# THEORY

Equation 1 describes Beer-Lambert’s law8 where α is the (decadic) absorption coefficient (usually given in cm-1), *I* and *I0* are the intensities after and before absorption respectively and *d* is the path length.

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|  | Equation 1 |

It is common, especially in the chemistry community, when reporting infrared spectra to use a decadic molar absorption coefficient (), which has units of L.mol-1cm-1. The relationship between the absorption coefficient and the molar absorption coefficient8 is;

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|  | Equation 2 |

where *C* is the concentration of the absorbing species.

## Molecular Approach to Absorption Intensity

For molecules the transition intensity *Ik* of the kth mode (calculated from the change in dipole moment along the mode displacement) can be converted to an integrated molar absorption coefficient, *Ak*, which can then be more readily compared with experiment. The theory for this is described by Wilson, Decius and Cross9 and results in expressions such as the two equations below (Equation 3). The first expression shows the relationship between the integrated molar absorption coefficient and the transition intensity and uses the number of molecules per unit volume (*N*), the velocity of light (*c*) and the degeneracy of the mode (*gk*). The second expression shows the appropriate conversion factors if the units for the integrated molar absorption coefficient are L.mol‑1cm‑2 (1 L.mol-1cm-2 = 0.01 km.mol-1) and the units for the transition intensity are D2.Å-2.amu-1, where D represents the Debye unit of dipole moment and amu is an atomic mass unit. The factor loge10 arises due to the choice of a decadic Beer’s law.

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|  | Equation 3 |

The derivation of the above expressions assumes that the rotational levels are not quantised and that the vibrational levels are thermally occupied according to a Boltzmann distribution. In order to use the calculated molecular intensities to predict a spectrum it is usual to assume9 that each transition is associated with a Lorentzian line shape with a full width at half maximum (FWHM) of *σk*. It is common, when reporting comparison between theoretical and experimental spectra, to assume that the line widths are the same for all modes.10,11 Recent work on terahertz absorption in crystalline pentaerythritol tetranitrate (PETN) using molecular dynamics calculations12 in combination with the direct calculation of the cubic anharmonic couplings of the normal modes13 has shown that the FWHM of the intense absorptions may vary between 10 and 25 cm-1. Assuming a Lorentzian line shape, the molar absorption coefficient for the kth mode at wavenumber, , can be written as a function of frequency or wavenumber ();

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|  | Equation 4 |

The maximum height of the Lorentzian, clearly depends upon the value of *σk*. As can be seen in Equation 5, the choice of normalisation for the Lorentzian means that integration of the molar absorption coefficient over wavenumber returns the integrated molar absorption coefficient and a sum over all the bands provides the total molar absorption coefficient as a function of wavenumber, calculated from the intensities of each band. The final expression in Equation 5 shows the relationship between the absorption and the molar absorption coefficients. *C* is the concentration usually expressed in mol/L.

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|  | Equation 5 |

A comment should be made about the various units which can be used for these quantities. A common unit for the transition intensity is (D/Å)2/amu, another is km/mol. However, it should be pointed out that strictly speaking the latter unit refers to the integrated molar absorption coefficient as defined above in Equation 3 and therefore relies on the assumptions made in its derivation ( 1 (D/Å)2/amu is equivalent to 42.256 km/mol ).

## Solid State Approach to Absorption Intensity

The optical properties of a solid are determined by its complex, frequency dependent relative permittivity () and in particular the imaginary refractive index component tensor, , of the complex refractive index, where;

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|  | Equation 6 |

The intensity of absorption is given by the effect of the imaginary component of the refractive index on the incident light assuming an isotropic material10;

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|  | Equation 7 |

Comparison with the definition of the absorption coefficient from Beer-Lambert’s law (Equation 1) gives;

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|  | Equation 8 |

Since the refractive index is dimensionless, the absorption coefficient (*αsol*) is specified in cm-1. The superscripts ‘sol,’ for solid, and ‘mol,’ for molecular, are used here to distinguish between the two methods of calculating the absorption (α) and molar absorption coefficients (a). In the calculation of the imaginary component of the refractive index it is necessary to choose the solution which gives a positive value. This is consistent with the Kramers-Kronig relationship between the real and imaginary components.15

