamma}$; it must be represented by a sum of powers of time. This result has also been noted by Sancho et al. [142] for a slightly more general reaction.

3.8.3 Late-time behavior

In the late-time limit, and examination of Eq. (3.94) shows that $c_{A\gamma}$ tends to the value

$$\langle c_{A\gamma} \rangle_{t \to \infty}^{\gamma} = c_{A0} \Delta_{Ax} \Delta Ay / (L_x L_y)$$
 (3.115)

which represents the concentration formed by spreading the initial mass of species A evenly over the domain. Because $\langle c_{A\gamma} \rangle^{\gamma}$ is essentially constant, one can spatially average Eq. (3.104) to immediately determine

$$\langle c_{B\gamma} \rangle_{t \to \infty}^{\gamma} \propto c_{B0} \frac{\Delta_{Bx} \Delta_{By}}{L_x L_y} exp[-k_B^0 \langle c_{A\gamma} \rangle_{\infty}^{\gamma} t]$$
 (3.116)

This is equivalent to the classical kinetics for a fully-mixed system.

In between these two regimes, no simple scaling law exists for the behavior of the time exponents. However, the effectiveness factor can be used to describe the state of the system. This is described in the main body of the paper.

3.9 Validation of the inequality given by Eq. 3.32

In this appendix, we compute the quantity

$$\frac{cov_{AB}}{\sigma_A^2 + \sigma_B^2} \ll 1 \tag{3.117}$$

expressed as (3.32) in the main body of the paper. In Fig. 3.9, we have plotted this quantity as a function of time for the four initial condition cases considered. In each case, the inequality is met, but the degree to which the "much less than" criterion is met is somewhat subjective. In any event, for the late-time behavior the inequality is clearly valid. For intermediate times, the case for validity is not as strong; however, coupled with the correspondence between the direct numerical simulations and the upscaled model, the validity of the assumption appears to be warranted. In early-time applications to initial conditions that have structure distinctly different from those presented here, the validity of the assumption should be checked by at least an approximation of the quantities needed to compute (3.32).



Figure 3.9: The ratio given in (3.32) as a function of normalized time for the four initial conditions examined (Da = 100).

Chapter 4 – Computational pore-scale closures for Darcy's law

To be incorporated in abridged form in a monograph by Brian D. Wood, Sourabh Apte, Xiaoliang He, and Sassan Ostvar

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4.1 Preface

Proposed in analogy with Fourier's and Ohm's law, in Darcy's law the rate of fluid flow across a porous medium is linearly proportional to a net driving force (the sum of bulk pressure drop and body forces)

$$\langle \mathbf{v} \rangle^{\gamma} = \frac{\mathbf{K}}{\mu} \cdot (\nabla \langle p \rangle^{\gamma} + \mathbf{F}_{b}) \tag{4.1}$$

Since its conception as an empirical relationship, Darcy's law has found great utility in the Earth sciences to describe the macroscopic motion of creeping flow across porous media. Eq 4.1 introduces the notion of *permeability* as an effective property of a porous medium. In the original work of Henry Darcy and since, permeability has been treated as an experimental observable. Elucidation of K typically involves measuring the pressure drop across a sample at predetermined flowrates in a regime where the linearity of Eq 4.1 holds. There has also been interest in predicting K from a set of simple morphological quantifiers of porous media, such as porosity (ϕ) and specific surface area (S) among others [14], and more recently via computation.

Since its introduction, derivation of Eq 4.1 as a effective theory from microscopic physics has inspired much theoretical work. One can show that Darcy's law is equivalent to the volume-averaged form of the Stokes equations in macroscale homogeneous two-phase media [182]. The multiscale analysis starts with the microscale problem stated as

$$0 = \mu \nabla^2 \mathbf{v}_{\gamma} - \nabla p_{\gamma} + \mathbf{f}_b \tag{4.2}$$

$$\nabla \cdot \mathbf{v}_{\gamma} = 0 \tag{4.3}$$

$$\mathbf{v}_{\gamma} = 0 \quad \text{in} \quad \mathcal{A}_{\gamma\kappa}, \tag{4.4}$$

and appropriate external boundary conditions. The volume averaging approach to the derivation of Darcy's law poses the computation of K as a closure problem for Eq 4.1, where the tensor is defined as

$$\mathbf{K} = \left[\frac{\phi}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{b}_{p}\mathbf{I} + \nabla \otimes \mathbf{B}_{v}) dA\right]^{-1}$$
(4.5)

 \mathbf{B}_v and \mathbf{b}_p are the closure variables associated with permeability, and are defined analogously to the closure variable to diffusion (see Chapter 2). The full statement of the closure problem for an REV as Whitaker [182] would write it is

$$-\nabla \mathbf{b}_p + \nabla^2 \mathbf{B}_v = \frac{1}{\mathcal{V}_{\gamma}} \int_{\mathcal{V}_{\gamma}} [\nabla \mathbf{b}_p + \nabla^2 \mathbf{B}_v] dV, \qquad (4.6)$$

$$\nabla \cdot \mathbf{B}_v = 0, \tag{4.7}$$

B.C.1
$$\mathbf{B}_v = -\mathbf{I}$$
 in $\mathcal{A}_{\gamma\kappa}$ (4.8)

B.C.1
$$\mathbf{B}_{v}(\mathbf{r}+\ell_{i}) = \mathbf{B}_{v}(\mathbf{r}) \quad \mathbf{b}_{p}(\mathbf{r}+\ell_{i}) = \mathbf{b}_{p}(\mathbf{r}) \quad i = 1, 2, 3,$$
 (4.9)

$$\langle \mathbf{b}_p \rangle^{\gamma} = \langle \mathbf{B}_v \rangle^{\gamma} = 0 \tag{4.10}$$

The structure of (4.6 - 4.10) is very similar to the original problem. We can also appreciate the similarity with the closure problem for diffusion. Here too, the only source is a boundary constraint, with the subtle differences that (i) \mathbf{B}_v is divergence-free as guaranteed by the $\nabla \mathbf{b}_p$ term which acts similar to a Lagrange multiplier, and (ii) local curvature of \mathbf{B}_v is stabilized by nonlocal information as expressed by integral term. In principle, (4.6 - 4.10)can be solved directly to compute \mathbf{K} , but for reasons that we will outline in the proceeding, we are interested in performing direct numerical simulations of the microscale velocity and pressure fields first.

4.2 Goals for this study

In the present study, we are interested in direct numerical simulation of a Newtonian fluid in the creeping flow regime in triply-periodic monodisperse sphere packings. Our goals for the work are two-fold: (i) First, we are interested in treating the simulations as computational closures for the method of volume averaging. The main goal here is to compute the permeability tensor with high fidelity and study its behavior as a function of sample size. (ii) Second, we are interested in cross-examining the simulations with an experimental case that was previously reported on by our group [192]. Very briefly, this is a mildly laminar ($Re \approx 3.2$) unidirectional flow in a packing of 78 spheres that are confined to walls on the sides. The associated velocity field has been imaged using Particle Image Velocimetry (PIV) and cross-validated with direct numerical simulations.

4.3 Simulation of fluid flow in porous media

Numerical solutions of the Navier-Stokes equations in porous structures have received a great deal of attention in the past two decades. Various fundamental aspects of the problem including the statistics of the velocity field [105, 82, 43] and its correlation to the structure of the solid [151], the turbulent transition [72], and anomalous scalar transport induced by the heterogeneities of the velocity field [17] have been explored. The problem also finds immediate application in computing the permeability of natural and synthetic porous materials, which is the main focus of the present study.

