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Multiscale local porosity theory, weak limits, and dielectric response in composite and porous media

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A mathematical scaling approach to macroscopic heterogeneity of composite and porous media is introduced. It is based on weak limits of uniformly bounded measurable functions. The limiting local porosity distributions that were introduced in the work [Adv. Chem. Phys. **XCII**, 299–424 (1996)] are found to be related to Young measures of a weakly convergent sequence of local volume fractions. The Young measures determine frequency dependent complex dielectric functions of multiscale media within a generalized self-consistent effective medium approximation. The approach separates scales by scale factor functions of regular variation. It renders upscaled results independent of the shape of averaging windows upon reaching the scaling limit. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5063466>

I. INTRODUCTION

Averaging microscopic heterogeneities over mesoscopic **Representative Elementary Volumes** (REV's) is a crucial concept in theories of composite and porous media.^{1,2} Despite its popularity, the REV-concept has remained difficult to quantify precisely.

My objective in this contribution is to introduce weak limits from functional analysis as a mathematical basis for quantifying the elusive REV-concept. Averaged quantities such as porosity $\phi = \phi(\mathcal{S}, \mathbb{P}, \mathbb{V})$ or permeability $k = k(\mathcal{S}, \mathbb{P}, \mathbb{V})$ depend not only on the shape of the sample $\mathcal{S} \subset \mathbb{R}^d$ and the material substance filling the pore space $\mathbb{P} \subset \mathcal{S}$ but also on the shape of the averaging window $\mathbb{V} \subset \mathcal{S}$ although this dependence is usually suppressed.^{2–5} In Ref. 4, Eq. (18), the set \mathbb{V} is the set on which a window function is nonvanishing, in Ref. 3, the set \mathbb{V} is implicit in Eqs. (3.38), (2.6), and (2.7), and in Ref. 5, the set \mathbb{V} is implicit in Eqs. (15) and (16). On the other hand, for sufficiently homogeneous media, one expects

$$\lim_{\mathbb{V} \rightarrow \mathcal{S}} \phi(\mathcal{S}, \mathbb{P}, \mathbb{V}) = \phi(\mathcal{S}, \mathbb{P}, \mathcal{S}) = \phi(\mathcal{S}, \mathbb{P}) \quad (1)$$

to become independent of \mathbb{V} long before the limit is attained. Recent results for an almost perfectly homogeneous benchmark sample show that the convergence is much slower than expected.⁶ Extra large scale permeability calculations⁷ on the same benchmark sample might soon be able to test convergence for permeability REV's. Many publications seem to ignore the slow convergence to homogeneity or, equivalently, the strong dependence on the size, form, and shape of the representative elementary volume \mathbb{V} .

Deviations from homogeneity are often present on more than one scale.⁸ Examples of practical importance include carbonate rocks⁹ or cements.¹⁰ In such samples, it becomes difficult to identify the plateau regions postulated in numerous studies such as Ref. 2, Fig. 5, p. 35 and Ref. 11, Fig. 3, p. 17 or Ref. 12, Fig. 1.3.1, p. 17.

Geometrical deviations from homogeneity give rise to position and frequency dependent averaged transport properties. Low frequency electromagnetic waves with large penetration depths can detect such geometrical deviations. One of the motivations to study the low frequency dielectric response of complex geometries arises from imaging applications.^{13–16} Real and complex dielectric response functions carry rich geometrical information content. Its extraction requires solving the

direct problem as a prerequisite.^{17,18} Approximate expressions for effective dielectric functions are given below as a first step in this direction. More accurate expressions, though desirable, are lacking at present.

II. PROBLEM AND OBJECTIVE

The physical problem is to compute the dielectric properties of multiscale heterogeneous media consisting of two different homogeneous constituents. The geometric problem is to quantify the microstructure mathematically. The underlying fundamental theoretical problem is to establish rigorous quantitative links between heterogeneities on multiple scales.

Traditional volume averaging assumes implicitly that multiscale heterogeneity can be modelled mathematically on all scales by number valued functions. Here it is found that this assumption is too restrictive and has to be weakened to include probability measure valued functions. The latter were predicted physically in a previous study of the author as limiting local porosity distributions.¹⁹ In this work, measure valued functions are obtained mathematically from applying the concept of weak convergence to a rescaling limit.

The specific objective for applications is to generalize approximate mathematical expressions for electrical conductivity σ' and dielectric permittivity ϵ_r from local porosity theory^{17,19} to multiscale composite media. The real valued functions $\sigma' : \mathbb{R}^d \times [0, \infty) \rightarrow [0, \infty)$ and $\epsilon_r' : \mathbb{R}^d \times [0, \infty) \rightarrow [0, \infty)$ determine their complex valued counterparts through

$$\begin{aligned}\epsilon(\mathbf{x}, \omega) &= \epsilon'(\mathbf{x}, \omega) + i\epsilon''(\mathbf{x}, \omega) \\ &= \epsilon_r(\mathbf{x}, \omega) + i\frac{\sigma'(\mathbf{x}, \omega)}{\omega},\end{aligned}\quad (2a)$$

$$\begin{aligned}\sigma(\mathbf{x}, \omega) &= \sigma'(\mathbf{x}, \omega) + i\sigma''(\mathbf{x}, \omega) \\ &= \sigma'(\mathbf{x}, \omega) + i\omega(1 - \epsilon_r(\mathbf{x}, \omega)),\end{aligned}\quad (2b)$$

where $\omega = 2\pi\nu$ is the circular frequency, ν is the frequency, and prime $'$, respectively, double prime $''$ denote the real, respectively, imaginary, part.

The italic vector symbol \mathbf{x} generically denotes positions at any given scale or resolution. Position vectors at specific scales will below be identified notationally as $\mathbf{x}, \bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}$. In Eq. (2), $\mathbf{x} \in \{\mathbf{x}, \bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}\}$ can stand for any one of them.

III. MATHEMATICAL MODELING

A. Multiscale microstructure

Consider a large heterogeneous medium extending over hectometers or kilometers at nanometer resolution. At the nanometer scale, position vectors are denoted as $\mathbf{x} \in \mathbb{R}^d$. It is assumed without loss of generality that there are three intermediate scales of interest, the micrometer scale, denoted $\bar{\mathbf{x}} \in \bar{\mathbb{R}}^d$, the millimeter scale, denoted $\tilde{\mathbf{x}} \in \tilde{\mathbb{R}}^d$, and the decimeter scale, denoted $\hat{\mathbf{x}} \in \hat{\mathbb{R}}^d$. Dimensionless position vectors $\mathbf{x} \in \mathbb{R}^d$, $\bar{\mathbf{x}} \in \bar{\mathbb{R}}^d$, $\tilde{\mathbf{x}} \in \tilde{\mathbb{R}}^d$, and $\hat{\mathbf{x}} \in \hat{\mathbb{R}}^d$ become dimensional position vectors after multiplying with a length, i.e., $\tilde{\mathbf{x}} = \mathbf{x} \cdot 1\text{nm}$, $\hat{\mathbf{x}} = \bar{\mathbf{x}} \cdot 1\mu\text{m}$, $\tilde{\mathbf{x}} = \tilde{\mathbf{x}} \cdot 1\text{mm}$, and $\hat{\mathbf{x}} = \hat{\mathbf{x}} \cdot 1\text{dm}$. Equivalently, $\mathbf{x} = \tilde{\mathbf{x}}/\text{nm}$, $\bar{\mathbf{x}} = \hat{\mathbf{x}}/\mu\text{m}$, $\tilde{\mathbf{x}} = \tilde{\mathbf{x}}/\text{mm}$, and $\hat{\mathbf{x}} = \hat{\mathbf{x}}/\text{dm}$.

