**Morphological Optimization of Nano-structured Materials for Solar Thermochemical Applications**

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**ABSTRACT**

Solar thermochemical reactors are designed to take concentrated solar energy and convert it to energy stored in chemical bonds. The interaction between solar radiation and the chemically-active material is therefore central to the reactor performance. To optimize the thermochemical conversion process, we propose to design a porous material with features spanning many length scales; including features small enough that the wave nature of light cannot be ignored. The multi-scale nature of this problem raises the challenge of modeling a structure with wavelength-scale behavior on the scale of a macroscopic reactor. To facilitate this design, we propose a homogenization approach to thermal radiative transfer in nano-structured materials to obtain an effective radiative transport equation (RTE). The approach is founded on the concept of moment-linking—the macroscopic moments of the effective RTE must match the macroscopic moments of the underlying electrodynamic solution. As a proof of concept, we show that this approach recovers the expected behavior in the dilute limit where the RTE is expected to strictly hold.

**1. Introduction**

The emerging field of high-temperature solar thermochemistry holds tremendous promise to disrupt the conventional paths of producing fuels, energy-intensive commodity materials and generating dispatchable power. Direct solar irradiation is concentrated by mirrors, captured by a receiver, converted into high-temperature process heat, often exceeding 1000 K, and used to drive highly-endothermic processes for production of chemical fuels and materials including synthesis gas, carbon black, ammonia, lime, and metals [1]. Solar reactors typically feature heterogeneous chemically reacting media in the form of micro-structures, macro-structures, or particles [2-4]. The disparate length scales found in the reactive structures and the reactor itself leads to a challenging multi-scale problem. Effective simulation techniques bridging the length-scales are crucial for quantifying the effects of a given design decision on reactor performance.

The rapid and efficient transfer of energy from a concentrated solar source to the redox material to drive reactions—i.e. the transfer of energy from photons to chemical bonds—is the core critical research aspects towards achieving a high-output and efficient reactor design. For efficient radiative transfer, the active material should feature efficient absorption of the incident concentrated solar radiation with moderate to low spatial variation of the absorbed volumetric radiative power and confinement of the emitted thermal radiation in the close vicinity of the reaction site.

Radiative transfer in complex macro-structured media has garnered attention in the recent decade [5]. When the heterogeneous features of such media are sufficiently large the radiative transfer equation (RTE) can be applied at discrete levels, which drastically simplifies the analysis. Recent developments provide a strong theoretical foundation for the use of the single and multiple RTE continuum approaches in macro-structured media consisting of multiple components with arbitrary-shaped discrete-level geometry and arbitrary radiative properties of the constituents [6]. Studies on predicting thermal characteristics, in particular radiative properties, of nano- and micro-structured media encountered in high-temperature applications are nearly absent in the literature and pose serious challenges to model. The connection between the true electrodynamic behavior of light and ray description that underlies the RTE in discrete and continuous random media has been explored by numerous authors and been shown to be valid in limiting cases [8,9]. In this work we propose a method for the multi-scale simulation of porous materials exhibiting wavelength-scale features where the RTE may not be strictly valid, but where the energy transfer within the media can be captured by it. That is, we propose a homogenization method for finding an effective RTE to model strongly heterogeneous materials with small features.

**2. Proposed methodology**

We consider the consider the simplest case of the RTE written in terms of a specific intensityfor a cold participating medium,

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Hereis the scattering coefficient,is the *i*th component of the velocity vector, andis the scattering phase function. Space and time are denotedand. Note that here the specific intensity has the units of Wm-2µm3, i.e. flux per wavevector and the scattering phase function is properly normalized and should ensure that scattering only takes place within a certain wavenumber band.

We define the Wigner function as in [7],

,

Where the vectoris defined by

,

This quantity has been shown to be analogous to the specific intensity in that its zeroth and first moments correspond to the internal energy and the energy flux, respectively and satisfies a RTE under limiting circumstances (in the high frequency limit within an isotropic randomly perturbed refractive index) [7].

As one would expect, the local internal energy is given by [7],



Whereis the trace operation.