Previous works span a wide range of flow regimes from viscous-dominated [176, 156, 152, 192], to inertial [58, 73, 15] and turbulent. Different simulation paradigms including Lattice-Boltzmann methods [73, 176], and finite-volume methods [17, 112, 57, 75] have been explored. Siena et al. [152] recently compared three diverse simulation platforms for Darcy flow and found them to be consistent with each other. The geometrical setups studied also come in a wide variety that includes periodic crystalline arrays of mono- [73] and bidisperse particles [15], random arrangements of obstacles [51], synthetic correlated structures [75, 151], and x-ray microtomographic reconstructions of rock [68, 156, 198], bone [37], and fibrous materials [111].

4.3.1 The fictitious domain method

The simulations in this study were performed via an immersed boundary (IB) implementation using the fictitious domain method (FDM). The IB is a robust approach to fully resolving the Navier-Stokes equations in domains with arbitrary boundaries, e.g. flow in porous materials, and particle-laden flows. In IB methods, the solid phase is modeled as an analogous fluid that undergoes rigid body motion [147, 10]. The particular FDM implementation used here has been outlined in detail in [58, 154]. Very briefly, the force necessary to cancel local fluid velocities and impose stationarity (or rigid body motion) in the solid phase is computed and added to the momentum balances as an external source. To do so, the solver uses a superlattice of Lagrangian material points. At each timestep, the force necessary to cancel motion at loci that correspond to the solid is calculated on the superlattice by interpolating the regular grid. This interpolation step is critical to the accuracy of the solver, so the three-point delta function proposed by Roma et al. [140] was used here. This function has continuous first derivatives, and can be shown to converge to a sharp representation of the $\gamma - \kappa$ interface as the spatial grid is refined.

4.4 Computation of the permeability tensor

4.4.1 Solver validation and setup

Prior to the study we assessed the solver using as the series solution of Zick and Homsy [200] for drag in simple cubic arrays, where the drag coefficient is defined as

$$C_d = \frac{f_d}{3\pi N\mu D\langle v \rangle} \tag{4.11}$$

We found very good agreement between the simulations and the analytical solution (Figure 4.1A). The results are obtained for flow driven by a volumetric body force, and $Re < 10^{-4}$. Following [192] we made sure that a baseline grid refinement of $\Delta/D \ge 50$ was met. To match the analytical solution, we made sure the time step Δt was at least two orders of magnitude smaller than the time scale $t_v \sim \Delta x^2/\nu$ associated with viscous forces.

Next, we performed an REV analysis on periodically disordered sphere packings. These are structures that are generated by packing spheres in containers with periodic instead of wall conditions. Our main goal here was to match the permeability reported by Wood et al.



Figure 4.1: (A) Drag coefficient (4.11) as a function of solid volume fraction $1-\phi$ in a simplecubic array of spheres. (B) Comparison of the permeability obtained for the experimental system in [192] (dashed horizontal line), and direct simulations using the fictitious domain method in different REV sizes. Here $\kappa \equiv K_{\xi\xi}$ for flow in the ξ -direction.

[192] for a measured velocity field, so we parametrized the problem using values that match this particular experimental setup. We studied flow in the regime $Re \sim 1$. The results of computations for the component of the permeability tensor that corresponds to mean flow reproduced in Figure 4.1B show excellent agreement between the numerical simulations and the experiments.

4.4.2 Permeability from volume averaging

One way to compute **K** via volume-averaging is to solve the closure problem over an REV defined by the system (4.6 - 4.10). Although this approach is conceptually appealing and potentially interesting from the point of view that Chapter 2 was developed, solving for the tensor field \mathbf{B}_v tends to be arduous. Instead, we recall the definition of **K** in terms of the spatial fluctuations, \tilde{p}_{γ} , and $\tilde{\mathbf{v}}_{\gamma}$. To avoid having to invert matrices on the fly, we also use the following relationship between **K** and the net traction vector **H**:

$$\mathbf{H} = -\mu \,\mathbf{K}_{mva}^{-1} \cdot \langle \mathbf{v} \rangle^{\gamma},\tag{4.12}$$



Figure 4.2: (A) Schematic illustrating the setup for calculating the spatial pressure fluctuations, \tilde{p} . (B) Test of the linearity of pressure drop along the flow direction in a simple cubic array of 3 spheres with periodic side boundaries.

and finally derive the relationship

$$\mathbf{H} = \frac{1}{\mathcal{V}_{\gamma}} \int_{\mathcal{A}_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \left(-\tilde{p}_{\gamma} \mathbf{I} + \mu \nabla \otimes \tilde{\mathbf{v}}\right) \, dA. \tag{4.13}$$

Eq 4.13 gives us a direct means to compute the volume averaging permeability tensor using the microscale velocity and pressure fields in an REV via the decompositions:

$$\tilde{\mathbf{v}} = \mathbf{v} - \langle \mathbf{v} \rangle^{\gamma} \tag{4.14}$$

$$\tilde{p} = \mathbf{p} - \langle p \rangle^{\gamma}. \tag{4.15}$$

A key emphasis of the forthcoming monograph is the proper way to compute the pressure fluctuations, \tilde{p}_{γ} . Here we have to take into account the physical fact that the average pressure varies along the direction of the macroscopic pressure gradient. As a result, at each point in the REV a new value of $\langle p_{\gamma} \rangle^{\gamma}$ has to be computed using the proper averaging window (Figure 4.2). A desirable simplification is to assume that the average pressure declines linearly along the macroscopic gradient. In the following section, we will confirm this for our system.

4.4.3 Rolling average pressure

We recall the definition of the superficial averaging operator acting on the pressure field, p_{γ} as

$$\langle p_{\gamma} \rangle |_{\mathbf{x}} = \int_{\mathbf{r} \in \mathcal{V}_{\gamma}(\mathbf{x})} w(\mathbf{x} - \mathbf{r}) \ p_{\gamma}(\mathbf{r}) \ dV(\mathbf{r})$$
 (4.16)

Similar to Chapter 2, for simplicity we use the boxcar function $w = 1/\mathcal{V}_{\gamma}$. In periodic arrays of particles, this particular choice has been shown to potentially introduce wave-like interference in the averaged field. To suppress these perturbations, Quintard and Whitaker [134] propose a top-hat function that averages information over two periods of an array. To test whether or not this is necessary in our system, we computed the averaged pressure along the direction of the vector $\nabla \langle p_{\gamma} \rangle^{\gamma}$ using the boxcar function, in a 3-period 3D sc array of spheres with periodic side boundaries (Figure 4.2B). The results presented in Figure 4.2C show that the pressure field is linear to a good approximation. This results in significant simplification of one-the-fly computations since the average pressure field need be obtained for one time step only, once the flow is fully-developed.



Figure 4.3: Streamwise velocity components normalized by their superficial average value for (a) simple-cubic case of [200], (b) a triply periodic monodisperse sphere packing with 8 particles, and (c) a triply periodic monodisperse sphere packing with 40 particles. Note that to improve the visualization, we have allowed the color scheme to vary between the subfigures.

4.4.4 Flow in confined and triply-periodic REVs

Figures 4.3 and 4.4 show the streamwise components of the velocity field, and computations of the velocity distribution functions (the histogram of velocity components normalized by the superficial velocity), for the four cases studied here (the experimental case of [192], a simple-cubic array of spheres, and the 8- and 40-sphere periodic REVs). Given the simplicity of monodisperse granular materials, it is not surprising that we converge to the experimental permeabilities even for small REVs, but we must note though that the structure of the flow varies significantly as larger structures are sampled, and a wider distribution of velocities become accessible.

A transition from a periodic simple-cubic cell to periodically disordered packings of 40 spheres corresponds to (i) a more spread-out velocity distribution, and (ii) more prominent (and symmetric) transverse velocity components. The presence of randomness also appears to contribute to a more smooth transition from small to large velocities, as opposed to the mild bimodality observed in crystalline arrangements (see Chapter 3 in [58]). We can understand this as a consequence of extensive channeling when openings in a pore space line up to permit unobstructed flow. Figure 4.4 shows that significant channeling takes place in all 4 corners of the REV in single sphere case, but as the number of particles increases, channeling is more localized and distributed slightly more randomly throughout space.