In order to calculate the relationship between absorption and molar absorption coefficients it is necessary to know the concentration. For solid state calculations the required unit is; moles of unit cells per litre. One of the drawbacks of this molar absorption coefficient unit is that the number of molecules in a unit cell can change depending on whether a supercell, primitive or non primitive unit cell is being used. A more natural unit would be to use a mole of formula units, or a mole of molecules. In order to aid comparison between such calculations PDielec is able to calculate concentration in both moles of atoms and moles of molecules. However for the rest of this paper Equation 9 will be used, where *V* is the volume of the unit cell, and therefore the concentration *C* is moles of unit cell/litre.

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|  | Equation 9 |

The volume fraction, *f*, of the dielectric material in a supporting matrix of non-absorbing material is included in the expression for the concentration as it will be useful when the theory for mixtures is developed.

For a periodic system the permittivity tensor can be calculated as a sum over Lorentz oscillators, incorporating an imaginary loss component through the damping factor *σk*.16 The frequencies of the oscillators are the transverse optic (TO) phonon frequencies of the system.

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|  | Equation 10a |
|  | Equation 10b |
|  | Equation 10c |
|  | Equation 10d |
|  | Equation 10e |

*V* is the volume of the unit cell, is the dipole oscillator strength tensor for the kth transition, with a TO frequency of *vk* and the optical permittivity tensor, which represents the electronic contribution to the permittivity. The intensity of a transition, *Ik* is given by the trace of the oscillator strength tensor,**.** The damping factor removes any discontinuities at the TO frequencies. Since the oscillator strengths and phonon frequencies can be calculated routinely in solid state quantum mechanical packages, the calculation of the frequency dependent complex permittivity using Equation 10a is straightforward. In some cases, using Equations 10b and 10c, PDielec calculates the oscillator strengths from the Born charge matrix for atom *a,* , and the contribution of atom *a* to the kth phonon mode, .16 As shown in Equation 10d, at the Γ point the kth phonon mode is described by the eigenvector, and eigenvalue, of the mass weighted, dynamical matrix, , which is a 3Nx3N matrix, where N is the number of atoms in the unit cell. The eigenvalues are the squared frequencies of the phonon modes (Equation 10e). The displacement of each atom in the kth mode, is proportional to , where *m*a is the mass of atom *a*. The dynamical matrix has 3N eigenvectors and eigenvalues, of which three should be zero due to translational invariance. If there are any negative eigenvalues the system is unstable to some displacement and therefore not at an energy minimum.

For ionic systems it is common practice in solid state QM and MM programs to include a long wave-length, non-analytic correction to the mass weighted dynamical matrix at the Γ point, which describes the coupling of the longitudinal optic (LO) modes to the induced field resulting from the vibration. This may be written for atoms *s* and *t* and their Cartesian components *α* and *β* as;16

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|  | Equation 11 |

The mass weighting has been incorporated through the mass of the atoms, *M*s and *M*t. The correction depends upon the direction, **,** that the long wave-length limit is approached. Diagonalisation of the corrected matrix gives the squared frequencies of N-1 LO modes and 2N-2 TO modes (Equations 10d and 10e). In some of the examples given below the LO frequencies will be given for comparison with the TO frequencies.

## Effect of Particle Shape on Infrared Absorption

It has long been recognised that, especially for ionic materials, the local field within a crystal and its coupling with the transverse optic phonons has an important effect on the position and intensity of the absorption. Fröhlich17 was one of the first to point out that the frequency of absorption of a small ionic sphere embedded in a low dielectric medium is shifted to lie between the transverse and longitudinal optic frequencies of the material making up the sphere.