Imagine a copy $\mathbb{R}_{\mathbf{a}}^d$ of \mathbb{R}^d (nanometer resolution) attached to every point $\bar{\mathbf{x}} \in \bar{\mathbb{R}}^d$ (micrometer resolution) in such a way that the origin of the copy $\mathbb{R}_{\mathbf{a}}^d$ is attached to the point $1000\bar{\mathbf{x}} = \mathbf{a} \in \mathbb{R}^d$. The point $\mathbf{a} = 1000\bar{\mathbf{x}} \in \mathbb{R}^d$ is the point $\bar{\mathbf{x}}$ written in units of nanometers. Formally, an \mathbf{a} -shifted copy of \mathbb{R}^d is the set

$$\mathbb{R}_{\mathbf{a}}^d = \mathbb{R}^d - \mathbf{a} = \{\mathbf{x} - \mathbf{a} : \mathbf{x} \in \mathbb{R}^d\} = \mathbb{R}^d - a\bar{\mathbf{x}} = \mathbb{R}_{a\bar{\mathbf{x}}}^d, \quad (3)$$

where $\mathbf{a} = a\bar{\mathbf{x}} \in \mathbb{R}^d$ with $\bar{\mathbf{x}} \in \bar{\mathbb{R}}^d$ is given and fixed and $a = 1000$ is the scale factor separating nanometers from micrometers. The general idea is to study the vicinity of $\bar{\mathbf{x}}$ by investigating sequences of points approaching the origin in $\mathbb{R}_{a\bar{\mathbf{x}}}^d$ when $a \rightarrow \infty$ becomes large.

Let $\bar{\mathcal{S}} \subset \bar{\mathbb{R}}^d$ denote the porous sample at micrometer resolution. The attachment of $\mathbb{R}_{a\bar{x}}^d$ to $\bar{\mathbb{R}}^d$ is written as a Cartesian product $\mathbb{R}_{a\bar{x}}^d \times \bar{\mathbb{R}}^d$. The Cartesian product

$$\mathbb{R}_{a\bar{x}}^d \times \bar{\mathcal{S}} = \{(\mathbf{x}, \bar{\mathbf{x}}) : \mathbf{x} \in \mathbb{R}^d, \bar{\mathbf{x}} \in \bar{\mathcal{S}}\} \quad (4)$$

represents the sample at micrometer resolution as a (fibrewise) space to which an underlying substructure, resolved in nanometers, is attached. A sequence ($i \in \mathbb{N}$) of cross sections \mathfrak{s}_i defined as

$$\begin{aligned} \mathfrak{s}_i : \bar{\mathbb{R}}^d &\rightarrow \mathbb{R}_{a_i\bar{x}}^d \times \bar{\mathcal{S}} \\ \bar{\mathbf{x}} &\mapsto \mathbf{x}_i + a_i\bar{\mathbf{x}} \end{aligned} \quad (5)$$

with $|\mathbf{x}_i| < a_i^\gamma$ and $\gamma < 1$ will be used below to probe the nanoscale structure near $\bar{\mathbf{x}}$.

At the nanometer scale, the medium is taken to consist of only two subsets, denoted \mathbb{P} and \mathbb{M} , and referred to as the pore and matrix. Both sets $\mathbb{M}, \mathbb{P} \subset \mathbb{R}^d$ are assumed to be closed and measurable. The closed sets \mathbb{P} and \mathbb{M} are unbounded. They fill space so that

$$\mathbb{P} \cup \mathbb{M} = \mathbb{R}^d \quad (6)$$

holds. For given and fixed $\bar{\mathbf{x}} \in \bar{\mathbb{R}}^d$, the set

$$(\mathbb{R}_{a\bar{x}}^d, \bar{\mathbf{x}}) = ((\mathbb{P} \cup \mathbb{M})_{a\bar{x}}, \bar{\mathbf{x}}) \quad (7)$$

represents the shifted pore structure near the macroscopic point $\bar{\mathbf{x}} \in \bar{\mathcal{S}}$ of the sample. For infinite scale separation $a \rightarrow \infty$, the nanoscopic pore structure is idealized as infinitely extended. The index $a\bar{x}$ on $(\mathbb{P} \cup \mathbb{M})_{a\bar{x}}$ in Eq. (7) indicates the shift.

On the nanoscale, the two subsets \mathbb{P} and \mathbb{M} represent two homogeneous substances. For example, the solid matrix \mathbb{M} of the composite medium could be fused silica (amorphous SiO_2), and its pore space \mathbb{P} could be filled with liquid water (H_2O) or brine. Note that the nanoscale sets \mathbb{P} and \mathbb{M} are not random. They are considered to be given and fixed. In practical applications, $d = 3$. For $d = 3$, the sets $\mathbb{M}, \mathbb{P} \subset \mathbb{R}^3$ have a two-dimensional interface denoted as

$$\partial_{\mathbb{P}\mathbb{M}} = \partial\mathbb{P} = \partial\mathbb{M} = \mathbb{P} \cap \mathbb{M}, \quad (8)$$

where the last equality applies because \mathbb{M}, \mathbb{P} were both assumed to be closed sets.

B. Dielectric response

The propagation of electromagnetic fields in a multiscale composite is governed on all scales larger than nanometers by the upscaled Maxwell equations.²⁰ On the nanoscale, they read

$$\nabla \cdot \mathbf{D}(\mathbf{x}, t) = Q(\mathbf{x}, t), \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (9a)$$

$$\nabla \cdot \mathbf{B}(\mathbf{x}, t) = 0, \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (9b)$$

$$\nabla \times \mathbf{E}(\mathbf{x}, t) = -\frac{\partial \mathbf{B}(\mathbf{x}, t)}{\partial t}, \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (9c)$$

$$\nabla \times \mathbf{H}(\mathbf{x}, t) = \mathbf{J}(\mathbf{x}, t) + \frac{\partial \mathbf{D}(\mathbf{x}, t)}{\partial t}, \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (9d)$$

where $\mathbf{D}(\mathbf{x}, t)$ is the electric displacement, $\mathbf{B}(\mathbf{x}, t)$ is the magnetic induction, $\mathbf{E}(\mathbf{x}, t)$ is the electric field, and $\mathbf{H}(\mathbf{x}, t)$ is the magnetic field. Taking the divergence of Eq. (9d) gives the equation of continuity

$$\frac{\partial Q(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{x}, t) = 0, \quad \mathbf{x} \in \mathbb{R}^d = \mathbb{P} \cup \mathbb{M}. \quad (9e)$$

It relates the macroscopic charge density $Q(\mathbf{x}, t)$ and the macroscopic current density $\mathbf{J}(\mathbf{x}, t)$.

Causality and locality in space restrict the constitutive equations to convolutions in time given as

$$\mathbf{J}_c(\mathbf{x}, t) = \int_{-\infty}^t \sigma'(\mathbf{x}, t - t') \mathbf{E}(\mathbf{x}, t') dt', \quad (10a)$$

$$\mathbf{D}(\mathbf{x}, t) = \epsilon_0 \int_{-\infty}^t \epsilon_r(\mathbf{x}, t - t') \mathbf{E}(\mathbf{x}, t') dt', \quad (10b)$$

$$\mathbf{H}(\mathbf{x}, t) = \frac{1}{\mu_0} \int_{-\infty}^t \frac{\mathbf{B}(\mathbf{x}, t')}{\mu_r(\mathbf{x}, t - t')} dt', \quad (10c)$$

for $\mathbf{x} \in \mathbb{P} \cup \mathbb{M}$, where σ' is the electrical conductivity. The symbols ϵ_0 , ϵ_r denote the dielectric permittivities of the vacuum, respectively, the medium, and μ_0 , μ_r are the magnetic permeabilities of the vacuum, respectively, the medium with $\mu_0 = 4\pi \times 10^{-7}$ N/A² and $\epsilon_0 = 1/(\mu_0 c^2) \approx 8.8542 \times 10^{-12}$ F/m. The conduction current due to free charges \mathbf{J}_c appearing in Ohm's law, Eq. (10a), is related to the total current via the current of bound charges defined as $\mathbf{J}_b(\mathbf{x}, t) = \mathbf{J}(\mathbf{x}, t) - \mathbf{J}_c(\mathbf{x}, t)$. Fourier transformation gives

$$\mathbf{J}_c(\mathbf{x}, \omega) = \sigma'(\mathbf{x}, \omega) \mathbf{E}(\mathbf{x}, \omega), \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (11a)$$

$$\mathbf{D}(\mathbf{x}, \omega) = \epsilon_0 \epsilon_r(\mathbf{x}, \omega) \mathbf{E}(\mathbf{x}, \omega), \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (11b)$$

$$\mathbf{B}(\mathbf{x}, \omega) = \mu_0 \mu_r(\mathbf{x}, \omega) \mathbf{H}(\mathbf{x}, \omega), \quad \mathbf{x} \in \mathbb{P} \cup \mathbb{M}, \quad (11c)$$

where $\omega = 2\pi\nu$ is the angular frequency and ν denotes the frequency.