Confinement appears to constrain the transverse components of the velocity field as evident by the reduced variance, and prominent asymmetry of the histograms in Figure 4.4. We observe a similar asymmetry in the transverse velocity components of the 8-sphere case, which implies finite anisotropy effects in these structures [96]. Smaller REVs also exhibit inter-sample fluctuations as evident in the variance in permeabilities computed using the 8-sphere samples in Figure 4.1B.



Figure 4.4: Confined vs periodic vdfs in monodisperse packings of spheres with $\phi = 0.44$. Confinement biases the transverse components of the velocity field in favor of the streamwise component. The transverse vdfs are more symmetric in comparison for the periodic REVs.

Chapter 5 – Multiscale Model Describing Bacterial adhesion and Detachment

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Abstract

Bacterial surfaces are complex structures with non-trivial adhesive properties. The physics of bacterial adhesion deviates from that of ideal colloids due to cell-surface roughness and because of the mechanical properties of the polymers covering the cell surface. In the present study, we develop a simple multiscale model for the interplay between the potential energy functions that characterize the cell surface biopolymers and their interaction with the extracellular environment. We then use the model to study a discrete network of bonds in the presence of significant length heterogeneities in cell-surface polymers. The model we present is able to generate force curves (both approach and retraction) that closely resemble those measured experimentally. Our results show that even small-lengthscale heterogeneities can lead to macroscopically nonlinear behavior that is qualitatively and quantitatively different from the homogeneous case. We also report on the energetic consequences of such structural heterogeneity.

5.1 Introduction

Surface heterogeneity created by biopolymers is a characteristic feature of bacteria. Lipopolysaccharides, a host of extracellular polysaccharides, and various proteinaceous structures like pili and fimbriae are among the macromolecules that constitute the surface of bacterial cells[48, 6, 175, 177, 155]. It has been suggested that physical heterogeneity on biological surfaces generally leads to an improvement in adhesion [12], and some bacteria have specialized tools that allow them to modulate the spatial heterogeneity of surface structures in response to external stimuli [91, 100, 180]. As one would expect, the effects of these variations lead to measurable changes in adhesion at the cell scale [159].

Heterogeneity partly explains why colloid models, such as the classical DLVO theory, have been largely unsuccessful in characterizing bacterial adhesion[130, 174, 84, 114]. Although the presence of surface heterogeneity is well established (illustrations of representative surface heterogeneities are given in Figure 5.1), it is a challenging problem to determine how such heterogeneity influences the interaction between the cell and a substratum. A central difficulty in addressing the problem is the presence of different kinds of heterogeneity on cell surfaces. One could formulate related but conceptually very different questions depending on whether heterogeneity in electric charge or surface roughness is of interest. In

the present study we are concerned with the latter.

In order to answer questions about surface roughness, we first need a framework that resolves the effects of macromolecular deformations on adhesion. Bacterial surfaces may contain surface features that are 10's to 100's of nanometers in length; the deformations of these features occur over distances that are much larger than the characteristic lengths of the bonds they form with an external substratum [53]. The ubiquity of these features suggests that they should be treated directly as the interacting feature in the adhesion process. In fact, such approaches have been explored already for adhesion via bacterial pili[18].

A typical bacterial adhesion event (as resolved by an AFM measurement for instance) is illustrated in Figure 5.2. During the approach phase of the measurement, often only repulsive forces are seen. However, upon reversal of the process, one usually observes significant attractive forces as the polymers are stretched and eventually pull out of the potential energy well holding them to the surface; this is often observed as a series of discrete detachment events that give the retraction curve a 'rugged' appearance. Upon a complete cycle of such an experiment on bacterial surfaces, significant hysteresis if frequently observed in the force curves between approach (usually repulsive) and extension (usually attractive)[175],[115].

Current approaches to modeling bacterial adhesion treat the approach and retraction phases as separate processes. The former is commonly studied using modified DLVO theory with additional contributions borrowed from steric polymer brush models[26, 45], where uniformity of surfaces is an often unstated assumption. And the latter is modeled using polymer elasticity theories. Most frequently some variation of the worm-like chain (WLC), or the freely-jointed chain (FJC) is adopted[4, 19]. Either component of this framework has essentially no predictive or explanatory value for the other.

We adopt a somewhat different approach here. Our primary goal is to develop a framework where both adhesion and detachment can be modeled as a single integrated process. We propose a two-scale model that interprets adhesion as the result of an ensemble of discrete bonds between a substratum and a spatially heterogeneous, mechanically compliant polymer brush. There are two elements to this approach that are novel.

There are several elements to our approach that are novel. First, we explicitly represent processes at two distinctly different scales: (1) the nanoscale molecular adhesion events of the cell surface structures to the substratum (length scale I in Figure 5.1), and (2) the submicron-scale subsequent deformation of the polymer molecules (length scale II in Figure



Figure 5.1: Surface roughness on bactera. (A) An SEM image of *Burkholderia cepacia* showing polymers on the order of 50 nm on the surface. (B) An AFM image of an 0.8 μ m by 0.8 μ m area of a single cell of *Escherichia coli* JM109 (SF815A) imaged at the nanoscale (data from Amro et al.[6]). (C) Length distribution for the data associated with Figure 1B. (D) A quantile-quantile analysis shows that surface features are approximately normally distributed, but show some evidence of the distribution being short-tailed.

5.1). The first of these two processes is what binds the tips of the polymer molecules to the substrate. The second process represents the large-scale deformation of the polymer molecules that can occur specifically because their tips are bound to the surface. These two process scales are not independent. For example, the state of stress in the polymer molecule can determine if the polymer tip is able to escape its bond with the surface. The explicit representation of these two interacting process scales is novel in applications to bacterial

adhesion.

Second, we directly account for the presence of spatial heterogeneity in the polymer lengths on the cell surface. This is important for capturing both the overall behavior of the adhesion process, as well as representing the discrete rupture events that occur during detachment. The importance of bacterial surface heterogeneity has only begun to be formally recognized [130], and very few studies have tried to represent these effects.

The framework we implement here is general because one can substitute whatever functional form is appropriate for the cell polymer molecules. Thus, we do not promote a particular constitutive theory for describing the mechanics of the deformations of macromolecules. Instead, we develop a *modeling approach* that is capable of representing the essential physics of hysteretic force-distance curves without being overly complex.

5.2 Model

We represent the force between bacterial surface polymers and a substratum as the sum of individual adhesion events over the polymer molecules. For each polymer molecule, we assume that there are three contributions to the overall potential energy function as described above: (1) the nanoscale adhesion process; (2) subsequent sub-micron deformations of the macromolecules, and (3) the influence of external (e.g., electrostatic) fields.

Our modeling approach is similar in many ways to the approach used in the moleculardynamical finitely-extensible-nonlinear-elastic (FENE) models developed for describing the properties of polymers [197, 109]. Such bead-spring models are inherently multiscale in that the characteristic lengths associated with bead interactions can be orders of magnitude smaller than the characteristic length scale for the springs.

In contrast to these models, however, we adopt two significant simplifications. First, we do not consider polymer-polymer interactions as is done in molecular-dynamical-FENE models of polymers; this is not an uncommon assumption in modeling dilute polymers[2]. Secondly, we do not *explicitly* consider thermal fluctuations or particular conformations of the polymers (e.g., polymers with a tilt angle) because these effects are embedded already in the particular polymer chain model adopted.