In the development of the theory used in PDielec an important assumption is that the particle size of the crystallites in the sample is small compared with the wavelength of light. Using this approach Genzel and Martin18 were able to explain the observed infrared absorption of small spheres of MgO crystallites and the effect of the permittivity of the supporting medium on the spectrum. Studies of the infrared absorption by small particles of α-Fe2O3 using an effective medium theory and an absorption/scattering theory19,20 showed that in order to fit the experimental spectra it was necessary to adjust not only the damping factors in Equation 10a, but also the permittivity of the matrix and the volume fraction of the dielectric medium. The latter was used to account for aggregation effects as the volume fraction increased. It was also shown that effective medium theories were only applicable for particles smaller than the wavelength of light. For larger particles the scattering from the particles becomes increasingly important.

More recently Balan and others in a series of papers20-24 used density functional calculations together with an effective medium theory to calculate the infrared absorption of several minerals incorporating information about the crystallite shape. In an experimental and theoretical study of irradiated kaolinite24 it was shown that exposure to radiation resulted in shifts in the infrared spectrum which could be accounted for by increasing the polarisability of the particles through an increase in the optical permittivity tensor.

The underlying theory adopted by PDielec is based on similar premises to the work described above, namely that the dielectric response of small spherical, ellipsoidal, slab-like or needle-like crystallites randomly distributed in a non-absorbing medium such as PTFE, KBr or Nujol, is the same as that of an effective medium material whose frequency dependent dielectric response can be calculated from the frequency dependent permittivity tensor of the crystal (as calculated by solid state QM or MM calculations), the shape of the crystallites and the permittivity of the non-absorbing medium (taken to be a constant over the frequency range of interest).

The development of the theory reported here closely follows the work of Sihvola25. It will be assumed that the inclusion particles, which may be non-isotropic, ellipsoidal (including spherical, needle-like and plate-like), are randomly orientated in an embedding, non-absorbing medium such as PTFE, KBr or Nujol. It should be emphasized that whilst PDielec can take account of particle shape, particle and matrix permittivity there are many additional aspects of infrared absorption which need to be considered when comparing calculated and experimental results. Most notable of these are; the coupling between phonons and mobile electrons or holes (so called phonon-polariton coupling)26, the scattering which starts to dominate as the particles get larger24 and the agglomeration of particles as the volume fraction increases.

### The polarisability of an isolated particle

Figure 1 shows a schematic of the field and polarisation inside an inclusion with non-isotropic permittivity embedded in a supporting medium with permittivity. The internal field within the inclusion is indicated by , the external, applied field is indicated by and the induced polarisation in the inclusion is shown by .

Figure1_Polarisation_Picture.tif

Figure : Schematic showing the field and polarisation inside an inclusion with non-isotropic permittivity embedded in a supporting medium with permittivity. The internal field within the inclusion is indicated by , the external, applied field is indicated by and the induced polarisation in the inclusion is shown by

The electric field internal to the inclusion gives rise to a polarisation density which is no longer necessarily aligned with the field because the material is non-isotropic. The polarisation density in the inclusion can be expressed as the tensor product of the permittivity contrast between the inclusion and the supporting medium and the (as yet unknown) internal field.

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|  | Equation 12 |

For any ellipsoidal shape (including sphere, slab and needle) with volume *V*, the polarisation density throughout the particle is uniform and integrating over all space gives the field induced dipole moment of the inclusion, .

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|  | Equation 13 |

The dipole and the external field () are related by the polarisability tensor, **.**

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|  | Equation 14 |

Equations 13 and 14, allow the determination of the polarisability, once the field internal to the inclusion has been expressed in terms of the shape of the inclusion and its permittivity. The polarisation within the inclusion gives rise to a depolarisation field (), which depends on the shape of the inclusion through the symmetric and unit trace depolarisation tensor, .

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|  | Equation 15 |

The internal field is the sum of the external field and the depolarisation field.

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|  | Equation 16 |

The depolarisation tensor acts as a projection or screening operator describing the effect of the geometry of the inclusion on the depolarisation field which results from its polarisation. For instance, in the case of a needle, only polarisation perpendicular to the needle axis contributes to the depolarizing field, whilst for a slab only polarization perpendicular to the slab face may contribute. Similarly for a sphere, all directions contribute and so the depolarisation matrix is diagonal with a value of 1/3 for each diagonal element, as the trace of the depolarisation tensor must be 1. It follows from Equations 12, 15 and 16 that;

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|  | Equation 17 |

Rearrangement allows the internal field of the inclusion to be expressed in terms of the known permittivities, the shape of the inclusion and the external field.