We propose a post-processing of



We impose that the global spatial moments of in space and wavevector match. This imposition has been shown to give excellent agreement when approximating radiative transfer by a diffusion equation [9].

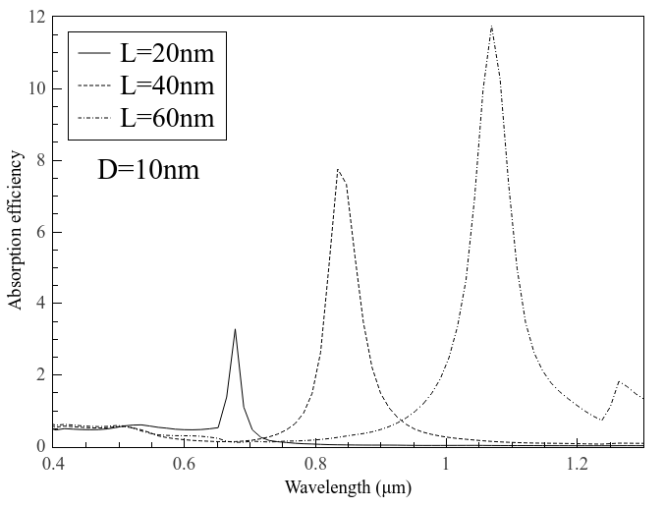
**3. Future work**

It is expected that the described approach will yield accurate predictions for the case of an independently scattering medium as considered in the works of Mishchenko et. al [8] since it has been shown that the RTE can be rigorously derived in this limit [7]. What we propose to test is how far this analogy can go to produce effective transport coefficients for effective RTE simulations of large-scale systems. With this in mind, we will conclude with a discussion the foreseen issues with this approach that will need to be resolved:

Excitation of the system

Time averaging

Ensemble averaging



**Figure 1. Calculated absorption efficiency of gold nanorods with different aspect ratios**

**References**

[1] Bader, R. & Lipiński, W. Solar thermochemical processes. In The World Scientific Handbook of Solar Energy (ed. Crawley, G. M.) (World Scientific, 2016).

[2] Scheffe, Jonathan R., Michael Welte, and Aldo Steinfeld. "Thermal reduction of ceria within an aerosol reactor for H2O and CO2 splitting." Industrial & Engineering Chemistry Research 53.6 (2014): 2175-2182.

[3] Chueh, William C., et al. "High-flux solar-driven thermochemical dissociation of CO2 and H2O using nonstoichiometric ceria." Science 330.6012 (2010): 1797-1801.

[4] Furler, Philipp, et al. "Thermochemical CO2 splitting via redox cycling of ceria reticulated foam structures with dual-scale porosities." Physical Chemistry Chemical Physics 16.22 (2014): 10503-10511.

[5] L.A. Dombrovsky and D. Baillis. *Thermal Radiation in Disperse Systems: An Engineering Approach*. Begell House, New York and Redding (CT), 2010.

[6] W. Lipiński, D. Keene, S. Haussener, and J. Petrasch. Continuum radiative heat transfer modeling in media consisting of optically distinct components in the limit of geometrical optics. *JQSRT*. 111:2474–2480, 2010.

[7] Leonid Ryzhik, George Papanicolaou, and Joseph B. Keller. Transport equations for elastic and other waves in random media. Wave Motion, 24(4):327 – 370, 1996.

[8] Michael I. Mishchenko, Janna M. Dlugach, Maxim A. Yurkin, Lei Bi, Brian Cairns, Li Liu, R. Lee Panetta, Larry D. Travis, Ping Yang, and Nadezhda T. Zakharova. First-principles modeling of electromagnetic scattering by discrete and discretely heterogeneous random media. *Physics Reports*, 632:1–75, 2016. First-principles modeling of electromagnetic scattering by discrete and discretely heterogeneous random media.

[9] K. Razi Naqvi and S. Waldenstrøm. Brownian Motion Description of Heat Conduction by Phonons. *Phys. Rev. Lett*., 95:065901, Aug 2005.