With these simplifications, we develop a simplified spring-bead model for the system as follows. For a system that consists of N_p deformable polymer chains each with a polymer molecule tip (bead) that bonds to the substratum, we write the potential energy function



Figure 5.2: Schematic representation of the two-scale interaction between the cell surface polymers and a substratum (AFM sphere probe) on approach and retraction. The process of adhesion is characterized by highly local short-range forces between the part(s) of polymer molecules that come in contact with the probe, and longer-range forces arising due to the compression or extension of the chains. Figure adapted from Ginn et al.[62]

for the i^{th} polymer molecule as

$$U_{T,i}(r) = U_{bead,i}(r) + U_{chain,i}(r) + U_{external,i}(r)$$
(5.1)

where $U_{bead,i}$ represents the interaction potential energy function between the bead and substate surface, and $U_{chain,i}$ represents the potential energy function of the polymer molecule.

At the molecular level, cellular adhesion to a substratum is often thought to be dominated by hydrogen bonds [98, 84, 150] thus, it is reasonable to represent the polymer tipsubstratum potential, $U_{bead,i}$, by a Lennard-Jones (L-J) 6–12 function [56]. Note that we are not necessarily suggesting that our choices of potential functions apply to all polymers and bonds; these are convenient empirical functional forms that capture the essential physics of the adhesion event, and such forms are frequently used to represent parts of the adhesion phenomena at cell surfaces[80, 124]

$$U_{bead}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(5.2)

Here ϵ is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, and r is the distance between the polymer tip (bead) and the substrate.

The potential function for the polymer molecule deformation, $U_{chain,i}$, can be as simple or complex as is reasonable for describing the deformation of the polymer, and can include polymer-polymer interactions. Although the contributions of enthalpic (e.g., bending) and entropic (thermal motion) forces are common to nearly all polymer models, the particular kind of polymer network, density of the network, and amount of deformation lead to tremendous variety in the models that predict polymer molecule force as a function of deformation. In this work we provide examples of the simplest kinds of models; more complex models can be adopted if there is sufficient knowledge about the particular system of interest to do so.

This model corresponds roughly to the following processes, illustrated in Figure 5.2. (A) The end of a single polymer chain (bead) is attracted into the L-J potential well (plus any external field potentials) to create adhesion of the bead and stretching of the chain. (B) Further approach leads eventually to chain compression and increasing repulsion. (C) On retraction, the polymer molecules remain trapped in the potential energy well, but begin to relax toward their equilibrium state. (D) Upon further retraction, the polymer molecules are stretched until either (1) the chain potential energy surpasses the maximum potential energy of the trapped bead (i.e. the depth of the potential well, ϵ) and the bead escapes the L-J well (D), or (2) the chain is ruptured. In the following material, we account for the first of these two options. The second option (chain rupture) is not discussed, but would be straightforward to incorporate in the model should conditions warrant it.

5.2.1 General force balance

In Figure 5.3 we have outlined the geometry of our system. The total separation between the substratum and the cell membrane (from which the cell surface features extend) is specified by the distance ξ , which is the *independent* variable in this analysis. The distance



Figure 5.3: (A) Geometrical setup of the problem defined by eq 5.6. The polymer base is assumed to be stationary. (B) A force balance for the bead-polymer system in a state of attraction toward the substratum (i.e. chain extension).

between the polymer tips and the substratum is given by $r(\xi)$, and this distance depends on the interaction between the L-J and chain forces.

For each polymer chain, the total force created by the potential energy function, $U_{T,i}$, is the negative of the gradient of the potential function. Thus, the total force balance on each polymer is given by

$$\frac{\partial (m_{eff,i}v_i)}{\partial t} = -\frac{\partial U_{bead,i}}{\partial r} - \frac{\partial U_{chain,i}}{\partial r} - \frac{\partial U_{external,i}}{\partial r}$$
(5.3)

For the remainder of this work, our primary focus is on the physics of the polymers; thus, we will not consider contributions from the external potential field $(U_{external,i} = 0)$; inclusion of this term if necessary is straightforward. We consider deflections only in the direction perpendicular to the substratum (which we label the r-direction). Computing the two

primary forces individually gives the results

$$F_{bead,i}(r(\xi)) = -\frac{\partial U_{bead}(r(\xi))}{\partial r} = 24\epsilon \left(\frac{\sigma^6}{r^7(\xi)} - \frac{2\sigma^{12}}{r^{13}(\xi)}\right)$$
(5.4)

and for the (yet unspecified) force associated with the polymer chain

$$F_{chain,i}(r(\xi)) = -\frac{\partial U_{chain,i}}{\partial r}$$
(5.5)

If we impose the approximation that the reconfiguration timescales for the polymers in response to changes in the distance r, are significantly smaller than the timescales that characterize the motion of the substratum, then then we can consider the process to be *quasi-steady-state*. If one were interested in the viscoelastic properties of the process, then this approximation would be invalid. However, it is a good starting point for the more general consideration of an adhesion cycle. Under these conditions, we have the balance

$$F_{bead,i}(r(\xi)) + F_{chain,i}(r(\xi)) = 0$$
(5.6)

Therefore, the forces on the polymer tips are equal (but with opposite sign) to the forces within the polymer molecule. With an appropriate model for $F_{chain,i}$, eq 5.6 is sufficient to determine $F_{chain,i}$ for each polymer. To determine the total force acting on the surface, it is necessary only to sum over all N_p polymer molecules

$$F_{adh}(\xi) = \sum_{i=1}^{N_p} F_{chain,i}(r(\xi))$$
(5.7)

In the next two sections, particular models (linear and nonlinear) for $F_{chain,i}$ are discussed.

5.2.2 Linear elastic model

Extension and compression of polymeric structures can involve a purely mechanical (enthalpic) response, a purely entropic response, or a combination of the two[22]. Regardless of source, some of the first statistical analyses of polymer chains and groups of chains led to linear (Hookean) spring laws for the deformation behavior[97, 141], and linear springs interacting with L-J potentials continue to be used to derive the mechanical properties of polymers [67]. Given that linear behavior is the limiting behavior of almost all known polymer force laws, it is not unreasonable to begin the investigation of particular polymer chain forces with the linear one. In this case, the force in the coarse-grained molecule is linearly proportional to the deformation from its equilibrium (zero force) length, ℓ_{eq} . For simplicity, we will drop the subscript "i" bellow.

$$F_{chain} = k_{chain} (\ell_{eq} - [\xi - r(\xi)])$$

$$(5.8)$$

where k_{chain} is the effective linear spring constant[22]. Equation 5.8 returns a force in the positive direction when the chain in compressed, and in the negative direction upon extension. Now the total force balance (Figure 5.3B) on one polymer is given by

$$k_{chain}(\ell_{eq} - [\xi - r(\xi)]) + 24\epsilon \left(\frac{\sigma^6}{r^7(\xi)} - \frac{2\sigma^{12}}{r^{13}(\xi)}\right) = 0$$
(5.9)

In this expression, all of the parameters are known except the value of $r(\xi)$. Although it is not possible to explicitly solve this equation for $r(\xi)$, it implicitly provides the value which can be determined by simple root finding. Once the value of $r(\xi)$ has been determined, the force in the chain (which is equal to the L-J force on the bead but with opposite sign) can be found by substituting this value into eq 5.8. A complete force-distance curve can be developed for every separation distance of interest for one polymer-bond complex by repeating this process for each value of ξ . Repeating this process for all chains then allows one to develop the information needed to find the total force function through eq 5.7.

