Letter

Theoretical Analysis of the Emissivity of a Plane Source with Carbon Nanotubes Array by Means of Radiative Heat Transfer

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ABSTRACT

By using the series solution of the effective emissivity in a semi-infinite cylindrical cavity with respect to a wall reflectivity shown in our previous literature, it can be analyzed theoretically that normally directed emission of the cavity from its aperture to a disk-type receiver holding a centerline in common with. Applying the results of this analysis, it can be evaluated that the hemispherical emissivity of a plane source with nano-sized cavities or tubes array that is consist of high-emissive material, such as carbon nanotubes. In some experiments, as high-density nanotubes are used, the represented single cavity is available; however, it cannot predict the top data by fabricating low-density nanotubes but can predict, considering the horizontal interreflection of fluxes penetrating the cavity's wall.

KEYWORDS: radiometry, cylindrical cavity, emissivity, radiative heat transfer, series method, carbon nanotubes

1. Background

As an ideal blackness absorber, or a blackbody radiator, vertically aligned carbon nanotubes (CNT) array has been investigated. One of the prospects is to aim at ultimate absorbent on the visible-light region of the spectrum\(^1\), the other is to realize the flatness of the spectral emissivity over the visible-light and infrared regions of the spectrum, nevertheless that of the flat surface of a bulk carbon- graphite is descended over 10\(\text{µm}^2\)\(^3\).

Theoretical backgrounds of these developments are mainly owing to electromagnetic reflection and refraction. Namely, the absorptivity is often estimated through the absorbent coefficient in connection with the refractive index on electromagnetism\(^4\).

Generally, the reflective and refractive Fresnel coefficients are dependent upon attributes of the incident, such as polarization, monochromatic, and coherency. For experimental apparatus however, it is often difficult to get their information sufficiently for exact evaluation of the absorption.

Therefore, theoretical researches are often confined to be qualitative as including some a priori supposition. For example, the amounts of reflective flux must be a simple average of s- and p- polarized ones in most tutorial reviews and books.

2. Theory

In our research, we have alternative principle to predict the absorptive characteristics, radiative heat transfer. According to Kirchhof’s law, absorptivity is equal to emissivity that can be self-containedly evaluated by calculating the thermal fluxes spontaneously emitting and multi-reflecting through the spacing among mutually faced surfaces of the enclosures, being free from any conditions of the incident flux which is necessary for estimation of absorptivity. For simplicity in our research, any surface of the system is perfectly diffusive.

Provided that the interreflection is a pivotal process for the CNT array to have high emissivity, we may introduce a circular cavity model to the spacing in an array of nanotubes shown in Figure 1.

![Figure 1 Schematic geometry of the CNT array](image)

Supposing the horizontal uniformity of the vertically aligned nanotubes array, the cavity spacing is seen to be rotational symmetric in its cross section. Therefore, the represented cavity model for the spacing in the CNT array should be a long circular cylinder. The sizes of the represented cavity are characterized the statistical average of the arrangement of the nanotubes in the array. Vertically, the average length of the nanotubes is simply to be the cavity length. On the other hand, horizontally, the cavity's diameter should be equal to the statistical average of the cross sections of circular spacing surrounded by
Table 1  The sizes of the CNT array seen in the references:

<table>
<thead>
<tr>
<th>References</th>
<th>a (um)</th>
<th>d (um)</th>
<th>a-d</th>
<th>l (um)</th>
<th>l/(a-d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>40-60</td>
<td>8-10</td>
<td>30-50</td>
<td>10-800</td>
<td>&gt; 172</td>
</tr>
<tr>
<td>(2)</td>
<td>d=2d</td>
<td>500+</td>
<td>0-10</td>
<td>0-200</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>(3)</td>
<td>15[um]</td>
<td>2[um]</td>
<td>1[um]</td>
<td>2-50[um]</td>
<td>&gt; 166</td>
</tr>
</tbody>
</table>

*Average values

neighboring nanotubes, as their arrangement is sufficiently uniform. The results are shown in Table 1.

It should be noted that the substantial parameter to the cavity's configuration on this analysis is only the aspect ratio of the cavity because of being free from any unit length such as wavelength for the logic of the radiative transfer. Also it is noted that we should sort out the case of low-density CNT as reference (1) from that of high-density CNT as reference (2) and (3).

Let us consider the influence of the bottom of the represented cavity. The cavity bottom is a metallic substrate of the CNT array, whose emissivity is rather low however; 0.2 and so on, we can adopt a bottomless long cavity, or a semi-infinite cylindrical cavity to, the CNT cavity model for all samples shown in the table, because of our examination in Appendix 3.