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|  | Equation 18 |

Substituting the internal field expression (Equation 17) into Equation 13 for the dipole moment and requiring the dipole moments calculated using the polarisation density to equal those calculated from the polarisability allows the polarisability to be written;

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|  | Equation 19 |

Although it has not been specified explicitly the permittivity of the inclusion, and therefore the polarisability tensor, are frequency dependent through the oscillator strengths of each phonon mode contributing to the permittivity according to Equation 10a. The calculation of the complex, frequency dependent polarisability tensor of the composite material is the key step in the calculation of its effective permittivity.

### The Effective permittivity of a mixture

To extend this approach to include the effect of a number of inclusions we need to introduce the concept of an effective permittivity (), which describes the behaviour of an average field, , where the angle brackets indicate an average over a volume of the composite material. It is required that the average electric flux density is the same in the effective medium as in the composite medium;

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|  | Equation 20 |

The averaging is necessary because the polarisation within a given inclusion has an effect on the field in other inclusions. The local field in the cavity left by a single inclusion embedded in the average polarisation field is given by;

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|  | Equation 21 |

The local field ‘excites’ the inclusion resulting in a dipole moment that is related to the polarisation through the number density of inclusions (*n*) and through the polarisability of the inclusion, which is already known from Equation 19.

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|  | Equation 22 |

The angle brackets around the product of the polarisability and the local field indicate that it is necessary to average the polarisation according to the distribution of alignments of inclusions. In this work it will be assumed that the inclusions are randomly aligned. Substituting the expression for the local field (Equation 21) gives;

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|  | Equation 23 |

### Mixing rules

There are many mixing rules which have been proposed to describe the homogenization of composite materials and a lot of work has been done in comparing their accuracy. Here two methods will be used. The first and the most commonly used method is the Maxwell-Garnett mixing rule.25 Indeed this has been implied by the use of Equation 20 to define the effective permittivity. The other commonly used method is the Bruggeman mixing rule,25 which differs substantially in the way the two components of the system are treated. It is usually stated that the Maxwell-Garnet mixing rule is good for low volume fractions of the inclusion and the Bruggeman approach should be better for higher volume fractions.27 In addition to these mixing rules one other approach will be described, namely the Averaged Permittivity (AP) mixing rule, which calculates the absorption spectrum ignoring the effects of the internal field on the absorption and can therefore be used as an indicator of the shifts in frequency and intensity which have occurred owing to the effect of particle shape.

### Maxwell-Garnett mixing rule

The Maxwell-Garnett approach for treating the properties of heterogeneous mixtures assumes that the average field and the average flux density result from volume fraction weighted sums. Substituting Equation 23 into Equation 20 gives the Maxwell-Garnett effective permittivity;

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|  | Equation 24 |

The fact that the polarisability tensor has a volume term in it (Equation 19) means that the terms in Equation 24 containing depend on the volume fraction *f*. Although written as a tensor, because the assumption has been made that the inclusions are randomly orientated, the effective permittivity has to be diagonal with equal complex values. Since the polarisability is complex and frequency dependent the effective permittivity is also and its calculation using Equations 24 and 19 needs to be calculated over the frequency range of interest.