5.2.3 Nonlinear elastic model

At large values of compression or extension, the stress in polymers generally behaves nonlinearly with distance. To represent these nonlinear effects, we have adopted the WLC approximation proposed by Broedersz and MacKintosh[22], which applies to semi-flexible polymers. We chose this model in because it provides the correct linear response in the low-deformation regime, and because it allows for some rigidity in the cell surface features. An additional linear spring term[199, 19, 61] has been added to represent nonspecific enthalpic contributions from mechanical deformation of the cell surface structures. The force function for the polymer molecule is

$$F_{chain} = k_{chain} (\ell_{eq} - [\xi - r(\xi)]) + \frac{9kT\ell_p}{\ell_c^2} \left[\left(1 - \frac{\ell_{eq} - [\xi - r(\xi)]}{\ell_c - \ell_{eq}} \right)^{-2} - 1 - \frac{1}{3} \frac{[\xi - r(\xi)] - \ell_{eq}}{\ell_c - \ell_{eq}} \right]$$
(5.10)

and the total force balance on a particular polymer molecule takes the form

$$k_{chain}(\ell_{eq} - [\xi - r(\xi)]) + \frac{9kT\ell_p}{\ell_c^2} \left[\left(1 - \frac{\ell_{eq} - [\xi - r(\xi)]}{\ell_c - \ell_{eq}} \right)^{-2} - 1 - \frac{1}{3} \frac{[\xi - r(\xi)] - \ell_{eq}}{\ell_c - \ell_{eq}} \right] + 24\epsilon \left(\frac{\sigma^6}{r^7(\xi)} - \frac{2\sigma^{12}}{r^{13}(\xi)} \right) = 0$$
(5.11)

Here, ℓ_c is the contour length of the polymer, ℓ_p is the persistence length, ℓ_{eq} is the zeroforce equilibrium length, k is the Boltzmann constant, and T is the absolute temperature. The model assumes that $\ell_c \leq \ell_p$, to ensure that the structures have stiffness [22].

As with the linear case, we can find the values of $r(\xi)$ for this force balance by simple root finding methods. We can calculate a force-distance profile using the polymer force function using eq 5.10 after determining a set of ξ and $r(\xi)$ pairs.

In the analysis that follows, we will characterize force-distance profiles using the adhesion energy, E^* , defined as the area under the retraction curve [54], and F_{max} defined as the maximum adhesive force in the retraction curve reached before detachment.

5.3 Simulations

Because we have multiple spatial scales in the phenomena of interest, and because of the nonlinearity involved in these phenomena, we rely on simple numerical simulations to com-



Figure 5.4: The landscape for a single polymer molecule. Maximum forces generated by the L-J potential obtained via a parametric sweep of ϵ and σ in eq 5.4 (background contours). Superimposed are the proposed energy scales of intermolecular hydrogen bonds[78, 83] (inclined hatches), bounds for (experimentally obtained) bacterial single-molecule specific forces [25] (dotted region), hydrogen bond strengths statistically inferred from AFM measurements on *L. monocytogenes*[64] (blue squares) and *E. coli*[3] (triangle) fitted to eq 5.4, and the parametrization used in the present study (crosses). The labeled contour lines mark the upper bound and mean of the measurements complied by Busscher et al.[25].

pute the force-distance relationships. We use a straightforward procedure where (1) ξ is fixed at increments along the direction of the interaction; (2) for each ξ , a numerical solution for an individual polymer molecule-bond system (eqs 5.9 or 5.11) is computed using a bisection method; and (3) the macroscale force is constructed by summing up individual contributions. We find that when the model parameters satisfy certain scale constraints, the force balances can have two stable solutions corresponding to the approach and retraction curves[116]. This observation confirms that eq 5.6 is self-contained in the sense that it can describe a complete hysteretic approach-retraction cycle.

5.3.1 Parametrization

The multiscale approach to simulating a cell surface requires information about the nanoscale processes and the macroscale statistical structure of the brush. There is, however, great variance in the values reported for the magnitude and length scales of the nanoscale adhesion forces and polymer brush thickness among different studies. Given these uncertainties, we find it more informative to first examine the ranges reported in the literature in our parametrization rather than to attempt to replicate specific experiments. In addition, to get representative results, we imposed order-of-magnitude constraints on some of the parameters. For instance, we find heuristically that the solutions to the linear chain model of eq 5.9 are hysteretic when $8\epsilon/k_{chain}\sigma^2 \gg 1$; we also find that normally-distributed roughness only becomes consequential when the bond length and the standard deviation in chain length satisfy $\sigma/s_{\ell_{eq}} \ll 1$.

In setting the L-J parameters we refer to the list of single-bond molecular recognition forces compiled by Busscher et al. [25], which occupies a range between 0.032 nN to 0.257 nN, with a mean of 0.095 nN. This interval overlaps with estimates obtained via statistical analysis of AFM force spectra [64, 3, 187]. Figure 5.4 is a graphical representation of these bounds superimposed on values obtained from eq 5.4 (via a simple parametric sweep within the typical energy scales of hydrogen bonds [78, 83]). We generally adhere to these bounds and use Figure 5.4 as a rubric for tuning the molecular bonds. In our simulations we consider one bond per polymer molecule for simplicity.

To infer the statistics of ℓ_{eq} we refer to the average brush thickness computed using AFM data. Studies on *E. coli* [3, 159], *Listeria monocytogenes* [128, 64], and *Pseudomonas aeruginosa* [79] have obtained mean brush thicknesses, $\mu_{\ell_{eq}}$, within a range between 2 nm to 212.4 nm, with mean-normalized standard deviations $(s_{\ell_{eq}}/\mu_{\ell_{eq}})$ in the range of 0.15 to 0.59 (these bounds are representative but not necessarily exhaustive). Alternatively, we can deduce the surface roughness (defined as the standard deviation in equilbrium chain lengths) from topographical data. We used the data from Amro et al.[6] to compute the statistics of the polymer molecules reported for strains of *E. coli*. We found that the surface features are normally distributed, with roughness on the orders 9.4 \pm 1.9 nm and 18.2 \pm 5.0 nm (Figure 5.1C), consistent with other studies on *E. coli* [3].

In our simulations, we have studied ensembles of statistically generated brushes with a mean ℓ_{eq} of 20 nm. To generate heterogeneous surfaces, we sample distributions with preset means and variances. To facilitate comparison with homogeneous surfaces, we fix the first and second moments of samples drawn from the generator distribution (regardless of sample size), but allow the higher-order moments to fluctuate. It is important to note that for both the homogeneous and heterogeneous polymer brushes, the *average* polymer length is the same. In the results that follow, we focus primarily on normally distributed roughness but also present one sample calculation for a surface described by multi-modal distributions.

Finally to construct the brushes, we sample a range of numbers of polymers involved, N_p , for representing the interaction of a surface with a bacterial polymer surface. This range overlaps with statistically inferred values reported by Gordesli and Abu-Lail [64], values derived from inverse modeling using the steric model of Butt et al. [128], and the more conservative estimates by Busscher et al. [25]. The parameter k_{chain} is treated as a general degree of freedom that tunes the energy and length scales of the interaction, and is constant for all chains in a given simulation (details below). Table 5.1 summarizes the parameters used in the present study.