Water and glass are homogeneous and isotropic materials at the length scales of interest. In the low frequency limit, the material parameter functions

$$\sigma'(\mathbf{x}, \omega) = \sigma'_{\text{H}_2\text{O}} \chi_{\mathbb{P}}(\mathbf{x}) + \sigma'_{\text{SiO}_2} \chi_{\mathbb{M}}(\mathbf{x}), \quad (12a)$$

$$\epsilon_r(\mathbf{x}, \omega) = \epsilon_{\text{H}_2\text{O}} \chi_{\mathbb{P}}(\mathbf{x}) + \epsilon_{\text{SiO}_2} \chi_{\mathbb{M}}(\mathbf{x}), \quad (12b)$$

$$\mu_r(\mathbf{x}, \omega) = 1 \quad (12c)$$

are assumed to be frequency independent with

$$\sigma'_{\text{H}_2\text{O}} = 4.8 \text{ S/m}, \quad (13a)$$

$$\sigma'_{\text{SiO}_2} = 0 \approx 10^{-18} \text{ S/m}, \quad (13b)$$

$$\epsilon_{\text{H}_2\text{O}} = 79, \quad (13c)$$

$$\epsilon_{\text{SiO}_2} = 3.75 \quad (13d)$$

for the material constants. The function $\chi_{\mathbb{X}} : \mathbb{R}^d \rightarrow \{0, 1\}$ defined as

$$\chi_{\mathbb{X}}(\mathbf{y}) = \begin{cases} 1, & \mathbf{y} \in \mathbb{X}, \\ 0, & \mathbf{y} \notin \mathbb{X} \end{cases} \quad (14)$$

is the characteristic (or indicator) function of a subset $\mathbb{X} \subset \mathbb{R}^d$. Equation (12c) assumes that magnetic effects are negligible at the frequencies of interest. Because glass is a good insulator, its electrical conductivity is set to zero in Eq. (13b). The electrical conductivity of water in Eq. (13a) corresponds to that of sea water at 20 °C. For drinking water, a value around 5×10^{-3} S/m could be used. Defining the relaxation frequency of water as

$$\omega_{\text{H}_2\text{O}} = \frac{\sigma'_{\text{H}_2\text{O}}}{\epsilon_0 \epsilon_{\text{H}_2\text{O}}} \approx 6.9 \text{ GHz} \quad (15)$$

makes ω a pure number multiplying $\omega_{\text{H}_2\text{O}}$.

Equation (12) implies that the material parameters are discontinuous at the interface. Physically this requires specifying boundary conditions at $\partial\mathbb{P} = \partial\mathbb{M}$. Mathematically the equations are interpreted in a weak sense as equations for distributions. Depending on the boundary conditions, a

suitable domain could be a Sobolev space for the potentials, respectively, a space of potential fields for the electromagnetic fields.^{21,22} The boundary conditions at the interface are

$$\mathbf{n}(\mathbf{x}) \cdot (\mathbf{B}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{B}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = 0, \quad (16a)$$

$$\mathbf{n}(\mathbf{x}) \cdot (\mathbf{D}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{D}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = Q_{\partial}(\mathbf{x}, \omega), \quad (16b)$$

$$\mathbf{n}(\mathbf{x}) \times (\mathbf{E}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{E}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = 0, \quad (16c)$$

$$\mathbf{n}(\mathbf{x}) \times (\mathbf{H}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{H}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = \mathbf{J}_{\partial}(\mathbf{x}, \omega), \quad (16d)$$

for $\mathbf{x} \in \partial\mathbb{P} = \partial\mathbb{M}$, where $Q_{\partial}(\mathbf{x}, \omega)$ (respectively, $\mathbf{J}_{\partial}(\mathbf{x}, \omega)$) are the Fourier transforms of (possibly time dependent) surface charge (respectively, surface current) densities with support in $\partial\mathbb{P} = \partial\mathbb{M}$. The notation $\mathbf{B}_{\partial\mathbb{P}}(\mathbf{x}, \omega)$ (respectively, $\mathbf{B}_{\partial\mathbb{M}}(\mathbf{x}, \omega)$) is the limiting value of the vector field as the point $\mathbf{x} \in \partial\mathbb{P} = \partial\mathbb{M}$ is approached from within \mathbb{P} (respectively, from within \mathbb{M}).

It is assumed that there is neither volume nor surface charges or currents inside the medium so that $Q = 0$, $Q_{\partial} = 0$, $\mathbf{J} = 0$, and $\mathbf{J}_{\partial} = 0$.

The nanoscopic details of an exact solution are of little interest at hectometer scales. The problem is to compute an effective dielectric function at larger scales. Its definition is given in Eq. (21). The effective frequency dependent dielectric functions at the micrometer scale, $\bar{\epsilon}_e(\bar{\mathbf{x}}, \omega)$, at the millimeter scale, $\tilde{\epsilon}_e(\tilde{\mathbf{x}}, \omega)$, and at the decimeter scale, $\hat{\epsilon}_e(\hat{\mathbf{x}}, \omega)$, are expected to be again position and frequency dependent due to the heterogeneity assumed in (12).

IV. METHODS AND APPROXIMATIONS

A. Weak convergence

The method employed in this paper to obtain scaling results for multiscale heterogeneous media is based on the following well known facts from the theory of Young measures for weakly convergent sequences.^{23,24}

Theorem 1 (Ref. 23). *Let $\mathcal{S} \subset \mathbb{R}^d$ be Lebesgue measurable, and let $f_i : \mathcal{S} \rightarrow \mathbb{A} \subset \mathbb{R}^m$ be a sequence of Lebesgue measurable functions that is uniformly bounded in $L^\infty(\mathcal{S}, \mathbb{R}^m)$ (but not necessarily convergent) taking (at almost every $\mathbf{x} \in \mathcal{S}$) its values in \mathbb{A} . Then there exists a subsequence $f_j(\mathbf{x})$ of $f_i(\mathbf{x})$ and a family of probability measures $\mu_{\mathbf{x}}$ parameterized by $\mathbf{x} \in \mathcal{S}$ with support in the closure $\text{cl}(\mathbb{A})$ of \mathbb{A} such that for every real continuous function $F : \mathbb{A} \rightarrow \mathbb{R}$, the sequence $F_j(\mathbf{x}) = F(f_j(\mathbf{x}))$ converges weak* in $L^\infty(\mathcal{S}, \mathbb{R}^m)$ to the limiting function*

$$\langle F \rangle(\mathbf{x}) = \int_{\mathbb{R}^m} F(\mathbf{a}) d\mu_{\mathbf{x}}(\mathbf{a}) \quad (17)$$

at almost every $\mathbf{x} \in \mathcal{S}$. The limiting measure $\mu_{\mathbf{x}}$ is called the Young measure and it depends measurably on \mathbf{x} in the sense that the limiting function $\langle F \rangle(\mathbf{x}) : \mathcal{S} \rightarrow \mathbb{R}$ is measurable.

The closure $\text{cl}(\mathbb{X})$ of a set $\mathbb{X} \subset \mathbb{R}^d$ is defined as the intersection of all closed sets containing \mathbb{X} .

Corollary. *If the original sequence $f_i : \mathcal{S} \rightarrow \mathbb{A}$ converges weak* in $L^\infty(\mathcal{S}, \mathbb{R}^m)$ to the limiting function $f_\infty(\mathbf{x})$, then*

$$f_\infty(\mathbf{x}) = \langle f \rangle(\mathbf{x}) = \int_{\mathbb{R}^m} \mathbf{a} d\mu_{\mathbf{x}}(\mathbf{a}) \quad (18)$$

at almost every $\mathbf{x} \in \mathcal{S}$, where $\langle f \rangle(\mathbf{x})$ is the barycenter of $\mu_{\mathbf{x}}$. The values $\langle f \rangle(\mathbf{x})$ are not restricted to \mathbb{A} , but are, in general, elements of the convex hull of the closure $\text{cl}(\mathbb{A})$ of \mathbb{A} .

If the sequence $f_i(\mathbf{x})$ does not converge, then $\langle F \rangle(\mathbf{x}) \neq F(\langle f \rangle(\mathbf{x}))$ in general.

