

An accurate and simple universal curve for the energy-dependent electron inelastic mean free path[†]

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The values of inelastic mean free paths (IMFPs) calculated from optical data for the three material categories of elements, inorganic compounds and organic compounds are re-assessed to provide a simple equation giving an estimate of the IMFP, knowing only the identities of the elements in an analysed layer and the atomic density of that layer. This simple equation is required for quantification of the thicknesses for layers of mixed elements in which the required parameters for use of the popular equation, TPP-2M, are insufficiently known. It describes the published values, calculated from optical data for energies above 100 eV, to a similar root mean square (RMS) deviation as that for TPP-2M in the three material categories. The RMS deviation for all three categories averages 8.4%, provided the inorganic data are 'corrected' for the published sum rule errors. If, in an analysed layer, only elements are identified and the atomic density is unknown, i.e. only the average *Z* value of the layer is known, a simpler relation is provided for the IMFP in monolayers with only one unknown parameter *Z* that exhibits an RMS deviation from the IMFPs calculated from optical data of 11.5%. Copyright © 2011 Crown copyright.

Keywords: attenuation lengths; elements; IMFP; inelastic mean free path; inorganic materials; organic materials

Introduction

The first measurements relating to the rapid attenuation of low-energy electrons appear in the mid-1960s.^[1] In studies of clean metallic overlayers on single crystal surfaces monitored by Auger electron spectroscopy (AES) and low-energy electron diffraction, Palmberg and Rhodin in 1968^[2] fitted the exponential AES signal changes with a characteristic parameter that they termed the mean free path, measured in monolayers. In similar studies monitored by AES and a quartz crystal oscillator, Seah in 1974^[3] described this characteristic as the product of the inelastic mean free path (IMFP) and a geometrical term to allow for the angle of emission of the detected electrons. Many other measurements of this characteristic parameter were made in the ensuing decade, to be followed by three compilations of data to provide surface analysts with estimates of the characteristic values to be used.^[4–6] Powell^[5] introduces the term attenuation length and equated this to the total IMFP, whereas Seah^[6] felt that the measured characteristic of the exponential decay in the overlayer method would be somewhat smaller than the IMFP as a result of elastic scattering. In the last of these compilations,^[6] universal curves were provided with simple expressions showing how experimental data fitted these curves but with rather large scatter factors of ~1.4. The scatter factor describes the standard deviation of the experimental data about the mean curve on a log value plot, replacing the usual '+' or '–' by '×' and '÷'. Three similar equations were given, one each for elements, inorganic compounds and organic compounds with different coefficients. Thus, at that time a single universal curve for all materials had not been achieved.

In the early studies, most of the scatter arose from the difficulty of making valid experiments where, following the original suggestion of Lander,^[7] layers of one material were deposited

on another, generally *in-situ* in the ultra-high vacuum spectrometer. Methods were not available to confirm that the intended layer-by-layer growth pattern had occurred. The experiments provided a parameter that is now called the attenuation length (AL) and is used to describe the change in the overlayer and substrate intensities via the Beer–Lambert law, rather than the inelastic mean free path (IMFP) that describes the attenuation of electrons in the absence of elastic scattering. The distinction between the measured AL and the IMFP was clarified by Gries and Werner.^[8] The AL and IMFP are easily converted to each other now with straightforward relations,^[9,10] and so the AL will not be considered further here although the AL is the parameter ultimately required for thickness measurements of thin films.

In 1988, Powell^[11] published a paper titled 'The Quest for Universal Curves to Describe the Surface Sensitivity of Electron Spectroscopies', reviewing many different 'universal curves' to describe the IMFP. There followed a number of papers leading to calculations of the IMFP from optical data for elements,^[12,13] inorganic materials^[14] and organic materials^[15] and, with the latter, the generic semi-empirical equation known as TPP-2M by which users may calculate IMFPs. This equation is also embodied in the software systems SRD71^[16] and SRD82.^[17] Here, we shall

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only consider TPP-2M of these semi-empirical descriptions as the most commonly used equation. This provides a single equation suitable for all three categories of materials with six subsidiary equations and nine fitting constants but only requiring four material parameters: density ρ , atomic or molecular mass M , number of free valence electrons N_v and band gap E_g . The accuracy of the theoretical calculations of the IMFPs from optical data for elements has been confirmed to a root mean square (RMS) deviation of 11% for 13 elements in the energy range 100–5000 eV using experimental data from elastic peak electron spectroscopy (EPES) measurements.^[18] The EPES approach avoids the need for depositing the thin uniform overlayers. A similar low scatter of 12.3% was found between the IMFPs calculated from optical data and the formula TPP-2M.^[13] Powell and Jablonski^[19] note that IMFPs calculated from optical data have uncertainties around 10% and a similar uncertainty applies to TPP-2M, although uncertainties could be larger for a small number of materials with extreme values of certain parameters not tested in the EPES measurements. Of the 41 elemental materials studied,^[13] RMS deviations above 25% occur for C (graphite), C (diamond) and Cs between the IMFPs calculated from optical data and TPP-2M.