Parameter	Range	Units
ϵ	1 - 10	kΤ
σ	0.1 - 0.6	nm
k_{chain}	0.0002 - 0.02	$N \cdot m^{-1}$
ℓ_{eq}	$\sim 20^{\dagger}$	nm
ℓ_c	$\sim 100^{\dagger}$	nm
ℓ_p	$\sim 300^{\dagger}$	nm
N_p	100	-
$s_{\ell_{eq}}$	0 - 5	nm
T	298	Κ
-		

Table 5.1: Ranges of parameters used in the simulations

[†]These ratios are kept constant in the statistically generated surfaces

5.4 Results

Before discussing the brush simulations, it is helpful to examine the behavior of individual polymer molecule-bond complexes. The model systems of eq 5.9 and eq 5.11 admit hysteretic solutions when the strain energy imposed on the chain can generate deformations that are larger than the L-J bond length (σ). A simple perturbation analysis on the rigidity of the chain shows that we can generally find a polymer in two states with respect to a given bond: (1) *stiff*: this is when the chain deformations are very small ($||\Delta \ell|| / \sigma \leq 1$), and the retraction curve traces the approach curve exactly (i.e. no hysteresis); or, (2) *compliant*:



Figure 5.5: Sample force-distance profiles for linear (A and B) and nonlinear (C and D) models with different generator distributions for ℓ_{eq} (insets). Bond strengths are tuned to $\epsilon = 5$ kT and $\sigma = 0.5$ nm. Linear chains are constructed with $k_{chain} = 0.01$ N/m, and nonlinear chains with $k_{chain} = 0.0002$ N/m and the values of ℓ_{eq} , ℓ_c , and ℓ_p as reported in Table-5.1. $s_{\ell_{eq}}/\ell_{eq} = 3$, and $N_p = 100$ in all simulations.

the chain has enough spatial degrees of freedom to allow for deformations on the order $\|\Delta \ell\|/\sigma \gg 1$, and the retraction curve begins to deviate from the approach curve[117]. This characterization helps us define an upper bound for chain rigidity by constraining the range of k_{chain} in eq 5.9, and the combinations of k_{chain} , ℓ_{eq} , ℓ_c , and ℓ_p in eq 5.11 to the compliant regime[118]·[119]. For our simulations, we generally observe that $\ell_p \geq \ell_c > \ell_{eq}$, and that there is a strong correlation between triplets of ℓ_{eq} , ℓ_c , and ℓ_p for heterogeneous surfaces.

Figure 5.5 shows example force curves for both the linear (A and B) and nonlinear
(C and D) models, for two very simple scenarios: (1) surfaces with no roughness, and (2) surfaces with normally-distributed roughness. These examples contain most of the observed differences between homogeneous (A and C) and heterogeneous (B and D) brushes. On approach, the homogeneous brush creates a jump-into-contact event with a lengthscale on the order of σ . The normally-distributed brush forms a longer-range force that emerges from the accumulation of out-of-phase contributions from chains of different lengths during compression. In retraction, the homogeneous brush creates a sharp step discontinuity upon detachment, but the heterogeneous brush goes through numerous smaller detachment events, creating a 'rugged' and spread-out macroscale force-distance curve.

Figure 5.5 demonstrates that the linear and nonlinear models show similar physical behavior, but differ in the magnitude and length scales of the forces they generate. Another key difference between the two is the asymmetry of elasticity in the nonlinear chain model (forces and deformations on retraction are much larger than on approach). This effect has been observed in measured force-distance profiles previously compared [63, 54].

In Figure 5.6 we present two sample profiles of adhesion energy (E^*) versus distance for the linear and nonlinear cases. We observe a ~70% decrease in adhesion energy for a linear-elastic brush made up of 100 normally-distributed polymers, compared with a uniform brush. Interestingly, we observe negligible sensitivity to roughness in adhesion energy for a nonlinear-elastic surface with the same standard deviation in polymer length. It is clear that the presence of nonlinearities influence the overall energy distribution in ways that are not necessarily intuitive.

Figure 5.7 illustrates one attempt to simulate an force-distance profile obtained experimentally for a bacterium of *S. epidermidis*[33]. In this figure, we have adopted a multimodal distribution for ℓ_{eq} (illustrated in the inset) to represent three different populations of polymers on the surface of *S. epidermidis*; the model results appear in Figure 5.7A. In Figure 5.7B, we have plotted the observed AFM measurements generated by Chen et al. [33].

5.5 Discussion

5.5.1 Adhesion as a multiscale process

Under proper length and energy constraints, a simple but carefully-constructed setup of two interacting potential functions reproduces the general features of a typical hysteretic



Figure 5.6: Sample adhesion energy profiles for the linear (A) and nonlinear (B) models, describing $N_p = 100$ chains. Linear brushes are constructed using $\epsilon = 5$ kT, $\sigma = 0.5$ nm, and $k_{chain} = 0.01$ N/m. Nonlinear brushes are constructed using the same bond strength, $k_{chain} = 0.002$ N/m, and the values of ℓ_{eq} , ℓ_c , and ℓ_p as reported in Table-5.1. While decreased by heterogeneity in the linear brush, the total adhesion energy stored in a nonlinear brush remains largely unaffected even for large standard deviations in ℓ_{eq} (note the difference in length and energy scales in the two plots).

force-distance curve (e.g. Figure 5.5B, D). Despite its simplicity, the quasi-steady-state solution to our model describes both the approach and retraction processes; previously, multiple mutually-independent models were generally used to interpret the two parts of the cycle[128, 132].

In the proposed framework, we can understand hysteresis as a multiscale phenomenon. Our model yields results that can be interpreted on two distinct levels (1) on the molecular level, hysteresis is a consequence of a single polymer's compliance to the force exerted by the small-scale bond; (2) on the macroscale, hysteresis is also a consequence of how molecular-level contributions scale; when roughness is present this scaling is governed by how synchronously the cell surface structures engage with the substrate. In our proposed model, the geometry of contact itself dynamically adapts to the interactions it helps modulate. Consistent with this picture, considering a "soft" charged layer in calculating the surface potentials of electrostatic forces on bacteria has improved the predictions of the



Figure 5.7: (a) An example of the force-distance curve for a trimodal brush (parameters are the same as in Figure 5.5). (b) An example of an AFM measurement on *S. epidermidis* reproduced from Chen et al. [33]. We observe significant qualitative similarities between our modeled results and observations, and the role of surface roughness is consistent with the discussion of adhesion properties provided by the authors [33].

DLVO theory [64, 123, 21, 71].

Because the approach and retraction processes are coupled in the present framework, the mechanism for detachment is escape from the potential energy well of the molecular bonds. Our approach relaxes the assumption that detachment is possible only via physically breaking the polymers responsible for adhesion. We can account for non-rupturing detachment events for cases where the detachment force is less than the rupturing force for the polymers of interest, and trivially expand the model to allow for chain breaking for cases where molecular-scale adhesion is strong.

5.5.2 Model performance

The ability for our model to reproduce the kinds of approach and retraction curves seen experimentally is illustrated in Figure 5.7. Although the computation presented in Figure 5.7A is largely intended only to show that one can qualitatively and quantitatively match experimental data, the model is not entirely heuristic. It is known that the surface of *S. epidermidis* has a wide variety of biomolecules involved in adhesion, including

polysaccharides, and a host of specific protein adhesins[139]. The work by Chen et al.[33], suggests that there must be cell surface structures with differing properties to explain their data; our analysis is consistent with their suggestion. Although our model is not a unique explanation of the data (for instance, we did not consider differences in bond strengths, which undoubtably occur when different molecules are involved), it does suggest that surface roughness created by structures of differing lengths may be part of the appropriate model for adhesion of this species. The rapid increase of F_{adh} as $\xi \to 0$ in Figure 5.7B can be attributed to contributions such as the turgor pressure, relative rigidity of the lipid bilayer, relative incompressibility of the periplasmic space; these phenomena are not included in the model.

Overall, we see that our model can provide a good representation of the observations in terms of length scales, maximum forces, and the shape of the force-distance profile. This is a unique result in terms of models for bacterial adhesion and detachment.

5.5.3 Surface roughness

Roughness has been incorporated into some studies of bacterial adhesion [3] using a 'rough' formulation of the van der Waals force in DLVO theory [136, 135]. The reduction in peak adhesion force observed in this work is phenomenologically consistent with these reports, as well as the reduced adhesion between rough abiotic surfaces on a range of scales [88, 89]. However, because macroscale deformations due to mechanical compliance (characteristic of bacterial surfaces) are usually not accounted for, the role of roughness in shaping the *length scales* of macroscale interactions is often ignored.