3. Approximating the apparent wall of the cavity

Both on a multi wall nanotubes array and on a single wall one, it may be regarded as the continuous wall of the cavity with a slit-like spacing parallel to the vertical line that the apparent side of a cylindrical spacing surrounded by the nanotubes.

For the case of high-density CNT, the effect of the slit-like spacing is to be negligible. That is, the cavity may have a simple continuous graphite wall. As the typical value of the graphite's emissivity is 0.85 ~ 0.9 at room temperature, the hemispherical emissivity is derived to be about 0.96 ~ 0.97 by using the 2nd order approximation with respect to a wall reflectivity of Appendix 1. Other results are shown in Table 2. It is remarked that the true hemispherical emissivity should be fixed between the 2nd order approximated amount and its inferior bound mentioned in Appendix 2, and that numerical data are shown to the decimal places whence the deviations are obvious respectively in the table, also in the following.

Table 2  The 2nd order approximated hemispherical emissivity of a semi-infinite cylindrical cavity and its inferior bound by using Appendix 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Wall emissivity</th>
<th>0.8000</th>
<th>0.8000</th>
<th>0.8000</th>
<th>0.90000</th>
<th>0.90000</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd order</td>
<td>0.9166</td>
<td>0.9167</td>
<td>0.9750</td>
<td>0.997613</td>
<td>0.99762</td>
</tr>
<tr>
<td>Inferior bound</td>
<td>0.9576</td>
<td>0.9677</td>
<td>0.9729</td>
<td>0.997612</td>
<td>0.99762</td>
</tr>
</tbody>
</table>

On the other hand, for the case of low-density CNT, the permeation through the slit on the cavity's wall cannot be negligible any longer. Let us consider where the permeate flux has gone. If the CNT array is horizontally infinite, the permeate flux will meet the wall of a nanotube somewhere, be absorbed, and re-emitted on it. Suppose that isothermal equilibrium has been kept horizontally in the CNT array as 2-dimensional system, the slit spacing on the cavity's wall must act the aperture of an ideal blackbody. Hence the hemispherical emissivity at the slit spacing on the cavity's wall may be equal to unit.

After all, the apparent wall emissivity of the cavity for the low-density CNT array is to be derived on the bold supposition that the occupied area-ratio by the slit on the wall is equal to that by the occupied area of the cavity spacing on the cross section of the CNT array, as follows:

$$\varepsilon = \varepsilon_0 \delta^2 + (1 - \delta^2), \delta = 0.5\pi (d/a).$$

(1)

$\varepsilon$ denotes the apparent wall emissivity “boosted” by the horizontal emission leaked from the slit on the wall.

4. Results and discussions

In Table 3, the results of the 2nd order calculation taken account of equation (1) are shown to discuss the experimental results of references (1)-(3).

Table 3  The 2nd order approximated hemispherical emissivity of a semi-infinite cylindrical cavity with the aid of supposition (1): $\varepsilon_0 = 0.85$.

<table>
<thead>
<tr>
<th>d/a</th>
<th>0.13</th>
<th>0.18</th>
<th>0.275</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>0.997006</td>
<td>0.996163</td>
<td>0.991090</td>
<td>0.970548</td>
<td>0.882190</td>
</tr>
<tr>
<td>2nd order</td>
<td>0.994502</td>
<td>0.990092</td>
<td>0.997674</td>
<td>0.992898</td>
<td>0.970295</td>
</tr>
</tbody>
</table>

First, let us discuss the influence of slit spacing on the cavity's wall. The experimental achievement of reference (1), three figures of 9, is endorsed theoretically on the radiative heat transfer as seen in the former two cases of that $d/a$ is from 0.13 to 0.275 in Table 3.

Additionally, let us discuss the relationship between the hemispherical emissivity and 1-dimensional occupied ratio of the CNT array, $d/a$ for the low-density CNT array. Fitting the above numerical data graphically, we may derive a following formula:

$$\eta_{hemispherical} = I \cdot 10^{-\delta} (60d/a)^2.$$

(2)
According to formula (2), in order to overcome four figures of 9, \( da \) should be less than \( 6 \times 10^{-10} \), or 0.053. Besides, formula (2) denotes that the hemispherical emissivity is depend upon a square of the occupied ratio, qualitatively in accordance with the result of calculating absorbitivity of aligned nanotubes system by using the Maxwell-Garnett formula on classical electromagnetism.

Second, the experimental results in reference (2), that the averaged one is 0.996, are thought to be correspondent to the case of low- or medium-density CNT, \( da \) is about 0.5, which are accordance with the calculation at least in visible-light region of the spectrum.