B. Quasistatic approximation

When the wavelength is large compared to the scale of heterogeneities, the time derivatives in Faraday's law (9) are small compared to spatial derivatives. Setting them to zero results in the

quasistatic approximation valid for small frequencies

$$\omega \ll \frac{1}{\ell \sqrt{\epsilon_0 \mu_0}} = \frac{c}{\ell} = \frac{299\,792\,458}{\ell} \text{ Hz}, \tag{19}$$

where ℓ denotes the scale of heterogeneities and c is the speed of light. For heterogeneities with $\ell \approx 10\text{--}100 \mu\text{m}$, one finds $\omega \ll 3\text{--}30$ THz approaching the infrared.

The quasistatic approximation decouples the full equations (9). Fourier transformation of Eqs. (9) results in the equations of quasistatic electrostatics

$$\nabla \cdot \mathbf{D}(\mathbf{x}, \omega) = 0, \tag{20a}$$

$$\nabla \times \mathbf{E}(\mathbf{x}, \omega) = 0, \tag{20b}$$

$$\mathbf{D}(\mathbf{x}, \omega) = \epsilon_0 \epsilon(\mathbf{x}, \omega) \mathbf{E}(\mathbf{x}, \omega), \tag{20c}$$

$$\mathbf{n}(\mathbf{x}) \cdot (\mathbf{D}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{D}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = 0, \tag{20d}$$

$$\mathbf{n}(\mathbf{x}) \times (\mathbf{E}_{\partial\mathbb{P}}(\mathbf{x}, \omega) - \mathbf{E}_{\partial\mathbb{M}}(\mathbf{x}, \omega)) = 0, \tag{20e}$$

where $\mathbf{x} \in \mathbb{P} \cup \mathbb{M}$ in Eqs. (20a)–(20c), $\mathbf{x} \in \partial\mathbb{P} = \partial\mathbb{M}$ in Eqs. (20d)–(20e), and where $\epsilon(\mathbf{x}, \omega)$ denotes the complex frequency dependent local dielectric function.

C. Self-consistent local porosity approximation

The effective macroscopic dielectric function ϵ_e of self-consistent effective medium approximations¹ is usually defined by averaging Eq. (20c),

$$\langle \mathbf{D}(\mathbf{x}, \omega) \rangle = \epsilon_0 \epsilon_e(\omega; \mathbf{\Pi}) \langle \mathbf{E}(\mathbf{x}, \omega) \rangle, \tag{21}$$

on macroscopic scales, where $\mathbf{x} \in \{\bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}\}$, $\epsilon \in \{\bar{\epsilon}, \tilde{\epsilon}, \hat{\epsilon}\}$. Depending on the specific model, the angular brackets $\langle \cdot \rangle$ denote (spatial or ensemble) averaging and $\mathbf{\Pi}$ are parameters of physical importance (such as porosity or connectivity) that arise from averaging the smaller scale heterogeneities.

Local porosity theory in its simplest formulation represents the complex geometry of the pore space \mathbb{P} approximately by its local porosity distribution $\mu(\phi)$ and its local percolation probabilities $\lambda(\phi)$.^{25,26} The local geometric parameters in Eq. (21) are assumed to be $\mathbf{\Pi} = (\phi, \Lambda)$, where ϕ is the local porosity at \mathbf{x} and $\Lambda = 1$ if the local geometry at \mathbf{x} is percolating, while $\Lambda = 0$ if it is not. Let $\mathbb{K} \subset \mathbb{R}^d$ be a convex and compact set with its centroid at the origin $\mathbf{0} \in \mathbb{R}^d$. Then

$$\mathbb{K}(\mathbf{x}) = \mathbf{x} + \mathbb{K} = \{\mathbf{x} + \mathbf{z} \in \mathbb{R}^d : \mathbf{z} \in \mathbb{K}\} \tag{22}$$

denotes its translate by a vector $\mathbf{x} \in \mathbb{R}^d$ and

$$|\mathbb{K}| = \int_{\mathbb{K}} d^d \mathbf{x} = \int_{\mathbb{R}^d} \chi_{\mathbb{K}}(\mathbf{x}) d^d \mathbf{x} \tag{23}$$

is its volume. The local porosity in a measurement cell $\mathbb{K}(\mathbf{x})$ placed at position \mathbf{x} is defined as

$$\phi(\mathbb{K}(\mathbf{x})) = \frac{|\mathbb{P} \cap \mathbb{K}(\mathbf{x})|}{|\mathbb{K}(\mathbf{x})|}. \tag{24}$$

Given a sequence \mathbf{x}_i of cell centers such that all $\mathbb{K}(\mathbf{x}_i)$ are mutually disjoint, the local porosity distribution can be defined as

$$\mu(\phi; \mathbb{K}) = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M \delta(\phi - \phi(\mathbb{K}(\mathbf{x}_i))), \tag{25}$$

where M denotes the total number of different placements of \mathbb{K} .

The local percolation probability $\lambda(\phi; \mathbb{K})$ is loosely defined as the fraction of measurement cells with local porosity ϕ that are percolating according to a suitable criterion. For details on the percolation criteria and precise definitions, see Refs. 17 and 27.

Given the geometrical functions $\mu(\phi; \mathbb{K})$ and $\lambda(\phi; \mathbb{K})$, the self-consistent local porosity equation for the effective dielectric function ϵ_e reads

$$\int_0^1 \left[\frac{\epsilon_{\text{loc}}(\omega; \phi, 0) - \epsilon_e(\omega)}{\epsilon_{\text{loc}}(\omega; \phi, 0) + (d - 1)\epsilon_e(\omega)} (1 - \lambda(\phi; \mathbb{K})) + \frac{\epsilon_{\text{loc}}(\omega; \phi, 1) - \epsilon_e(\omega)}{\epsilon_{\text{loc}}(\omega; \phi, 1) + (d - 1)\epsilon_e(\omega)} \lambda(\phi; \mathbb{K}) \right] \mu(\phi; \mathbb{K}) d\phi = 0, \tag{26}$$

where $\epsilon_{\text{loc}}(\omega; \phi, 0)$ respectively $\epsilon_{\text{loc}}(\omega; \phi, 1)$ are average local dielectric functions for blocking ($\Lambda = 0$) respectively conducting ($\Lambda = 1$) configurations. The local functions are generally unknown, but are expected to obey

$$\sigma'_{\text{loc}}(\omega = 0; \phi, 0) = 0 \tag{27}$$

for all ϕ and

$$\sigma'_{\text{loc}}(\omega; 0, 1) = \sigma'_{\text{SiO}_2} = 0, \tag{28a}$$

$$\sigma'_{\text{loc}}(\omega; 1, 1) = \sigma'_{\text{H}_2\text{O}}, \tag{28b}$$

$$\epsilon'_{\text{loc}}(\omega; 0, 1) = \epsilon'_{\text{loc}}(\omega; 0, 0) = \epsilon'_{\text{SiO}_2}, \tag{28c}$$

$$\epsilon'_{\text{loc}}(\omega; 1, 1) = \epsilon'_{\text{loc}}(\omega; 1, 0) = \epsilon'_{\text{H}_2\text{O}} \tag{28d}$$

for all ω . A simple choice satisfying these requirements is

$$\epsilon_{\text{loc}}(\omega; \phi, 0) = \epsilon_{\text{SiO}_2}(\omega), \tag{29a}$$

$$\epsilon_{\text{loc}}(\omega; \phi, 1) = \epsilon_{\text{H}_2\text{O}}(\omega) \tag{29b}$$

independent of ϕ . This amounts to identifying connectivity with porosity $\Lambda = \phi$. Another choice is

$$\epsilon_{\text{loc}}(\omega; \phi, 0) = \epsilon_{\text{loc}}(\omega; \phi, 1) = \phi \epsilon_{\text{H}_2\text{O}}(\omega) + (1 - \phi) \epsilon_{\text{SiO}_2}(\omega) \tag{30}$$

which assumes local connectivity $\Lambda = 1 = \lambda(\phi; \mathbb{K})$ for all local configurations independent of local porosity ϕ . Inserting Eq. (29) into Eq. (26) and taking the limit $d \rightarrow \infty$ gives the mean-field result