Our results show that the nature of initial bonding on compliant heterogeneous surfaces can be quite different from homogeneous surfaces, even though the two share the same molecular bonding mechanisms. Figures 5.5B, and 5.5D illustrate that roughness transforms the spontaneous jump-into-contact events seen in Figure 5.5A and Figure 5.5C into longerrange apparently repulsive interactions. On a compliant heterogeneous surface, new bonds form sequentially only after longer polymer molecules have been sufficiently deformed, and therefore cost energy. This suggests that at least some of the (potentially repulsive) force experienced on approach could be explained by structural heterogeneities only, without having to resort to (exotic) long-range interactions [114]. Note that this effect is unique to heterogeneous (rough) surfaces, and can be qualitatively distinguished from steric repulsion (also present in homogeneous systems).

The effects of heterogeneity on the length scales of interactions and its importance in interpreting force measurements are perhaps more evident in the retraction portion of the adhesion cycle. Figures 5.5B and 5.5D also demonstrate that surface roughness increases the length scales of the force curve on retraction, while significantly decreasing the magnitude of F_{max} compared with a homogeneous surface. Thus, if F_{max} were the sole metric used (via an appropriate model) to elicit a structural or energetic property of the surface, failing to account for roughness could lead to incorrect inferences (e.g. bond strength or grafting density could be significantly underestimated).

It is interesting to note that surface roughness creates an apparent tradeoff between the maximum force that can be sustained during detachment versus the total length scale over which some adhesive force still remains upon deformation. For both the linear and nonlinear cases, the heterogeneous surfaces can withstand larger total deflections before becoming detached than can the homogeneous surfaces.

These observations suggest that for a system that satisfies the scale constraints studied here, length heterogeneities are of fundamental importance, and should be explicitly accounted for in modeling. There are conceptual parallels between this property of rough surfaces and similar deviation from effective descriptions observed for surfaces with charge heterogeneities. For example, the motion of colloids with charge heterogeneities is not always properly captured by the effective surface charge density or zeta potential [49, 81], and deviations from the classical colloid filtration theory are frequently observed [169, 170]. Similarly, when length-scale heterogeneities are present, homogenization of bacterial surfaces without explicitly accounting for heterogeneity might lead to the loss of essential physics that are detrimental to adhesion.

5.5.4 The role of roughness in the biology of adhesion

Unlike colloids, the structure of the exterior of living cells is the consequence of extensive information processing, and is therefore complex. This complexity is characterized by various different types of heterogeneities. Roughness, defined as the variation in a characteristic measure of length of the polymers that make up the surface, is particularly ubiquitous. An interesting aspect of bacteria is how their surfaces, and surface roughness, are responsive to external stimuli. In gram-negative bacteria, for example, co-expression of short (A- band: hydrophobic, electroneutral) and long (B-band: hydrophobic, negatively-charged) LPS chains has been found to impart the cell surface some control in expressing states with different overall hydrophobicities in response to changes in ionic strength [148]. The genetic circuits responsible for modulating these surface modalities are rather well-understood [196].

An interesting question here is whether or not this type of 'regulated' roughness could lead to adhesion *enhancement*, and therefore be a feature that affects selection under particular environmental conditions. In the multiscale framework adopted here, roughness might appear to hinder adhesion at first glance if one considers only the maximum adhesion force, F_{max} . But a closer examination reveals that there is a trade-off between the reduction in F_{max} and the corresponding increase in the characteristic length scale of the adhesion process (i.e., the maximum distance in which polymer molecules are still adhered is larger for the heterogeneous case). Such an increase could potentially boost a cell's ability to stay adhered when there are environmental perturbations tending to cause detachment.

Adhesion energy is relatively less sensitive to roughness. For the the linear model here is a small energy penalty for rough versus smooth surfaces. Interestingly, however, the total adhesion energy for heterogeneous bacterial surfaces that exhibit nonlinear elasticity is far less sensitive to roughness. In fact, a small increase in total energy was observed for the rough versus smooth case in our computations. These observations hint at the possible existence of states where roughness could lead to *enhancements* in adhesiveness. Our results suggest that surface roughness may have significance in the ecological context by providing cells with properties that might make them more competitive under some environmental conditions.

5.6 Conclusion

This study serves as a first step in the validation of the concept of bacterial adhesion as a multiscale process. As such even very simple potential energy functions for the different components of the system can capture the essential features of experimental observations. The framework introduced here represents a shift of focus from increasing the phenomenological complexity of models that are constrained to a single scale, to one which instead implements basic physical phenomena within a multiscale framework. Using this framework we argue that some of the complexities of bacterial adhesion can be explicitly attributed to scale effects and structural heterogeneities without having to invoke explanations that involve exotic long-range interactions.

In this work, we have assumed that roughness is a normally distributed variable, which is a simple but physically reasonable first step. We have also focused on systems where the molecular bond potential function is more or less invariant, and almost all of the heterogeneity can be found in the lengths of the polymer molecules[120]. In subsequent studies the proposed model should be expanded to include (1) variations in bond strength and chemical characteristics, and (2) more fully characterized polymer molecule length distributions on bacteria (e.g., Whitfield et al. [186]). Additionally, the ideal that bacterial surface heterogeneity may confer ecological advantages is an interesting idea that is only hinted at by our results. However, the idea is an important one, and this idea should be explored more fully.

	Table 5.2: List of Symbols
F_{adh}	Adhesion force; force-distance trace for a brush
$F_{chain,i}$	Adhesion force of the i-th polymer; force-distance trace for a single polymer
F_{max}	Peak adhesion force in the retraction curve
E^*	Total adhesion energy for a brush (defined as the area under the retraction curve)
$U_{chain,i}$	Polymer chain potential energy function
$U_{bead,i}$	Bond potential energy function
$U_{external,i}$	Per chain external potential energy field contribution (e.g. electrostatic, etc.)
$U_{T,i}$	Total potential energy of a chain-bond complex
N_p	Number of polymers
ϵ	Bond energy parameter for the Lennard-Jones potential
σ	Bond length parameter for the Lennard-Jones potential
$k_{chain,i}$	Spring constant for the i-th chain
$\ell(\xi)$	Length of the i-th chain at a given ξ
ℓ_{eq}	Equilibrium length of the i-th chain
ℓ_c	Contour length of the i-th chain
ℓ_p	Persistence length of the i-th chain
$m_{e\!f\!f,i}$	Mass associated with a an individual polymer
v_i	Velocity associated a polymer chain in the ξ -direction
r	Distance between the probe and the bond-forming part of the chain
ξ	Total distance between the probe and graft base
$S_{\ell_{eq}}$	Standard deviation of an ℓ_{eq} set
$\mu_{\ell_{eq}}$	Mean of an ℓ_{eq} set
T	Temperature
k	Boltzmann's constant

APPENDICES

100

Pressure fluctuations in confined porous media subject to biofilm growth

Sassan Ostvar, Dorthe Wildenschild, and Brian D. Wood

TBD In Preparation as a Short Communication

Abstract

Biofilm growth in 3D porous media under a constant flow rate generates fluctuations in the bulk pressure drop measured across the system. These fluctuations emerge out of the dynamic co-evolution of the pore-space geometry and the flow field, and in response to cycles of growth and decay in established surface-associated colonies. The inherent nonlinear nature of the process raises the question of whether or not the dynamics are predictable from the point of view of a macroscale observer with no access to pore-scale information. In this short paper, we explore this question via a symbolic analysis of pressure drop data by measuring the entropy rate (a measure of the persistent generation of uncertainty in a time series), and excess entropy (a measure of the length of the sample required to reach a maximally predictable state in the time series). Analysis of experiments conducted at three flowrates show bounded excess entropies and vanishing entropy rates, suggesting that the fluctuations in pressure are predictable and self-contained over the time scales that the experiments were conducted over.

.1 Background

The reciprocal effects of hydrodynamics and biofilm growth in tortuous geometries has attracted a great deal of attention from the biomedical and porous media research communities. The formation of biofilm streamers, connected cell-matrix agglomerations that could span many characteristic pore lengths, in such media can lead to catastrophic flow disruptions that are detrimental to the study of a wide range of designed and natural systems [50].