The agreement of IMFPs calculated from optical data and TPP-2M is not so good for the 15 inorganic compounds studied^[14] but is fine for the 14 organic compounds.^[15] The comparison in the original publication for inorganic compounds^[14] is for a slightly different generic equation, TPP-2, but TPP-2M exhibits an RMS deviation of 18.9% for inorganic and 8.5% for organic compounds.^[15] The higher scatter for the inorganic materials was thought^[14,15] to have arisen from inadequacies of the input optical data for the theoretical calculations rather than any shortcomings of TPP-2M.

Universal curve

The equation known as TPP-2M, shown below, is certainly a universal equation but does not show up as a universal curve because it is difficult to plot all the different materials scaled to a curve of only one variable and one dependent function. The formula for TPP-2M is, in nm,^[13,15]

$$\lambda_{\text{TPP-2M}} = \frac{0.1E}{E_p^2 [\beta \ln(\gamma E) - (C/E) + (D/E^2)]} \quad (1)$$

where $\lambda_{\text{TPP-2M}}$ is the IMFP for electrons of kinetic energy E in electronvolts and where

$$E_p = 28.8(N_v \rho / M)^{1/2} \quad (2)$$

$$\beta = -0.10 + 0.944(E_p^2 + E_g^2)^{-1/2} + 0.069\rho^{0.1} \quad (3)$$

$$\gamma = 0.191\rho^{-0.50} \quad (4)$$

$$C = 1.97 - 0.91U \quad (5)$$

$$D = 53.4 - 20.8U \quad (6)$$

$$U = N_v \rho / M \quad (7)$$

These equations depend on N_v , M , E_g and ρ that are, respectively, the number of valence electrons per atom (for elements)

or molecule (for compounds), the atomic or molecular mass in unified atomic mass units or daltons, the band gap energy in electronvolts and the mass density in grammes per cubic centimetre.

In practical analysis, where a layer whose thickness is to be determined may be composed of many elements, the values of parameters such as the band gap, the mass density and the effective number of free electrons may not be obvious and it may not be at all clear how to deduce them. In TPP-2M, for example, the density occurs in E_p^2 which directly scales λ in Eqn (1) with the density ranging over a factor of 42 in the 41-element study of Tanuma, Powell and Penn.^[13] Similarly, N_v ranges over a factor of 11 and E_p^2 or U , to which λ is linearly proportional, over a massive factor of 110. The density and number of free electrons would each need to be known to 7% for any analysed layer to be able to use TPP-2M to 10%. It is therefore of interest to see if a much simpler and more transparent relation may be obtained, with some sacrifice, if necessary, in accuracy in order to provide a universal curve with parameters that may be easily input by the analyst. In the past, simpler equations of the form $\lambda = kE^m$ have been considered^[18] and have been found to be useful to illustrate behaviour, but not very accurately, with both k and m varying in an unpredictable manner. The power dependence of E can only be approximate because this power changes slightly with the electron energy.

The advantage of a simple power law is that users easily recognise the functional behaviour. To allow for the failure of the simple power dependence at low energies, we add an energy-independent term to kE^m and first consider a relation with only two material parameters Z , which is directly obtained from the spectroscopic analysis, and the atomic volume a^3 , where a only varies over a factor of 2.75 in the 41-element study of Tanuma, Powell and Penn:^[13]

$$\lambda = (P + QE^n)a^{(1+A)}/Z^d \quad (8)$$

The variations of ρ , N_v , E_p^2 or U , used in TPP-2M, and a , for the solid elements, are shown in Fig. 1 with the total ranges shown to the right. In Eqn (8), λ is in nm and the constants A , P , Q , n and d are initially to be found by fitting to the calculated IMFP values λ_{Opt} for the 41 elemental materials^[13] where theoretical calculations are more recent and more extensive. The aforementioned relation has been chosen because, by inspection, Z and