$$\epsilon_e(\omega; \mathbb{K}) = p(\mathbb{K}) \epsilon_{\text{SiO}_2}(\omega) + (1 - p(\mathbb{K})) \epsilon_{\text{H}_2\text{O}}(\omega), \tag{31}$$

where

$$p(\mathbb{K}) = \int_0^1 \lambda(\phi; \mathbb{K}) \mu(\phi; \mathbb{K}) d\phi \tag{32}$$

is the total fraction of percolating cells. Choosing Eq. (30) instead of Eq. (29) gives the same result except that $p(\mathbb{K})$ is replaced with

$$\bar{\phi}(\mathbb{K}) = \int_0^1 \phi \mu(\phi; \mathbb{K}) d\phi, \tag{33}$$

the average local porosity. Equation (26) can also be solved for $d = 1$. With Eq. (29), this gives

$$\epsilon_e(\omega; \mathbb{K}) = \left(\frac{p(\mathbb{K})}{\epsilon_{\text{H}_2\text{O}}(\omega)} + \frac{1 - p(\mathbb{K})}{\epsilon_{\text{SiO}_2}(\omega)} \right)^{-1}, \tag{34}$$

while Eq. (30) gives

$$\epsilon_e(\omega; \mathbb{K}) = \left(\int_0^1 \frac{1}{\phi \epsilon_{\text{H}_2\text{O}}(\omega) + (1 - \phi) \epsilon_{\text{SiO}_2}(\omega)} \mu(\phi; \mathbb{K}) d\phi \right)^{-1}, \tag{35}$$

a different result. The difference between Eqs. (34) and (35) highlights the importance of connectivity in one dimension. While Eq. (34) has a percolation transition at $p(\mathbb{K}) = 1$, Eq. (35) exhibits no such transition. The total fraction of percolating cells $p(\mathbb{K})$ is an important control parameter which seems to correlate strongly with many transport quantities²⁷⁻²⁹

For $d = 3$, a specific choice fulfilling conditions (28) is

$$\epsilon_{\text{loc}}(\omega; \phi, 1) = \epsilon_{\text{H}_2\text{O}}(\omega) \left[1 - (1 - \phi) \left\{ \left(1 - \frac{\epsilon_{\text{SiO}_2}}{\epsilon_{\text{H}_2\text{O}}(\omega)} \right)^{-1} - \frac{\phi}{3} \right\}^{-1} \right] \tag{36}$$

for a water coated quartz sphere and

$$\epsilon_{\text{loc}}(\omega; \phi, 0) = \epsilon_{\text{SiO}_2} \left[1 - \phi \left\{ \left(1 - \frac{\epsilon_{\text{H}_2\text{O}}(\omega)}{\epsilon_{\text{SiO}_2}} \right)^{-1} - \frac{(1 - \phi)}{3} \right\}^{-1} \right] \tag{37}$$

for a hollow quartz sphere filled with water. At larger length scales, an effective local dielectric response from a smaller length scale could be used as well (see Refs. 30 and 31).

Self-consistent local porosity approximations for the dielectric response and fluid flow in porous media have been explored and developed in several publications of the present author.^{28,30,32-36} The results have subsequently found numerous applications to heterogeneous sandstones,^{37,38} carbonates and chalk,^{39,40} ceramics,⁴¹ cements,^{10,42} polymer blends,^{16,43} polymer electrolyte membranes,⁴⁴ clays and shales.^{45,46}

V. SCALING LIMIT

A scale factor function (magnification factor, shrinkage factor, or zoom factor) is defined to be a positive and measurable function $b: [1, \infty) \rightarrow (0, \infty)$ such that

$$\lim_{x \rightarrow \infty} \frac{b(\lambda x)}{b(x)} = g(\lambda) \tag{38a}$$

or equivalently

$$\lim_{x \rightarrow 0} \frac{b\left(\frac{1}{\lambda x}\right)}{b\left(\frac{1}{x}\right)} = g\left(\frac{1}{\lambda}\right) \tag{38b}$$

holds for some $\lambda > 0$ and an arbitrary function $g: (0, \infty) \rightarrow (0, \infty)$. Scale factor functions are oftentimes power laws with slowly varying corrections. This follows from the following:

Theorem 2. *Given a scale factor function $b: [1, \infty) \rightarrow (0, \infty)$, let $B \subset \mathbb{R}$ be the set of all $\lambda > 0$ such that (38) holds. If the set B has positive measure, then (38) holds for all $\lambda > 0$ and there exists a number $\alpha \in \mathbb{R}$ with $g(\lambda) = \lambda^\alpha$.*

For the proof, see Ref. 47, p. 17. For $\alpha \neq 0$, the function b is called regularly varying at infinity. The function $b(1/\cdot)$ is called regularly varying at zero. For $\alpha = 0$, the functions are called slowly varying. The theorem implies that scale factor functions have the form

$$b(x) = x^\alpha s(x), \tag{39}$$

where $s(x)$ is a slowly varying function. For $\alpha > 0$, this corresponds to magnification, and for $\alpha < 0$ to shrinkage.

Consider a scale factor function $b: [1, \infty) \rightarrow (0, \infty)$ with $0 < \alpha$ and define a sequence of scale factors as $b_i = b(i)$ for $i \in \mathbb{N}$. Given the sequence b_i , and given the heterogeneous nanoscale set \mathbb{P} with characteristic function $\chi_{\mathbb{P}}$, consider a sequence of functions $\phi_i = \mathfrak{q} \circ (\chi_{\mathbb{P}} \times \text{id}_{\mathbb{R}^{-d}}) \circ \mathfrak{s}_i : \overline{\mathbb{R}^d} \rightarrow \{0, 1\}$ defined as

$$\phi_i(\overline{\mathbf{x}}) = \mathfrak{q} \left\{ (\chi_{\mathbb{P}} \times \text{id}_{\mathbb{R}^{-d}}) [\mathfrak{s}_i(\overline{\mathbf{x}})] \right\} = \chi_{\mathbb{P}}(b_i \overline{\mathbf{x}} + \mathbf{x}_i) \tag{40}$$

on the micrometer scale, where s_i is a sequence of cross sections [see Eq. (5)] probing the vicinity of $b_i\bar{x}$. Here $\text{id}_{\mathbb{R}^d} : \mathbb{R}^d \rightarrow \mathbb{R}^d$ is the identity map and q is the projection map $q : \{0, 1\} \times \mathbb{R}^d \rightarrow \{0, 1\}$. The sequence $\mathbf{x}_i \in \mathbb{R}^d$ is arbitrary subject only to $|\mathbf{x}_i| \leq b_i^\gamma$ with $\gamma < 1$. The condition $\gamma < 1$ ensures that $b_i\bar{x} + \mathbf{x}_i$ stays near $b_i\bar{x}$. The functions ϕ_i are measurable because \mathbb{P} was assumed to be measurable. The sequence ϕ_i is uniformly bounded in $L^\infty(\mathbb{R}^d, \mathbb{R})$ because ϕ_i assumes only the values 0 or 1.

Theorem 1 can be applied with $\mathbb{S} = \mathbb{R}^d$, $m = 1$, and $\mathbb{A} = \{0, 1\}$ to obtain the Young measure $\mu_{\bar{x}}$ associated with the sequence ϕ_i in the scaling limit $i \rightarrow \infty$. In this limit, Theorem 1 also gives $\text{supp}(\mu_{\bar{x}}) = \text{cl}(\mathbb{A}) = \{0, 1\}$ so that for almost all \bar{x} there exists a constant $c_{\bar{x}}$, $0 \leq c_{\bar{x}} \leq 1$, with

$$d\mu_{\bar{x}}(\phi) = (1 - c_{\bar{x}})\delta(\phi) + c_{\bar{x}}\delta(\phi - 1), \tag{41}$$

where δ denotes the Dirac measure. By Theorem 1, the coefficient

$$c_{\bar{x}} = \bar{\phi}(\bar{x}) = \int_{\mathbb{R}} \phi \, d\mu_{\bar{x}}(\phi) \tag{42}$$

defines a measurable function $\bar{\phi} : \mathbb{R}^d \rightarrow [0, 1]$ with values in the full unit interval because the unit interval is the convex hull of $\{0, 1\}$.

