A Modified Maxwell Garnett Model: Hysteresis in phase change materials

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Abstract. The dielectric properties of materials undergoing phase transitions are key to a number of modern and developing technologies, particularly when hysteresis is demonstrated in the response. This paper presents a modified Maxwell Garnett model for analysing electromagnetic hysteresis, using an asymmetric effective medium approximation to describe intermediate states in the phase change, establishing a link between effective medium and hysteresis analysis. The model has few input parameters and provides a phenomenological approach to describing electromagnetic hysteresis in various phase change materials.

1. Introduction
Phase change materials such as chalcogenide glasses switch between two phases with greatly different properties, with critical technological applications including rewritable optical discs and non-volatile electronic memory [1,2]. The control of intermediate states in these materials is also of interest in, for example dynamically tuneable antennae, beam steering and multi-level memory. Transitions between phases involves complicated atomic and electronic changes, a topic of significant study in condensed matter physics and material science [3-5]. The use of intermediate states also has a range of emerging potential applications [6-9] and understanding of the mechanisms and dynamics of phases transitions is therefore of great importance.

Hysteresis is often evident in phase change materials: for thermally triggered phase changes, this signifies different properties upon heating and cooling at the same temperature. In memory applications, large and controllable hysteresis is integral to function [10]. Some analytical models have been developed for analysing hysteresis [11,12]. The choice of model, often with modification, depends on the specific material and/or properties under study. The lack of a comprehensive and accurate single modelling approach signifies that, while these models are perceived as powerful analytical tools, their usefulness for design and in technological applications is limited.

This paper presents an analytical model for describing electromagnetic hysteresis, based on the Maxwell Garnett effective medium approximation. The analysis presented in this paper is based on vanadium dioxide (VO$_2$) a material which exhibits a hysteretic insulator-metal transition close to 68°C. At low temperatures, VO$_2$ has an infrared complex permittivity of a typical lossy dielectric and at high temperatures, the complex permittivity shows characteristics of a metal, with negative real and large imaginary component. In intermediate states during the phase transition, these two phases exist simultaneously in complicated nanostructures, the analysis of which is generally performed using effective medium models such as the Maxwell Garnett effective medium model [5]. This type of model is typically considered to be inapplicable to scenarios where hysteresis is prominently observed.
The model presented in this paper uses an asymmetric effective medium approximation to describe intermediate states in the phase change, establishing a link between effective medium and hysteresis analysis. The model is simple, requires very few input parameters, and provides a phenomenological approach to describing electromagnetic hysteresis in various phase change materials.

2. Modified Maxwell Garnett effective medium model
As an effective medium theory, the Maxwell Garnett model is frequently used to predict the effective complex permittivity $\varepsilon_{\text{eff}}$ of a composite formed by two constituents: the host material (permittivity $\varepsilon_{\text{host}}$) and the inclusion which consists of many randomly distributed particles with permittivity $\varepsilon_i$. The effective complex permittivity of the material is given by:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{host}} \left( \frac{\varepsilon_i(1 + 2\phi) + \varepsilon_{\text{host}}(2 - 2\phi)}{\varepsilon_i(1 - \phi) + \varepsilon_{\text{host}}(2 + \phi)} \right)$$

where $\phi$ is the normalised volume fraction (or filling factor) of constituent 1 relative to the total volume (ranging from 0 to 1). This equation describes the additional contribution to the polarisation of the material arising as a result of Maxwell-Wagner Interfacial polarisation of the two surfaces on either side of the particle, which results in the particle exhibiting an induced dipole moment. This polarisation is defined by the existence of “particles”, with the variation with frequency and volume fraction related to both constituents but scaled only by the host.

The equation is therefore asymmetric with respect to the two constituents. For complicated distributions of constituents, it is often subjective whether a constituent is the inclusion or the host. As can be seen from the equation, this will produce a different effective permittivity depending on the choices made, an effect which has been viewed as a flaw of the model [13].

The modified Maxwell-Garnett approach uses this inherent asymmetry to model hysteretic phase change. During heating, the VO$_2$ phase transition is generally considered to occur via the nucleation and growth of nanoscale metallic “particles” inside a host consisting of the low temperature dielectric phase [3]. As the temperature increases, the particles expand and coalesce into a continuous metallic film. The reverse cooling transition is generally considered to occur in reverse with the metallic particles shrinking until a continuous dielectric remains.
The model presented here [14] is based on the concept that irreversibility in the transition process arises from a change in host versus inclusion depending on the direction of the temperature change i.e. whether the material is heating or cooling. An illustration of the concept is shown in figure 1, with metallic particles forming and growing inside the dielectric host during heating. During cooling, dielectric particles form and grow inside the metallic host. The modified Maxwell Garnett model is therefore described by a pair of equations for the effective permittivity while heating and the effective permittivity while cooling:

\[
\varepsilon_{\text{eff,heating}} = \varepsilon_{\text{dielectric}} \frac{(1 + 2\phi)\varepsilon_{\text{metal}} + 2(1 - \phi)\varepsilon_{\text{dielectric}}}{(1 - \phi)\varepsilon_{\text{metal}} + (2 + \phi)\varepsilon_{\text{dielectric}}}
\]

\[
\varepsilon_{\text{eff,cooling}} = \varepsilon_{\text{metal}} \frac{2\phi\varepsilon_{\text{metal}} + (3 - 2\phi)\varepsilon_{\text{dielectric}}}{(3 - \phi)\varepsilon_{\text{metal}} + \phi\varepsilon_{\text{dielectric}}}
\]

Note that this model uses \( \phi \) to denote the volume fraction of one constituent phase: in this case metallic was chosen, so that both equations describe a pure dielectric phase at \( \phi = 0 \) and a pure metallic phase at \( \phi = 1 \). At other values of \( \phi \), \( \varepsilon_{\text{eff,heating}} \neq \varepsilon_{\text{eff,cooling}} \) giving an integral outcome of hysteresis.