Third, nevertheless the experiment of reference (3) corresponds to the case of low-density CNT array, the emissivity is rather correspondent to the case of high-density CNT array. Alignment of nanotubes of the CNT array have been said not to be always perfect, namely, to have a little tilt statistically. Because of its randomness, the effective occupied ratio is thought to be rather large.

Last, let us discuss the spectral properties of the hemispherical emissivity. We can derive the relationship between the descending deviation of the wall emissivity and that of the hemispherical emissivity of the cavity with the aid of Appendix 1, as follows:

\[
\Delta \eta_{\text{hemispherical}} = (\pi/2) - (4/3) + 8(1 - e) I_2 \Delta \omega
\]  

where \( \Delta \) denotes the deviation between a maximum spectral amount and minimum one descending over the visible-light and infrared regions of the spectrum.

If the average spectral emissivity of the cavity's wall such as graphite is 0.89, decreasing the hemispherical emissivity is suppressed to be 30% or slightly less by fabricating cylindrical cavity array however, the calculation according to equation (3) is rather insufficient to predict the flatness of spectral emissivity of the CNT array as seen in reference (3).

5. Conclusions

Theoretical analysis of the thermal emissive characteristics of CNT array based on the radiative heat transfer is done. In some cases, as high-density CNT, a semi-infinite cylindrical cavity with carbonaceous continuous sidewall whose surface is perfectly diffusive is available; however, it has found insufficient for the case of low-density CNT. On condition that the sidewall is penetrable for that case, considering the horizontal interference by the penetrating fluxes, realization of the top data in reference (1) may be proved theoretically with the dependence of the emissivity upon the occupied area-ratio of aligned nanotubes, that is qualitatively accordance with the theoretical results by classical electromagnetism.

It should be remarked that those results have not been excluded to reckon a specular or a non-classical optics in the emissive process.

Acknowledgement

The author would like to thank H. Minato for his discussion to thermal radiation sources and detectors, and to thank K. Mizuno and J. Ishii belonging to NIMS of AIST respectively for their introducing to the reference (3) on CNT forest fabricated by water-assisted chemical vapor deposition. The author also would like to thank N. Tanigaki and M. Watanabe for their encouragement.

References

Appendix 1. Derivation of the 2nd order approximated hemispherical emissivity of a semi-infinite circular cylindrical cavity with respect to reflectivity

Main purpose of the train of our researches is to get analytical formulae that are not only convenient but also based on a rigorous deduction, and may give results reliable to some degree for practical situations treated numerically by senior researchers.

In our research, we adopt the situation same as reference (6) except using a semi-infinite long cavity. Results are presented for a finite sized disk-type receiver of the same radius as the cavity opening, holding the same centerline as that of the cavity and aligned normally. Rigorous formulation is carried out for a general case that has finite distance of the receiver from the cavity opening. It cannot be formulated analytically because the convolution integral of the calculated effective emissivity and of the known angle factor to a circular element in the interior wall of the cavity from a surface of the receiver is elliptic even in the 1st order with respect to a wall reflectivity however, asymptotical formulae in the 2nd order can be derived for some limit cases. One is that the receiver is joined to the cavity opening, the other is that the receiver is far from the opening. It should be remarked that the limit formula for the former case is equated with a hemispherical emissivity of the cavity. On the other hand, the asymptotic one for the latter case is corresponded to a normal emissivity.

A schematic geometry is in accordance with the upper portion of the figure 1 drawn in reference (6). A semi-infinite long circular cylindrical cavity of radius $R$, whose wall is diffusive, is at the right and faced to the left. A finite diffusive disk of radius $R$, by which the radiant flux out of the cavity opening is sensed, is faced to the cavity at the left. Its normal is aligned with the cavity's principal axis. Along the principal axis of the semi-infinite cavity, the amount of a radiant flux leaving the cavity's interior wall per unit area varies. Recently, we have shown the variety of the normalized radiant flux, or the effective emissivity, can be formulated rigorously with respect to a wall reflectivity $\rho_1$ that has sufficient accuracies in the 2nd order as $\rho_0 < 0.2$.