VI. RESULTS

Young measures $\mu_{\bar{x}}(\phi)$ are closely related to local porosity distributions $\mu(\phi; \mathbb{K})$. This basic result can be seen formally as follows. Comparison of the density $d\mu_{\bar{x}}(\phi)$ at the micrometer scale from Eq. (41) with Eq. (2.10) in Ref. 17, p. 63 for small \mathbb{K} suggests that formally

$$\lim_{|\mathbb{K}| \rightarrow 0} \mu(\phi; \mathbb{K}) = \mu_{\bar{x}=\mathbf{0}}(\phi) \tag{43}$$

the local porosity distribution for small cells converges to the Young measure at the origin $\bar{\mathbf{0}} \in \mathbb{R}^d$, because the neighbourhood of the origin in \mathbb{R}^d approaches \mathbb{R}^d in the scaling limit.

To establish the connection between Young measures and limiting local porosity distributions more rigorously, consider a fixed, convex, and compact averaging window located at $\bar{x} \in \mathbb{R}^d$,

$$\bar{\mathbb{V}}(\bar{x}) = \bar{x} + \bar{\mathbb{V}}, \tag{44}$$

at the micrometer scale. Let f be any real continuous function with compact support in $[0, 1]$. Volume averaging of $f(\phi_i)$ over $\bar{\mathbb{V}}(\bar{x})$,

$$\frac{1}{|\bar{\mathbb{V}}|} \int_{\bar{\mathbb{V}}(\bar{x})} f(\phi_i(\bar{y})) \, d\bar{y} =: \mu_{\bar{x}, \bar{\mathbb{V}}, i}(f), \tag{45}$$

defines a positive continuous linear functional $\mu_{\bar{x}, \bar{\mathbb{V}}, i} : C_c([0, 1]) \rightarrow \mathbb{R}$ on the space $C_c([0, 1])$ of continuous functions $f : [0, 1] \rightarrow \mathbb{R}$ with compact support. According to Riesz's representation theorem (see Ref. 48, Sec. 29), the set of positive linear functionals on $C_c([0, 1])$ can be mapped bijectively to the set $M_+([0, 1])$ of positive Radon measures on $[0, 1]$. In this way, volume averages are in one-to-one correspondence with positive measures on $[0, 1]$.

The positive Radon measure $\mu_{\bar{x}, \bar{\mathbb{V}}, i}$ is normalized because $\phi_i(\bar{y})$ is well defined for all $\bar{y} \in \bar{\mathbb{V}}(\bar{x})$. It gives the probability distribution for the values of ϕ_i in $\bar{\mathbb{V}}(\bar{x})$. This becomes evident when expressing its density as

$$d\mu_{\bar{x},\bar{V},i}(\phi) = \frac{1}{|\bar{V}|} \int_{\bar{V}(\bar{x})} \delta(\phi - \chi_{b_i\mathbb{P}}(\bar{y})) d\bar{y} \tag{46}$$

in terms of Dirac measures at $\phi = 0$ and $\phi = 1$. Note the similarity with the definition of the local porosity distribution μ in Eq. (25). The main difference to Eq. (25) is that Eq. (46) is formulated at the micrometer scale and involves the scaling factor function, while Eq. (25) is formulated at the nanometer scale. This observation indicates a link between the present approach to macroscopic heterogeneity and the approach in Ref. 19, p. 341. In the scaling limit $i \rightarrow \infty$, the measures $\mu_{\bar{x},\bar{V},i}$ converge to a limiting measure

$$\mu_{\bar{x},\bar{V},i} \xrightarrow{w^*} \mu_{\bar{x},\bar{V}} \tag{47}$$

in the weak* (also called vague) topology on $M_+([0, 1])$.⁴⁸ Theorem 1 can now be applied again to establish the connection between the theory of Young measures and local porosity theory. Multiplying Eq. (46) by any given continuous function $F(\phi)$ and integrating gives

$$\begin{aligned} \int_0^1 F(\phi) d\mu_{\bar{x},\bar{V},i}(\phi) &= \int_0^1 \frac{F(\phi)}{|\bar{V}|} \int_{\bar{V}(\bar{x})} \delta(\phi - \chi_{b_i\mathbb{P}}(\bar{y})) d\bar{y} d\phi \\ &= \frac{1}{|\bar{V}|} \int_{\bar{V}(\bar{x})} F(\chi_{b_i\mathbb{P}}(\bar{y})) d\bar{y}, \end{aligned} \tag{48}$$

where the integrand on the right-hand side converges by virtue of Theorem 1. Combined with Eq. (47), one finds

$$\int_0^1 F(\phi) d\mu_{\bar{x},\bar{V}}(\phi) = \frac{1}{|\bar{V}|} \int_{\bar{V}(\bar{x})} \int_0^1 F(\phi) d\mu_{\bar{y}}(\phi) d\bar{y} \tag{49}$$

or

$$\mu_{\bar{x},\bar{V}} = \frac{1}{|\bar{V}|} \int_{\bar{V}(\bar{x})} \mu_{\bar{y}} d\bar{y} \tag{50}$$

in short. Given a fixed continuous F ,

$$\lim_{|\bar{V}| \rightarrow 0} \int_0^1 F(\phi) d\mu_{\bar{x},\bar{V}}(\phi) = \int_0^1 F(\phi) d\mu_{\bar{x},\{\bar{x}\}}(\phi) \tag{51a}$$

$$= \lim_{|\bar{V}| \rightarrow 0} \frac{1}{|\bar{V}|} \int_{\bar{V}(\bar{x})} \int_0^1 F(\phi) d\mu_{\bar{y}}(\phi) d\bar{y} \tag{51b}$$

$$= \int_0^1 F(\phi) d\mu_{\bar{x}}(\phi) \tag{51c}$$

for almost every \bar{x} by virtue of Lebesgue’s differentiation theorem. Choosing a countable dense set of functions implies that the probability distribution $\mu_{\bar{x},\bar{V}}$ of local porosities in $\bar{V}(\bar{x})$,

$$\mu_{\bar{x},\bar{V}} \xrightarrow{w^*} \mu_{\bar{x}}, \tag{52}$$

converges as $\bar{V}(\bar{x}) \rightarrow \{\bar{x}\}$ in the weak* topology in $M_+([0, 1])$ to the Young measure $\mu_{\bar{x}}$. This establishes a mathematical connection between Young measures and the large scale local porosity distributions in Ref. 19, p. 343.

The preceding discussion can be generalized. The nonrandom local porosity function $\chi_{\mathbb{P}}$ from the discussion above is generalized into a function called ϕ in the sequel. The notation $\text{int}(\mathbb{X})$ denotes the interior of a set \mathbb{X} . The interior $\text{int}(\mathbb{X})$ is the union of all open sets contained in \mathbb{X} . The notation $b\mathbb{X} = \{b\mathbf{x} : \mathbf{x} \in \mathbb{X}\}$ denotes magnification or shrinkage of \mathbb{X} with $b > 0$.

Theorem 3. Let $b_\phi: [1, \infty) \rightarrow (0, \infty)$ be a regularly varying magnification factor function with index $\alpha_\phi > 0$ and $b_V: [1, \infty) \rightarrow (0, \infty)$ a shrinkage factor function ($b_V(\infty) = 0$) regularly varying with index $\alpha_V < 0$. Let $\phi: \mathbb{R}^d \rightarrow [0, 1]$ be a nanoscale nonrandom local porosity function, let $\mathbf{x}_i \in \mathbb{R}^d$ be a nanoscale sequence such that $|\mathbf{x}_i| \leq b_\phi(i)^\gamma$ with $\gamma < 1$ for all $i \in \mathbb{N}$, and let

$$\begin{aligned} \phi_i: \bar{\mathcal{S}} \subset \bar{\mathbb{R}}^d &\rightarrow [0, 1] \\ \bar{\mathbf{x}} &\mapsto \phi_i(\bar{\mathbf{x}}) = \phi[b_\phi(i)\bar{\mathbf{x}} + \mathbf{x}_i] \end{aligned} \tag{53}$$

with $\bar{\mathbf{x}} \in \text{int}(\bar{\mathcal{S}})$ be a sequence of local porosity functions. If $\bar{V}(\bar{\mathbf{x}}) \subset \bar{\mathcal{S}}$ is a measurement cell centered at $\bar{\mathbf{x}}$ and $\mathbb{A} \subset [0, 1]$ is any measurable subset of the unit interval, then

$$\mu_{\bar{\mathbf{x}}}(\mathbb{A}) = \lim_{\lambda \rightarrow \infty} \lim_{i \rightarrow \infty} \frac{|\{\bar{\mathbf{y}} \in b_V(\lambda)\bar{V}(\bar{\mathbf{x}}) : \phi_i(\bar{\mathbf{y}}) \in \mathbb{A}\}|}{|b_V(\lambda)\bar{V}(\bar{\mathbf{x}})|} \tag{54}$$

exists and gives the probability to find a local porosity value $\bar{\phi} \in \mathbb{A}$.