3. Results and Discussion

3.1. Analysis of complex permittivity

The effective permittivity during heating and cooling for VO\(_2\) was calculated with the permittivity values in the electromagnetic range of interest for the pure phases taken and extrapolated from experiments (for full details and references, see [14]). From the model, heating and cooling indeed would have very different values over this frequency range, with permittivity in intermediate states during phase transition not confined by the values of the two pure phases, particularly at low frequencies.

Figure 2 shows the calculated effective permittivity during heating (left figures) and cooling (right figures) for VO\(_2\). This is calculated as a range of values of \( \phi \) using the model. The data is plotted as separate real (figure 2(a)) and imaginary (figure 2(b)) parts as a function of frequency in the range of interest, as well as Cole-Cole plots of \( \varepsilon' \) against \( \varepsilon'' \) (figure 2(c)). The individual lines on each figure represent the same volume fraction value as shown in the legend.

Comparison of each pair of figures, (a), (b) and (c) show that, as expected, the curves for the pure phases (\( \phi = 0 \) and \( \phi = 1 \)) are identical, but also that the transition stages are both progressive but very distinctive for the heating and cooling processes.

For the heating case, the change in phase is the transition from a dielectric to metallic. Examining the Cole-Cole plot (figure 2(c)), it can be observed that there is a progressive change in what appears to be a dielectric from the volume fraction value of 0 up to 0.7, followed by a rapid change to the metallic form for a volume fraction of 1. This can be verified by examining figure 2(a) where there is a gradual change in the form of \( \varepsilon' \) up to \( \phi = 0.7 \), which then undergoes rapid change to the form for \( \phi = 1 \).

Contrasting this with the cooling case, where the change in phase is the transition from metallic to dielectric, the Cole-Cole plot demonstrates a gradual change in what appears to be a metal-like behaviour from a volume fraction of 1 down to 0.3, followed by a rapid change to the curve for \( \phi = 0 \). This is confirmed by examination of figure 2(a) which shows a gradual change in \( \varepsilon' \) from negative values to positive, and examination of figure 2(b) which demonstrates gradual change in \( \varepsilon'' \) down to a value \( \phi = 0.3 \), followed by a substantial change in the form of the curve for the value \( \phi = 0 \).

This demonstrates a noticeably different behaviour between the two processes and illustrates the hysteresis inherent in the model.
Figure 2. Complex permittivity of VO$_2$ calculated based on the modified Maxwell Garnett model for pseudo heating (left figures) and pseudo cooling (right figures), shown as (a) the real part of the permittivity, $\varepsilon'$, (b) imaginary part of the permittivity, $\varepsilon''$, and (c) Cole-Cole plots of $\varepsilon''$ against $\varepsilon'$. The individual lines on each figure represent the same volume fraction value as shown in the legend. Comparison of each pair of figures, (a), (b) and (c) show that, as expected, the curves for the pure phases ($\phi = 0$ and $\phi = 1$) are identical, but also that the transition stages are progressive but very distinctive for heating and cooling.
Figure 3. Complex permittivity of VO₂ calculated based on the modified Maxwell Garnett model as a function of volume fraction shown as separate real (left figures) and imaginary (right figures) parts. The data is shown for the heating (solid line) and cooling (dashed line) processes for several frequency points across the analysed range, demonstrating decreasing hysteresis as the frequency increases.
3.2. Analysis of hysteresis: reflectivity

The two extremes of the frequency range analysed correspond to practical IR wavelengths with applications in communications, imaging and sensing. It is clear from figure 2 that the change in permittivity with volume fraction and the form of the hysteresis is different.

Figure 3 shows a more detailed analysis of the change in complex permittivity for four values of frequency(wavelength) across the calculated spectrum range. There are several shared characteristics: first, that both the real and imaginary part of the permittivity show hysteresis and second, that at large values of ϕ, the real part is negative, and the material effectively behaves as a metal. Both characteristics agree with common understandings of the behaviour of the material. In addition, the degree of hysteresis decreases as the frequency increases.

The modified model also predicts characteristics that are counter-intuitive. First, a typical hysteresis loop possesses two-fold rotational symmetry. By contrast, the individual process curves are asymmetric and where hysteresis is strong, distinctly so. Indeed, the imaginary part at 24THz shows a crossover within the loop. Secondly, a typical hysteresis loop shows the biggest contrast in its output if the input is at the centre of the loop. Again, at 24THz, the biggest difference between heating and cooling is at ϕ = 1, close to one end of the loop and this changes distinctly with frequency. Finally, in a typical hysteresis loop, the output changes monotonically with the input. This general observation is obviously invalid for all curves shown in figure 3.

4. Conclusions

An analytical model for electromagnetic hysteresis in phase change materials has been presented, based on modification of the Maxwell-Garnett effective medium model and using the inherent asymmetry in the conventional Maxwell Garnett approximation to establish a method for the analysis of hysteresis. The permittivity of VO₂ thin films was numerically calculated to demonstrate the use of the model. The model is simple, only requiring the volume fraction and the experimental permittivity of each pure phase, providing a phenomenological approach to interpreting hysteresis and intermediate states of transition between two solid phases of various materials.

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