On the above mention, we derive the radiant flux arriving at the receiver per unit area from a wall of the cavity denoted by $H_1$ as follows:

$$H_1(x_0) = \int_{\mathbb{R}} \phi(x-x_0) K_1(x) dx,$$  \hspace{1cm} \text{(A1)}

where $K_1(x)$ is angle factor from the surface of the cavity's interior wall to that of the finite diffusive disk out of the cavity opening:

$$K_1(x) = (2x^2 + 1)(x^2 + 1)^{1/2} - 2x.$$  \hspace{1cm} \text{(A2)}

$\phi(x)$ is the effective emissivity at the surface of the interior wall of the cavity. For the case of a semi-infinite cylindrical cavity, it can be formulated as a series solution:

$$\phi(x) = 1 + \rho_1 \rho_2 + \rho_2^2 \rho_3 + \ldots + \rho^{n-1} \rho^n + \ldots.$$  \hspace{1cm} \text{(A3)}

In equation (A3), the coefficient $\rho_n(x)$ is defined recursively as follows:

$$\rho_1 = x - (2x^2 + 1)(2(x^2 + 1)^{1/2})^{-1},$$  \hspace{1cm} \text{(A4)}

$$\rho_{n+1}(x_0) = \int_{\mathbb{R}} \rho_n(x) K'(x_0, x) dx,$$  \hspace{1cm} \text{(A5)}

where the cavity's angle factor is

$$K'(x_0, x) = K'(x_0-x) = 1 - |x-x_0| \left[ 2(x-x_0)^2 + 3 \right] \left[ 2(x-x_0)^2 + 1 \right]^{-1}.$$  \hspace{1cm} \text{(A6)}

Comparing equation (A2) with equation (A4), we find that $K(x)$ is equal to $-(1/2) \rho_1$. Putting solution (A3) into equation (A1), we can derive:

$$H_1(x_0) = -4 \int_{\mathbb{R}} \rho_1(x) dx - \sum_{n=1}^{\infty} 4 \int_{\mathbb{R}} \rho_n(x) \rho_1(x) dx.$$  \hspace{1cm} \text{(A7)}

On the other hand, the radiant flux arriving at the receiver per unit area from an ideal blackbody is as $H_b$ following:

$$H_b(x_0) = -4 \int_{\mathbb{R}} \rho_1(x) dx.$$  \hspace{1cm} \text{(A8)}

Therefore, the normalized flux at the receiver from the cavity source is derived from the definition shown in reference (6):

$$\eta_{n=a}(x_0) = \frac{H_1(x_0)}{H_b(x_0)} = 1 + \sum_{n=1}^{\infty} \rho_1 \rho_2 \rho_3 \ldots \rho_n(x-x_0) \rho_1(x) dx,$$  \hspace{1cm} \text{(A9)}

As already mentioned, the normalized flux at the receiver (A9) should be equivalent to the hemispherical emissivity of the cavity at the limit that the receiver is joined to the cavity opening, hence $\eta_{\text{hemispherical}} = \eta_{n=a}(x_0 = 0)$.

Besides, in our previous research (5), we also pointed out that only the 1st order's coefficient of the series solution of the effective emissivity, $\rho_1$, could be formulated analytically, but the 2nd order's one could be evaluated keeping sufficient accuracy by adopting the approximation using a logistic function.

After all, the 2nd order approximated amount of the hemispherical emissivity can be equated to:
\eta_{n=2, \text{hemispherical}} = 1 - \rho \left( (\pi/2) - (4/3) \right) + \rho^2 I_2 \int_{\phi=0}^\pi \rho_1 (x) \, dx,
I_2 = \int_{u=-\infty}^{\infty} \frac{1}{\sqrt{1 - (15\pi/64 - 1/4) u}}
+ (15\pi/32 - 11/8) u^2 \exp \left\{ -2u \right\} \left[ u - (u^2 + 1)^{1/2} \right]
+ (2u^2 + 1)^{1/2} \right\} \, dx
\int_{\phi=0}^\pi \rho_1 (x) \, dx = -1/4. \quad (A10)

HIL (u) is Hill's logistic function. We substitute 3 for q to be more accurate, because the Hill's function is integrand in this research.

First integral of I_2 in (A10) can be formulated analytically through rather verbose but irresistible calculation; second integral, however, can be estimated only through some numerical quadrature because of elliptic integral. In this research we use the quadrature package of IMSL. Hence I_2 is evaluated as follows:

\begin{align*}
I_2 &= 30\pi/256 - 17/64 \left\{ \mathbf{H}_0(2) - N_0(2) \right\}
- (30\pi/256 - 13/64) \left\{ \mathbf{H}_0(2) - N_0(2) \right\}
+ \text{Elliptic} \left( \text{HIL} (u) \right)
= 0.031116... + \text{Elliptic} \left( \text{HIL} (u) \right) = 0.031148...
\text{as} \text{Elliptic} \left( \text{HIL} (u) \right) \approx 3.1703 \times 10^{-6}, \quad (A11)
\end{align*}

where \mathbf{H}_0 (u) and N_0 (u) are 0th order Struve function and Neumann function, respectively.