The proof follows from the application of Theorem 1 and its corollary with $m = 1$ and $f_i = \phi_i$. In fact, the result is not restricted to rescaled local porosity functions ϕ_i . It holds for any observable that gives a uniformly bounded sequence of functions ϕ_i .

Theorem 4. Let $\phi: \mathbb{R}^d \rightarrow [0, 1]$ be a nonrandom local porosity function, let $b: [1, \infty) \rightarrow (0, \infty)$ be a regularly varying scale factor function of index $\alpha > 0$, let $\mathbf{x}_i \in \mathbb{R}^d$ be a nanoscale sequence with $|\mathbf{x}_i| \leq b_\phi(i)^\gamma$ with $\gamma < 1$ for all $i \in \mathbb{N}$, and let $\phi_i: \bar{\mathcal{S}} \subset \bar{\mathbb{R}}^d \rightarrow [0, 1]$ with $\phi_i(\bar{\mathbf{x}}) = \phi[b_\phi(i)\bar{\mathbf{x}} + \mathbf{x}_i]$, $i \in \mathbb{N}$, and $\bar{\mathbf{x}} \in \text{int}(\bar{\mathcal{S}})$ be a sequence of local porosity functions. If $\mu_{\bar{\mathbf{x}}}$ is the limiting local porosity distribution in Eq. (54) and $F: [0, 1] \rightarrow \mathbb{R}$ is any continuous function, then

$$\begin{aligned} \lim_{i \rightarrow \infty} \int_{\bar{\mathcal{S}}} F[\phi_i(\bar{\mathbf{x}})]f(\bar{\mathbf{x}}) d\bar{\mathbf{x}} &= \\ \int_{\bar{\mathcal{S}}} f(\bar{\mathbf{x}}) \int_0^1 F(\phi) d\mu_{\bar{\mathbf{x}}}(\phi) d\bar{\mathbf{x}} & \end{aligned} \tag{55}$$

holds for all integrable functions $f \in L^1(\bar{\mathcal{S}}; \mathbb{R})$.

When f is peaked at some point, the average over limiting local porosity distributions amounts to volume averaging over infinitely extended and rescaled representative elementary volumes. Repeated rescaling allows one to bridge scales.

VII. DISCUSSION

A. Multiple scales

The results above can be extended to multiple scales. Given a porous medium \mathbb{P} with heterogeneities at length scales $\ell \in \{\bar{\ell}, \tilde{\ell}, \hat{\ell}\}$, let $\phi \in \{\bar{\phi}, \tilde{\phi}, \hat{\phi}\}$ denote the corresponding local porosity functions at these scales starting from $\phi(\mathbf{x}) = \chi_{\mathbb{P}}(\mathbf{x})$ at the nanoscale. Choosing a scale factor function $b_\phi: [1, \infty) \rightarrow (0, \infty)$ then yields limiting local porosity distributions $d\mu_x(\phi)$ from Eq. (54) with $\mathbf{x} \in \{\bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}\}$ and $\phi \in \{\bar{\phi}, \tilde{\phi}, \hat{\phi}\}$ by iteration. The sequence ϕ_i is defined in analogy with Eq. (53), and the local porosity function for the next length scale is obtained as

$$\phi(\mathbf{x}) = \int_0^1 s d\mu_x(s) \tag{56}$$

from the limiting local porosity distribution of the previous sequence for the scale below.

B. Classification of macroscopic heterogeneity

The following classification and terminology emerges naturally from the results.

Definition. A microscopically nonrandom multiscale porous medium with limiting local porosity distributions $\mu_{\mathbf{x}}$ with $\mathbf{x} \in \{\bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}\}$ is called macroscopically

1. homogeneous and nonrandom if

$$d\mu_{\mathbf{x}}(\phi) = \delta(\phi - \phi_{\mathbb{P}}) \tag{57a}$$

for all \mathbf{x} ,

2. homogeneous and random if

$$d\mu_{\mathbf{x}}(\phi) = d\mu(\phi) \tag{57b}$$

for all \mathbf{x} ,

3. heterogeneous and nonrandom if

$$d\mu_{\mathbf{x}}(\phi) = \delta(\phi - \phi(\mathbf{x})), \tag{57c}$$

4. heterogeneous and random in all other cases.

C. Multiscale dielectric functions

Inserting the limiting local porosity distributions $d\mu_{\mathbf{x}}(\phi)$ with $\mathbf{x} \in \{\bar{\mathbf{x}}, \tilde{\mathbf{x}}, \hat{\mathbf{x}}\}$ into the local porosity equation Eq. (26) gives

$$\int_0^1 \left[\frac{\epsilon_{\text{loc}}(\omega; \phi, 1) - \epsilon_e(\mathbf{x}, \omega)}{\epsilon_{\text{loc}}(\omega; \phi, 1) + (d - 1)\epsilon_e(\mathbf{x}, \omega)} \lambda_{\mathbf{x}}(\phi) + \frac{\epsilon_{\text{loc}}(\omega; \phi, 0) - \epsilon_e(\mathbf{x}, \omega)}{\epsilon_{\text{loc}}(\omega; \phi, 0) + (d - 1)\epsilon_e(\mathbf{x}, \omega)} (1 - \lambda_{\mathbf{x}}(\phi)) \right] d\mu_{\mathbf{x}}(\phi) = 0, \tag{58}$$

where $\epsilon \in \{\bar{\epsilon}, \tilde{\epsilon}, \hat{\epsilon}\}$ and $\lambda_{\mathbf{x}}(\phi)$ is the limiting local percolation probability corresponding to $d\mu_{\mathbf{x}}(\phi)$. The limiting total fraction of percolating cells $p(\mathbf{x})$ and the effective dielectric functions $\epsilon_e(\mathbf{x}, \omega)$ become \mathbf{x} -dependent. This result generalizes the local porosity equation (26) to multiscale heterogeneous media. Note that the dependence on size, shape, and form of the measurement cell \mathbb{K} is reduced to its location \mathbf{x} .

D. From deterministic to disordered systems and back

The theory developed above has noteworthy fundamental implications. Starting from the deterministic nanoscale local porosity function $\chi_{\mathbb{P}}(\mathbf{x})$ with values in $\{0, 1\}$, the microscale distribution $\mu_{\bar{\mathbf{x}}}$ is random consisting of two Dirac measures. Consider the quasistatic problem (20) with $\mathbf{x} = \bar{\mathbf{x}}$ at the microscale. If accurate approximations for the ϕ -dependence of the local dielectric function $\bar{\epsilon}_{\text{loc}}(\omega; \phi)$ are available, then Eq. (20) can be turned into a stochastic partial differential equation by replacing

$$\bar{\epsilon}(\bar{\mathbf{x}}, \omega) = \bar{\epsilon}_{\text{loc}}(\omega; \phi_{\bar{\mathbf{x}}}) \tag{59}$$

in Eq. (20), where $\phi_{\bar{\mathbf{x}}}$ is a random realization drawn from $\mu_{\bar{\mathbf{x}}}$. In this way, a disordered system can emerge as an approximation to a deterministic system in the scaling limit.

The reverse phenomenon is also possible when at some scale the limiting distribution $d\mu_{\bar{\mathbf{x}}}(\phi) = \delta(\phi - \phi(\bar{\mathbf{x}}))$ becomes a single Dirac measure.

