Phys 160 Physical Review Report: Thermoplasmonics Modeling: A Green's function approach

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1 Introduction

This report features metallic nanoparticles known as "Thermoplasmonics." These particles have light absorption properties that bring about several interesting optical and heat transfer properties. In particular, these particles are able to absorb light and generate heat. Because of the diffusive nature of heat, it is generally difficult to examine heat microscopically. However, Thermoplasmonics give us some insight on how temperature regimes and heat transfer behave on a small length scale. In the paper, "Thermoplasmonics Modeling: A Green's function approach", Baffou et al describes temperature distributions for different nanoparticle configurations and provides methods for solving for them.

2 Discrete Dipole Approximation

The discrete dipole approximation is a method we use to investigate optical properties like absorption and scattering of nanoparticles. Baffou assumes that the particles and surrounding media are composed of only dielectric material and no magnetic material. If an external magnetic field were to be applied to a distribution of N metallic nanoparticles, then each particle would experience electric polarization. We can write the polarization amplitude of each particle as

$$\mathbf{p}_i = \alpha(\omega)\mathbf{E}_i^{ext}(\omega) \tag{1}$$

where α is the polarizability and $\mathbf{E}_i^{ext}$ is the external field subject to the particles plus the electric field emitted from the *ith* particle's neighbors.

Baffou then defines

$$\alpha = \frac{\alpha_0}{1 - \frac{2}{3}ik^3\alpha_0} \tag{2}$$

and

$$\alpha_0 = 4\pi\epsilon_0 a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \tag{3}$$

where ϵ is the electric permittivity of the nanoparticle and ϵ_m is the permittivity of the surrounding medium.

3 Thermal Field

3.1 Thermal field of a nanoparticle

We can model the temperature of the N particle system by using Poisson's equation for steady state heat transfer.

$$\kappa\nabla^2 T(\mathbf{r}) = -q(\mathbf{r}) \tag{4}$$

where κ is the thermal conductivity and $q(\mathbf{r})$ is the heat source density.

However, for now, let's just look at the case of just one particle i.e. $N = 1$, then we can later generalize to a system of arbitrary number of independently interacting particles. Because there are no heat sources outside of the single particle, for $N = 1$, the heat source density $q(\mathbf{r})$ goes to 0. This means our PDE for heat transfer reduces to its homogenous counterpart: Laplace's Equation.

$$\nabla^2 T(\mathbf{r}) = 0 \tag{5}$$

From here on out, behaviors of the thermal field and temperature gradient will eerily resemble the electrostatic potential and electrostatic field respectively. However, this is no coincidence. $\nabla^2 T(\mathbf{r}) = 0$ holds the same form as $\nabla^2 V(\mathbf{r}) = 0$ from electrostatics, so we should expect these two scenarios to be analogous of one another.

If we take these metallic nanoparticles to be spheres of radius a, then $\nabla^2 T(\mathbf{r}) = 0$ implies the use of spherical coordinates. We find the solution of this PDE to be

$$T(\mathbf{r}) = T_0 \frac{a}{|\mathbf{r} - \mathbf{r}_i|} \tag{6}$$

for $|\mathbf{r} - \mathbf{r}_i| \geq a$, which is outside the radius of the particle.

The approximate temperature inside the particle is

$$T(\mathbf{r}) = T_0 \tag{7}$$

This turns out to be a good approximation for nanoparticles with greater thermal conductivity than the medium they reside in.

We can calculate the heat power Q of the nanoparticle by taking a surface integral of the temperature gradient over the surface of the sphere.

$$Q = \int_S -\kappa\vec{\nabla} T(\mathbf{r}) \cdot d\mathbf{S} \tag{8}$$

Evaluating this expression yields

$$T_0 = \frac{Q}{4\pi\kappa a} \tag{9}$$

which we can substitute it into (6) to get

$$T(\mathbf{r}) = \frac{Q}{4\pi\kappa|\mathbf{r} - \mathbf{r}_i|} \tag{10}$$

As I've mentioned before, (10) looks very similar to the electric potential of a point charge. We can write (10) in terms of Green's functions $G(\mathbf{r}, \mathbf{r}_i) = \frac{1}{4\pi\kappa|\mathbf{r}-\mathbf{r}_i|}$. Thus, we can write the temperature profile of an independent metallic nanoparticle as

$$T(\mathbf{r}) = QG(\mathbf{r}, \mathbf{r}_i) \tag{11}$$

If we generalize to a 1 dimensional system of N particles, then we can take a summation over (11).

External Temperature

$$T(\mathbf{r}) = \sum_{j=1}^{N} G(\mathbf{r}, \mathbf{r}_j)Q_j \tag{12}$$

Internal Temperature

$$T_i = \sum_{j=1}^{N} G^{int}(\mathbf{r}_i, \mathbf{r}_j)Q_j \tag{13}$$

where $G^{int}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{4\pi\kappa a}$

External temperature describes the temperature profile of the medium, disregarding the interior of the metallic particles. Internal temperature describes the temperature profile inside each nanoparticle.

3.2 Method of Images

Rather than calculating thermal field of a distribution of charges in a single medium, we can also consider the presence of a neighboring medium with a different thermal conductivity.

