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Optical and thermal radiative properties of plasmonic nanofluids containing core–shell composite nanoparticles for efficient photothermal conversion

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ABSTRACT

Nanofluid has been proposed for use in direct absorption solar collector because of its unique thermal and optical radiative properties. The improvement of solar absorption efficiency was shown to be significantly influenced by the particle material, size, shape, volume fraction, etc. However, it was rare for simultaneously investigating the thermal and optical properties, especially the spectral ones that are critical for efficient photothermal application. Nonmetallic nanoparticles with metallic nanoshells can improve the spectral solar absorption efficiency since the effect of localized surface plasmon resonance (LSPR) exists at the surfaces of these core–shell composite nanoparticles. In this paper, the effect of LSPR at the surfaces of some typical composite nanoparticles (with Si or SiC core and Au, Ag, Cu or Al shell) on the optical and thermal radiative properties of water-based plasmonic nanofluids is numerically investigated by varying the particle radius ratio, outer radius and type of material of the composite nanoparticles in the dependent scattering regime through setting the volume fraction or particle distance. The scattering, absorption or extinction coefficient for these nanoparticles are calculated using the Mie scattering theory and the Rayleigh scattering approximation. The order of magnitude of near field interactions between the nanoparticles is demonstrated by two parallel nanoparticle arrays, based on the near field radiation heat flux between two nanoparticles using the fluctuation electrodynamics. The contributions of the optical absorption and thermal radiation in the near field are compared with the effective thermal conductivity of the nanofluids. The results show that the structure itself can simultaneously influence the average and the near field radiative properties of the composite nanoparticles and thus the plasmonic nanofluids. These coupling effects can be efficiently utilized for tuning the radiative properties of plasmonic nanofluids used in photothermal application.

1. Introduction

Optical and thermal radiative properties of advanced materials are critically needed for solar energy conversion systems, photothermal management, etc. Nanofluid has been proposed for use in direct absorption solar collector because of its unique thermal and optical properties [1] since it was first reported with abnormally high thermal conductivity [2]. For example, Yousefi et al. [3] experimentally investigated the effect of Al_2O_3/H_2O nanofluid on the efficiency of flat-plate solar collectors. Their results show an increased efficiency of 28.3% comparing with water when the mass concentration is 0.2%. Tyagi et al. [4] theoretically studied the capability of using nanofluid in non-concentrating direct absorption solar collector and found that its efficiency is up to 10% higher than that used in a flat-plate collector. Otanicar et al. [1] experimentally studied the effect of different nanofluids used in solar thermal collectors and obtained an efficiency improvement up to 5%. The efficiency improvements were shown to be significantly influenced by the particle material, size, shape, volume fraction, etc [5]. However, it was rare in the literature for simultaneously investigating the thermal and optical properties, especially the spectral ones.

The research on the scattering and absorption characteristics of a simple particle with diameter smaller than the radiation wavelength can be traced back to the works by Rayleigh and later Lorenz, Mie, Debye, et al. More details about the history of scattering can be referred to, e.g., Modest's book [6]. Recently, with the

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Nomenclature

a	particle radius (m)
c	speed of light (m/s)
C	cross-section (m^2)
d	center-to-center distance (m)
D	diameter (m)
f	volume ratio
f_v	volume fraction
F	form factor
g	pair distribution function
$\mathbf{G}$	Green's function
h	Planck constant (J s)
$\hbar$	reduced Planck constant (J s)
k_B	Boltzmann constant (J/K)
k_{eff}	effective thermal conductivity (W/(m K))
k_r	average radiative thermal conductivity (W/(m K))
k_{nf}	average near field radiative thermal conductivity (W/(m K))
K	optical constant
n	refractive index
N_T	particle number in unit volume
P	radiation heat transfer power volume ratio
Pr	Prandtl number
Q	scattering efficiency mean energy of an oscillator (J)
r	radius (m) distance from the central scatterer (m)
R_λ	blackbody radiation intensity (J/(m Hz))
s	radiation heat transfer area (m^2)
S	Poynting vector, near field radiation heat flux (W/m^2)
t	radius ratio
T	temperature (°C)
x	non-dimensional size parameter

Greek symbols

α	polarizability, polarization
ε	dielectric function
Φ	phase function
Γ	scattering rate
λ	wavelength (m)
Θ	angle between directions of propagation and observation (rad)
σ	extinction coefficient Stefan Boltzmann constant (J/(s m^2 K^4))
ω	frequency (rad/s)
Ω	solid angle (sr)

Subscripts

0	vacuum
1	core
2	shell
∞	high frequency contribution
a,abs	absorption
bf	base fluid
cr	critical
ext	extinction
p	nanoparticle plasma
s,sca	scattering

Superscripts

e	perpendicular polarization
m	parallel polarization
M	Mie scattering
SD	dependent scattering
SM	Mie scattering
TE	perpendicular polarization
TM	parallel polarization

development of nanoparticle (NP) and its potential application in fluids for solar energy conversion, the radiative properties of nanoparticles including the absorption and scattering coefficients and the induced extinction coefficient were attracting much attention [7]. For example, the optical properties of metallodielectric nanostructures, such as the optical absorption and scattering cross sections as well as the local electromagnetic fields and induced charge densities at the surfaces of the nanostructures, can be obtained by the finite difference time domain (FDTD) method [8,9]. The material and the shape of nanoparticle are two important factors influencing the spectral properties of fluids. An effective method for obtaining the spectral properties of fluids is by using and controlling the core–shell composite nanoparticles [10,11]. Core–shell composite nanoparticle can be prepared by many chemical reaction method [12–15]; however, the absorption and scattering characteristics of these novel nanoparticles need to be verified.

Three scattering regimes can be defined using the non-dimensional size parameter $x = \pi D/\lambda$ where D is the nanoparticle diameter and λ is the wavelength of the incident radiation: Rayleigh scattering ($x \ll 1$), Mie scattering ($x = 1$), and geometric scattering ($x \gg 1$) [16]. When nanoparticle size is close to the wavelength, the coupling effects between particles including multiple interference, near field radiation or the surface plasma should be considered. For instance, Volz et al. [17] investigated the near-filed radiative heat transfer in nanoparticle based composite media and obtained the effective thermal conductivity due to the near field radiation. Lu et al. [18] developed the three critical point pole pairs (CP3) model to better describe the dielectric functions for the dispersions of metal nanoparticles and used the FDTD method to study the effect of the interaction between the SiO_2/Au core–shell composite nanocylinder pair on the localized surface plasmon resonance (LSPR) spectra. Phan et al. [19] studied the near field heat transfer between gold nanoparticle arrays using the coupled dipole method and found that the near field radiation reduces with increasing nanoparticle size. These investigations show that details about the effect of the material and the size of nanoparticle needs for further discussion.

In this paper, we will investigate the optical and thermal radiative properties of water-based plasmonic nanofluids containing core–shell composite nanoparticles through absorption, extinction and near filed radiation heat transfer in the nanoparticles at wavelength scale by changing the material, size, structure and volume fraction, in order to vary the spectral absorption properties of these nanofluids that could be used in direct absorption solar collector.

2. Theory

2.1. Absorption and extinction

The optical radiative properties involving light absorption and scattering in a media is related to the extinction effect. During the absorption and scattering processes, surface plasmon resonance (SPR) plays an important role that influence the extinction coefficient. SPR is the collective oscillation of surface electrons