Bioclogging occurs over multiple time scales in porous media, making it a complex process even in morphologically simple and homogeneous media. Cells undergo cycles of growth and death, and the spatial distribution of biofilms undergoes configurational changes that are linked to the efficiency of solute transport, and shear. In a recent experimental study in 3D model systems, we observed that these pore-scale processes create fluctuations in bulk pressure drops on multiple time-scales (ranging from <1 hr to ~2 days). Even at very small flowrates, the pressure signal is complex despite the simplicity of the flow field itself.

We expect the temporal ordering of the processes that generate these fluctuations to be different in different hydrodynamic regimes. For instance, at lower flowrates growth can be oxygen-limited but more local, so catastrophic clogging events could be more common - in higher flowrates sloughing is more prevalent so clogging and pressure build-ups occur over longer time scales. The imaging work uncovered that this is in a sense a difference in mechanisms: although the processes are the same, the way they manifest over time is different: lower flowrate columns clogg locally but fast, and then transition into an oxygen/nutrient-limited state. In contrast, higher flowrate columns clogg globally (small erosions are more frequent on shorter timescales and big pressure depression happen over longer scales).

The emergence of these fluctuations raises a number of questions, including (i) how long does the pressure drop signal need to be to be representative of the pore-scale dynamics? (ii) will the dynamics access stable states by optimizing the morphology of the biofilm-fluid interface, or is there an irreducible level of stochasticity involved in the process?

The framework of computational mechanics [146] and information-theoretic analysis are particularly well-suited to answer these types of questions. Computational mechanics and information theory have been applied to several notoriously complex physical systems that operate in a regime that is chaotic but not random. Examples include 2D Turbulence [29, 28], Geomagnetisms [34], atmospheric turbulence [127], disordered condensed matter [179].

.2 Flow experiments

The details of the flow experiments can be found in [77]. A schematic of the setup is reproduced in Figure 8A. Briefly, biofilm was allowed to develop under constant flowrate conditions in tubular flow reactors filled with spherical beads to simulate a porous medium. Growth was promoted over a 2 week period and the bulk pressure drop across the columns measured continuously. A total of 6 columns were studied, two at each flowrate; and 3 total flow regimes were studied that correspond to initial Re of 0.1, 1.0, and 10. A snapshot of a biofilm-altered column is reproduced in



Figure 8: Schematic of the flow experiments (A), and a sample of the imaged biofilm (B). In (B), biofilm=blue, and grains=gray.

Figure 8B.

This particular experimental design creates a semi-constrained tubular flow that is especially responsive to temporal variations in porosity and flow field reorientation. In this setting, we can expect the bulk pressure drop fluctuations to be not entirely random, but directly related to pore-scale processes that affect the global dynamics of the flow. In this constant flowrate setting, the pressure drop pressure serves as an indicator of the continuous rearrangements of the velocity field.

.3 Time series analysis

We first performed a spectral analysis via a fast Fourier transform. Figure 9 shows the scaling of power spectral densities in different flow regimes. Color of noise, defined by the exponent λ is a reliable characterizer of dynamics in noisy systems. Most natural system tend to operate optimally near $\lambda = 1$, or pink noise. Closely correlated systems operate near $\lambda = 2$, or Brownian dynamics. Figure 10A illustrates that a transition from creeping flow to mildly laminar flow corresponds to a transition from Brownian



Figure 9: spectral analysis

scaling to pink noise in our system.

Next, we were interested in measuring the crypticity of the signal; this is a measure of the amount of irreducible uncertainty in a time series. In other words, it measures how much we would still not know about a signal even if we sample an infinite string from it. If this parameter is nonzero for the biofilm data, it would imply that porescale bioclogging is essentially stochastic, and to some extend unpredictable.

To perform the analysis, we first tested the time series data for stationarity. This was done via the Augmented Dickey-Fuller (ADF) test, which rejected nonstationarity for all the experimental samples. Next, we needed to isolate the gradual accumulation of biomass in the system and the associated ramping of the pressure drop. We are only interested in the fluctuations. Detrending was done using a simple Hanning filter.

Symbolic data analysis time series data to be *alphabetized* by dividing the amplitudes into a finite number of bins, n, and assigning the values contained in each bin to a unique *letter*. Each point in a *binned* time series is a member of the set (alphabet) $\mathscr{S}_n = \{s_1, s_2, ..., s_n\}$. The time series can then be expressed as a string of letters drawn from \mathscr{S} . This string S can be divided into two halves \overleftarrow{S} , and \overrightarrow{S} , where $S = \overleftarrow{S} \cup \overrightarrow{S}$.

Next we are interested in constructing *words*, blocks of L consecutive letters. The Shannon entropy of blocks of L letters can then be computed as

$$H(L) \equiv -\sum_{s_1 \in \mathscr{S}} \dots \sum_{s_L \in \mathscr{S}} Pr(s_1, \dots, s_L) log(Pr(s_1, \dots, s_L))$$
(12)

As $L \to \infty$ the Shannon entropy diverges. A more stable measure of information called *entropy rate* or *metric entropy* is defined as

$$h_{\mu} \equiv \lim_{L \to \infty} \frac{H(L)}{L}.$$
(13)

Entropy rate is the entropy associated with a symbol if all the preceding symbols are known. In other words, how predictive we can be if we have perfect memory. Now we understand that h_{μ} is an asymptotic value. We can study the growth toward this value by a simple difference equation

$$h_{\mu}(L) \equiv H(L) - H(L-1), \quad L = 1, 2, \dots$$
 (14)

The quantity $h_{\mu}(L)$ is referred to as block entropy, and helps us define the notion of convergence to entropy rate more concretely. It also helps us define the following metric

$$\mathbf{E} \equiv \sum_{L=1}^{\infty} [h_{\mu}(L) - h_{\mu}] = \sum_{L=1}^{\infty} [H(L) - h_{\mu}L], \qquad (15)$$

that is referred to as *excess entropy*. \mathbf{E} has a very intuitive interpretation: it describes the length of the string that we must record for the signal to be maximally predictable.

In Figure 10B,C we have reproduced the computations of $h_{\mu}(L)$ and **E** for the detrended pressure drop time series for an alphabet size of 6. The results clearly show that $h_{\mu} \rightarrow 0$, implying that the pressure fluctuations follow repeating motifs at all flowrates. In addition, the excess entropy is remarkably consistent among different samples and flowrates. These observations support the notion that despite the difference in the dynamics at different flowrates (as measured by λ), all time series become predictable within the time span of the experiments.



Figure 10: (A) Scaling of the power spectral density, S(f), of the pressure drop time series at different loading Reynold's numbers. Pressure fluctuations show a smooth transition from near-Brownian scaling at Re=0.1 to pink noise scaling at Re = 10. (B) Block entropy and entropy rates for the 6 columns - all samples have vanishing entropy rates. (C) Excess entropies associated with (B) as a function of loading Reynolds number.

.4 Conclusions

Vanishing entropy rates suggest that the pressure fluctuations induced by biofilm growth in confined porous media had been adequately sampled. The results highlight the potential for information-theoretic investigation of transport phenomena with a chaotic component. The results also suggest that the coupled biofilm growth - flow system can relax toward stable asymptotic states, where fluctuations are still present in the system, but statistically predictable. The excess entropy \mathbf{E} can be transformed into a time scale that represents the initial establishment of biofilm in porous media.

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[1] Note that in our definition, for any three vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} , the dyad $\mathbf{a} \otimes \mathbf{b}$ is defined by the identity

$$(\mathbf{a} \otimes \mathbf{b}) \cdot \mathbf{c} = \mathbf{a}(\mathbf{b} \cdot \mathbf{c})$$

notation of Gibbs [188].

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