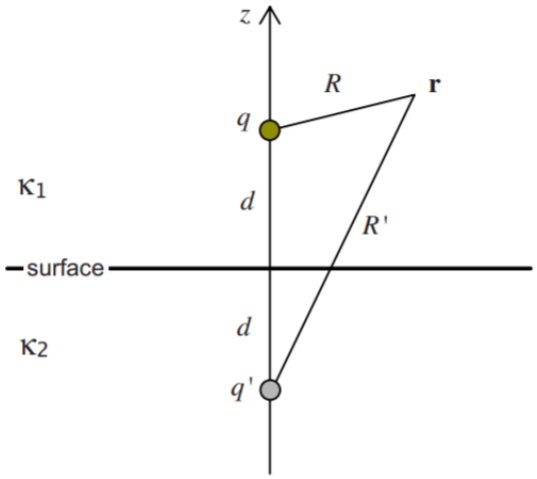

Figure 1: Method of Images

Since such a problem would introduce complicated interface conditions, it is often a useful tool to apply the method of images. The method of images states that if we have a physical particle q generating some potential in a medium with thermal conductivity κ_1 that has a neighboring medium of a different thermal conductivity κ_2, then we can effectively remove the interface and instead insert some image charge q', which is essentially a reflection of q. Rather than accounting for the boundary, we can instead simply sum the potentials of the physical and image charges to form the temperature profile.

For this interface problem, Baffou solves Green's functions as

$$G(\mathbf{r}, \mathbf{r}_i) = \frac{1}{4\pi\kappa_1}[\frac{1}{R} + (\frac{\kappa_2 - \kappa_1}{\kappa_2 + \kappa_1})\frac{1}{R'}] \tag{14}$$

for $z \geq 0$
and

$$G(\mathbf{r}, \mathbf{r}_i) = \frac{1}{4\pi\kappa_2}\frac{1}{R}(\frac{2\kappa_2}{\kappa_2 + \kappa_1}) \tag{15}$$

for $z \leq 0$
and

$$R = \sqrt{(x - x_i)^2 + (y - y_i)^2 + (z - d)^2} \tag{16}$$

$$R' = \sqrt{(x - x_i)^2 + (y - y_i)^2 + (z + d)^2} \tag{17}$$

3.3 Experimental Factors

Baffou also mentions experimental factors/phenomenon that we don't take into account into our calculations.

The first of these factors relates to thermal fields of single nanoparticles as in **3.1**. Baffou says that it is experimentally shown that thermal resistance on the surface of these nanoparticles don't effect the overall temperature profile, but it does effect the heat power of the nanoparticle.

Secondly, he mentions that when we have an interface of two mediums with different thermal conductivity as in **3.2**, thermo-induced fluid convection can occur. This is similar to the Marangoni effect where mass disperses away from regions of low to high surface tension.

4 Simulations

Displayed below are temperature profiles of 1D nanoparticle chains in different medium configurations. There are 10 particles per photo, and the particles are gold spheres with 15nm in diameter and 2nm seperation between each sphere. We see that images a and b correspond to nanoparticles submerged in homogeneous isotropic materials as we saw in **3.1**. Whereas images c,d,e,and f correspond the method of image problems in **3.2**.

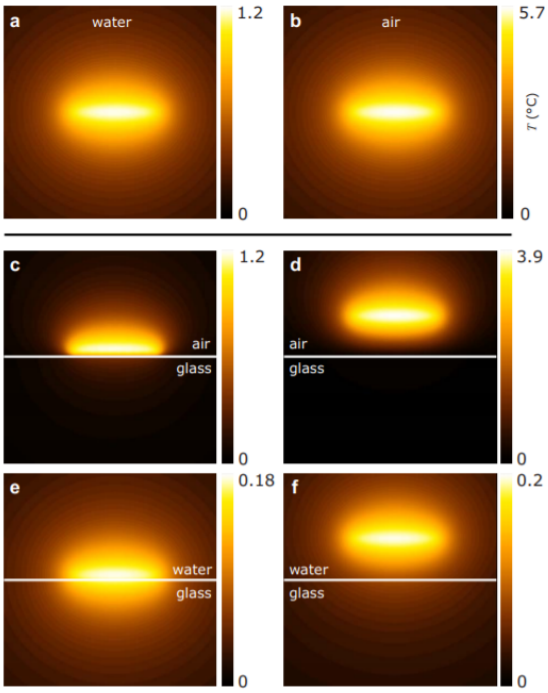

Figure 2: Temperature Profiles

Baffou concludes that the trend here is "the higher the thermal conductivity, the lower the temperature of the structure."

5 Conclusion

Thus far, we've learned how to calculate the thermal field of a single nanoparticle and for a chain of nanoparticles in different surrounding media. The fact that we found $\nabla^2 T(\mathbf{r}) = 0$ for temperature fields reveals the intimate connection to the several methods and results prevalent in electrostatics. For instance, (10) closely resembles the electric potential of a point charge. And, we even make use of the method of images in **3.2**, which is also a method for solving for the electric potential in electrostatics. We also derived the heat power Q emitted by each nanoparticle and the temperature profile in terms of Green's functions in (12) and (13). These equations are the generalized case of the Thermoplasmonics problem, and graphical results of the 1d chain in different media can be seen in Figure 2.

References

[1] Guillaume Baffou, et al.,"Thermoplasmonics modeling: A Green's function approach"

`https://link.aps.org/doi/10.1103/PhysRevB.82.165424`