### Bruggeman mixing rule

In the Maxwell-Garnett mixing formalism there is a distinction between the inclusion and the supporting medium which results in an asymmetry in the treatment of the two species in the mixture. Instead the Bruggeman mixing rule assumes that each species is polarized against the background of the effective medium and therefore the polarisation in the two components cancel each other out;

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|  | Equation 25 |

where the components are now labeled 1 and 2 rather than external and internal. The polarisation for species 1 and 2 with a number density of species represented by *n1* and *n2* can be obtained from the polarisability of the species (Equation 22);

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|  | Equation 26 |

Substituting Equation 26 into Equation 25 leads to the requirement that;

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|  | Equation 27 |

Taking Equation 19 and generalizing it for species *I*, (where *I* is 1 or 2) embedded in an effective permittivity given by ;

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|  | Equation 28 |

Equation 27 has to be solved for . Since the systems considered here are isotropic with random inclusions, a solution has to be found for a complex value of the Bruggeman permittivity at each frequency considered. An issue in the use of Equation 28 is that the same depolarisation matrix is being used for both species, which is clearly not always appropriate. The solution of Equation 27 can be achieved either by iteration or by casting the equation as a minimization problem. The iterative approach implemented in PDielec involves repeated application of Equation 29 until convergence.28 The starting point for the iterations is taken as the Maxwell-Garnett solution for the first frequency and then the solution at the previous frequency is used to start the iterations.

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|  | Equation 29 |

Although the Bruggeman permittivity is written here as a tensor, the polarisabilities in Equation 27 have to be averaged over the random orientation of the inclusions and therefore the homogenized material is isotropic with a single complex value for the diagonal tensor. Also, as with the Maxwell-Garnett mixing rule, since the polarisability is complex and frequency dependent, the effective permittivity is also, and its calculation using Equation 29 needs to be performed over the frequency range of interest.

The choice between using the Bruggeman or Maxwell-Garnett model is often governed by the assumption that the Maxwell-Garnett model works well at low concentrations and the Bruggeman model works better at higher concentrations. Work by Karkkainen *et al*. using a finite difference method for random mixtures of non-absorbing materials indicated that the Bruggeman approximation works best when there is some clustering of the inclusions and the Maxwell Garnett model works best when there is no clustering.29

The Bruggeman solution has been shown to be unphysical in certain circumstances.30 In particular when the real components of the permittivity have different signs and when the absolute values of the real components are much larger than those of the imaginary components. Unfortunately, it may be that these conditions will apply to modelling infrared absorption. As a result only a few of the examples discussed below will include results using the Bruggeman mixing rule; the majority will use the Maxwell-Garnett mixing rule.

### Averaged-Permittivity mixing rule

It is useful to be able to compare the effective medium theories with the absorption predicted using no shape information, that is using only the TO frequencies.

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|  | Equation 30 |

Equation 30 defines an isotropic permittivity which can be used to calculate such an absorption coefficient. The angle brackets indicate an average of orientation. This mixing rule provides a useful comparison between the absorption calculated without any shape effects and that calculated including shape effects using the other mixing rules presented above. At low concentrations the peak positions of the AP mixing rule will be at the TO frequencies.

## Particle Size Effects

Meier and Wokaunn1 outlined an approach to treating large (metal) spherical particles, where particle size is incorporating terms up to 3rd order in the wave vector *k*. Using equations 12 and 16 we can write

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|  | Equation 31 |
|  | Equation 32 |
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Here *a* is the size of the particle and *q* is the dimensionless ‘size’ of the particle with respect to the wavelength of the incident light. The first term relating the depolarisation field to the polarisability is the same as that used above in equation 15. The second term is a dynamic depolarisation term and the third term is a radiation damping correction to the electrostatic solution. [N1]

A slightly different, but related, approach is presented by Sihvola [Sihvola book]. Starting from Equation 17, we introduce a size dependent term *G(x)* taken from the work of Peltoniemi [N3];

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| The modified equation for the relationship between the internal field and the external field based on equation 17 becomes; | Equation 33 |
|  | Equation 34 |
| This leads to a modified equation for the polarisability of spherical particles |  |
|  | Equation 35 |

Using the modified, sized dependent polarisability all the mixing schemes can be implemented in a way that incorporates size effects.

Generally speaking the on-set of changes in the calculated absorption is an indication that size effects are important and should be treated properly in some way.

Extended to small cubic and cuboids by Massa, Maier and Giannini(N2).

## Numerical Methods

FDTD –GMES a python package

N1) Meier and Wokaun

N2) Massa, Maier and Giannini

N3) Peltoniemi