Based on these considerations, limiting local porosity distributions can be used to define the probability distribution of discrete random media as discussed in Ref. 19, Eq. (2.9). Consider m points $\{\mathbf{x}_1, \dots, \mathbf{x}_m\}$ forming a cube shaped cubic grid in \mathbb{R}^d . Again $\mathbf{x}_i \in \{\mathbf{x}_i, \bar{\mathbf{x}}_i, \tilde{\mathbf{x}}_i, \hat{\mathbf{x}}_i\}$ for $1 \leq i \leq m$ depending on the scale of interest. Define the multipoint local porosity function

$$\phi(\mathbf{x}_1, \dots, \mathbf{x}_m) = (\phi(\mathbf{x}_1), \dots, \phi(\mathbf{x}_m)), \tag{60}$$

where $\phi(x)$ with $\phi \in \{\chi_{\mathbb{P}}, \bar{\phi}, \tilde{\phi}, \hat{\phi}\}$ is a one-point local porosity function. Applying the results above yields the limiting m -point local porosity distribution μ_{x_1, \dots, x_m} with $x_i \in \{\bar{x}_i, \tilde{x}_i, \hat{x}_i\}$ one scale above. The result can be deterministic or stochastic depending on whether the limiting distribution approaches a Dirac measure or not.

VIII. CONCLUSIONS

The results of the present paper eliminate the dependence of volume averaged quantities on the shape of the averaging volume \mathbb{V} . This emerges from a suitable scaling limit in which $|\mathbb{V}| \rightarrow \infty$. Conventional models assume implicitly that number valued functions emerge in this limit. This assumption is found to be too restrictive. Instead measure valued functions must be expected to arise in the scaling limit. Applied to volume fractions, these limiting measures have been identified as limiting local porosity distributions. A systematic characterization of macroscopic heterogeneity in porosity emerges from classifying the limiting measures with respect to their position dependence and support.

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- ¹ D. Bruggemann, *Ann. Phys.*, 5. Folge **24**, 666 (1935).
- ² M. Hubbert, *Int. Assoc. Sci. Hydrol. Bull.* **2**, 23 (1957).
- ³ S. Whitaker, *Transp. Porous Media* **1**, 3 (1986).
- ⁴ C. Marle, *Int. J. Eng. Sci.* **20**, 643 (1982).
- ⁵ M. Hassanzadeh and W. G. Gray, *Adv. Water Res.* **2**, 131 (1979).
- ⁶ A. Lemmer and R. Hilfer, *J. Comput. Phys.* **281**, 970 (2015).
- ⁷ K. Mattila, T. Puurtinen, J. Hyvälouma, R. Surmas, M. Myllys, T. Turpeinen, F. Robertsen, J. Westerholm, and J. Timonen, *J. Comput. Sci.* **12**, 62 (2016).
- ⁸ B. Biswal, P. Øren, R. Held, S. Bakke, and R. Hilfer, *Image Anal. Stereol.* **28**, 23 (2009).
- ⁹ S. Roth, B. Biswal, G. Afshar, R. Held, P. Øren, L. Berge, and R. Hilfer, *AAPG Bull.* **95**, 925 (2011).
- ¹⁰ J. Hu and P. Stroeven, *Cem. Concr. Res.* **35**, 233 (2005).
- ¹¹ S. Whitaker, *Ind. Eng. Chem.* **61**(12), 14 (1969).
- ¹² J. Bear, *Dynamics of Fluids in Porous Media* (Elsevier Publ. Co., New York, 1972).
- ¹³ J. Poley, J. Nooteboom, and P. de Waal, *Log. Anal.* **19**, 8 (1978).
- ¹⁴ R. Bayford, *Annu. Rev. Biomed. Eng.* **8**, 63 (2006).
- ¹⁵ A. Haas and A. Revil, *Water Resour. Res.* **45**, W10202, <https://doi.org/10.1029/2009wr008160> (2009).
- ¹⁶ A. Barbetta, C. Cametti, G. Rizzitelli, and M. Dentini, *Soft Matter* **8**, 1120 (2012).
- ¹⁷ R. Hilfer, *Phys. Rev. B* **44**, 60 (1991).
- ¹⁸ E. Haslund and B. Nøst, *Geophysics* **63**, 149–153 (1998).
- ¹⁹ R. Hilfer, *Adv. Chem. Phys.* **XCII**, 299 (1996).
- ²⁰ J. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon, Oxford, 1932).
- ²¹ E. Sanchez-Palencia, *Non-Homogeneous Media and Vibration Theory*, Lecture Notes in Physics (Springer Verlag, Berlin, 1980), Vol. 127.
- ²² V. Jikov, S. Kozlov, and O. Oleinik, *Homogenization of Differential Operators and Integral Functionals* (Springer, Berlin, 1994).
- ²³ J. Ball, in *Partial Differential Equations and Continuum Models for Phase Transitions*, Lecture Notes in Physics, edited by M. Rascle, D. Serre, and M. Slemrod (Springer, Berlin, 1989), Vol. 344, pp. 207–215.
- ²⁴ C. Castaing, P. Raynaud de Fitte, and M. Valadier, *Young Measures on Topological Spaces* (Kluwer, Dordrecht, 2004).
- ²⁵ F. Boger, J. Feder, R. Hilfer, and T. Jøssang, *Physica A* **187**, 55 (1992).
- ²⁶ R. Hilfer, *Physica A* **194**, 406 (1993).
- ²⁷ R. Hilfer, in *Räumliche Statistik und Statistische Physik*, Lecture Notes in Physics, edited by D. Stoyan and K. Mecke (Springer, Berlin, 2000), Vol. 554, p. 203.
- ²⁸ B. Biswal, C. Manwart, R. Hilfer, S. Bakke, and P. Øren, *Physica A* **273**, 452 (1999).
- ²⁹ R. Hilfer, *Transp. Porous Media* **46**, 373 (2002).
- ³⁰ R. Hilfer, J. Widjajakusuma, and B. Biswal, *Granular Matter* **2**, 137 (1999).
- ³¹ R. Hilfer, J. Widjajakusuma, and B. Biswal, *Physica A* **318**, 319 (2003).
- ³² C. Andraud, A. Beghdadi, E. Haslund, R. Hilfer, J. Lafait, and B. Virgin, *Physica A* **235**, 307 (1997).
- ³³ B. Biswal, C. Manwart, and R. Hilfer, *Physica A* **255**, 221 (1998).
- ³⁴ B. Biswal and R. Hilfer, *Physica A* **266**, 307 (1999).
- ³⁵ J. Widjajakusuma, B. Biswal, and R. Hilfer, *Comput. Mater. Sci.* **16**, 70 (1999).
- ³⁶ J. Widjajakusuma, C. Manwart, B. Biswal, and R. Hilfer, *Physica A* **270**, 325 (1999).
- ³⁷ P. Yin and G. Zhao, *Int. J. Rock Mech. Min. Sci.* **70**, 82 (2014).
- ³⁸ J. Thovert, F. Yousefian, P. Spanne, C. Jacquin, and P. Adler, *Phys. Rev. E* **63**, 061307 (2001).

- ³⁹ J. Liu, G. Pereira, and K. Regenauer-Lieb, *J. Geochem. Explor.* **144**, 84 (2014).
- ⁴⁰ M. Talukdar, O. Torsaeter, M. Ioannidis, and J. Howard, *Transp. Porous Media* **48**, 101 (2002).
- ⁴¹ J. Petrasch, F. Meier, H. Friess, and A. Steinfeld, *Int. J. Heat Fluid Flow* **29**, 315 (2008).
- ⁴² K. Wan and Q. Xu, *Sci. China* **57**, 953 (2014).
- ⁴³ R. Hilfer, B. Nøst, E. Haslund, Th. Kautzsch, B. Virgin, and B. D. Hansen, *Physica A* **207**, 19 (1994).
- ⁴⁴ Z. Fishman and A. Bazylak, *J. Electrochem. Soc.* **158**, B841 (2011).
- ⁴⁵ L. Keller, L. Holzer, P. Schuetz, and P. Gasser, *J. Geophys. Res.: Solid Earth* **118**, 2799, <https://doi.org/10.1002/jgrb.50228> (2013).
- ⁴⁶ P. Cosenza, D. Pret, A. Giraud, and S. Hedana, *Mech. Mater.* **84**, 55 (2015).
- ⁴⁷ N. Bingham, C. Goldie, and J. Teugels, *Regular Variation* (Cambridge University Press, Cambridge, 1987).
- ⁴⁸ H. Bauer, *Maß-und Integrationstheorie* (Walter de Gruyter, Berlin, 1992).