Appendix 2. Theoretical uncertainty to the hemispherical emissivity of a semi-infinite cylindrical cavity
From another viewpoint, it should be noted that the 2nd order formula (A10) is a superior bound for the true amount of a hemispherical emissivity of the cavity, which is a rigorous series solution of the receiver-joined normal emissivity \eta_{n=2} (x_0 = 0), as all coefficients \rho_1 (x) are non-positive with respect to overall \rho; hence:

\int_{\phi=0}^\pi \rho_1 (x_0 - x) \rho_1 (x) \, dx \int_{\phi=0}^\pi \rho_1 (x) \, dx < 0. \quad (A12)

On the other hand, as also shown in reference (5), the series solution of the effective emissivity \phi has an inferior bound:

\phi (x_0) > 1 + \rho_1 + \rho^2 \rho_2 - \rho^3 \varepsilon. \quad (A13)

Putting (A13) into (A11) with the area of the parity of each integrand, we have an inequality as follows:

\eta_{n=2} (x_0 = 0) > \eta_{n=2} (x_0 = 0) - \rho^3 \varepsilon. \quad (A14)

Hence, the right-hand term denotes the inferior bound of true amount of the hemispherical emissivity of the cavity.
After all, the theoretical uncertainty by truncation to the hemispherical emissivity U (\eta_{n=2} (x_0 = 0)) is derived:

\begin{align*}
2U(\eta_{n=2} (x_0 = 0)) &< \rho^3 \varepsilon. \quad (A15)
\end{align*}

Hence we take the reliance of at least two significant figures to the case of not only low- but also high-density CNT, as the reflectivity of the graphite is at most 0.2 at room temperature.

Appendix 3. Fitness of the hemispherical emissivity of a bottomless semi-infinite long cylindrical cavity to a finite long cylindrical cavity on a diffusive substrate
It seems that the finite long cylinder with a flat diffusive bottom is more suitable for the represented cavity model to the CNT thermal plate source with a metal substrate however, it cannot be evaluated with analytic method but with some numerical method.

In our investigation, net-radiation method, or radiation network method, is adopted, because;

(1) It does not need any initial conditions;
(2) Its result is deterministic, not be dependent on some randomness such as Monte Carlo method;
(3) Therefore, it can be clarified deductively to estimate the accuracy of results.

Its procedure is as follows:

(1) The sidewall and the bottom of the cylinder are divided into annular disks and rings respectively.
(2) Provided that the front of the disks are ideal black, angle factors of them are fixed.
(3) Taking account of the summation's law and the reciprocity's law respectively, the angle factors to the real surface elements of side of disks and that rings of bottom can be evaluated.
(4) The effective emissivities on the real surface elements can be derived as the solution of a simultaneous arithmetic equation whose coefficient consists of the angle factors.
(5) In order to solve the equation, Gauss-Jordan's method is adopted, which does not have an iteration process where some a priori initial condition is necessary.
(6) Optionally, a posteriori error estimate improved for the verified numerical calculation based on Banach's contraction mapping principal may be introduced.

It should be remarked that this method could be applied only to rotationally symmetric cavities, for which the position of a surface of its interior wall is a function only with respect to the coordinates of its principal axis.

Numerical results are shown in Table A to demonstrate little influence of the bottom to the hemispherical emissivity for a medium long isothermal cylinder.
Table A  Hemispherical emissivity of a long isothermal cylinder with a bottom: Aspect ratio 20, Meshnumber 400(side) and 10(bottom), respectively.

<table>
<thead>
<tr>
<th>Emissivity</th>
<th>0.010</th>
<th>0.000</th>
<th>0.200+</th>
<th>0.9000</th>
<th>0.9900</th>
<th>(semi-infinite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bottom</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2nd order approx.</td>
</tr>
<tr>
<td>0.9979</td>
<td>0.999500</td>
<td>0.999501</td>
<td>0.999501</td>
<td>0.999501</td>
<td>0.999501</td>
<td>0.999502</td>
</tr>
<tr>
<td>0.9000</td>
<td>-</td>
<td>-</td>
<td>0.975006</td>
<td>0.975006</td>
<td>-</td>
<td>0.975008</td>
</tr>
<tr>
<td>0.8100</td>
<td>-</td>
<td>-</td>
<td>0.950337</td>
<td>0.950337</td>
<td>-</td>
<td>0.950384</td>
</tr>
</tbody>
</table>

* Typical value of metallic substrate.

Besides, the numerical values of the hemispherical emissivity are slightly less than the 2nd order approximated ones for a semi-infinite cylinder, obeying the result shown in Appendix 2.