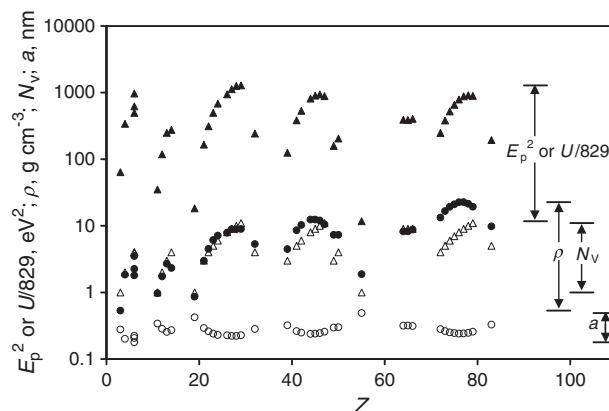


Figure 1. The variations of ρ (●), N_v (Δ), E_p^2 or $U/829$ (▲), used in TPP-2M and a (○) for the solid elements; ρ varies over a maximum to minimum range of a factor of 42, N_v varies over a range of 11, E_p^2 or U varies over a range of 110 and a varies over a range of 2.75 as shown to the right.

the atomic volume a^3 are significant and we wish to limit the number of material parameters used. The use of a and Z was also similarly chosen for the popular CS1 and CS2 equations of Cumpson and Seah^[20] for the attenuation length. Z is chosen in preference to M because the integer values are easily remembered. We choose a as the second parameter for its small range and also because it easily allows us to express λ in monolayers (ML) as λ/a directly (hence the $1 + A$ term in Eqn (8)). In determining layer thicknesses, a value in ML is often important. We could use ρ as the second parameter and similar quality results ensue but ρ is very much more dependent on the elements appearing in the analysis of the layer than is a . For completeness, the value of a in nm is computed using the equation

$$a^3 = \frac{10^{21}M}{\rho N_A(g+h)} \quad (\text{nm}^3) \quad (9)$$

where N_A is the Avogadro constant, M is the molecular mass in daltons for the relevant molecule G_gH_h and ρ , as before, is the density in grammes per cubic centimetre. Of course, for the elements so far discussed, $g=1$ and $h=0$.

It is not the objective of the present paper to describe the quantification of thin adsorbed layers, but it is useful to describe how to convert intensities quantified on commercial data capture systems where the quantification effectively provides a bulk atomic fraction X_i for the i th element. If one of these, element A , is in a part of a thin monolayer, the fractional monolayer coverage is, in the straight line approximation being used here, given approximately by Φ_A ^[21,22]

$$\Phi_A = (\lambda/a) \cos\theta (L/\lambda) X_A \quad (10)$$

where θ is the angle of emission of the detected electrons from the surface normal, and (L/λ) is the correction to the IMFP to provide the AL L ^[9,10] and is typically in the range 0.7–0.95.^[9] This shows why an expression of the IMFP in monolayers λ/a is important rather than simply λ in nm.

The points in Fig. 2 show the average value, at each energy, of $(\lambda_{\text{Opt}}/a)Z^{0.3}/a^{0.7}$ versus E for the 41 elemental materials, where $A=0.7$ and $d=0.3$. The smooth curve is for an ordinate equal to $7.1 + 0.104E^{0.872}$, i.e. $P=7.1$, $Q=0.104$ and $n=0.872$ in Eqn (8). The error bars are the RMS deviations for all 41 elemental materials from the smooth curve. To fit data below the minimum in

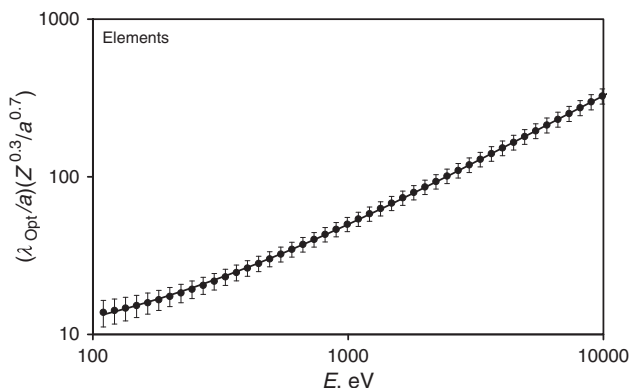


Figure 2. Plot of $(\lambda_{\text{Opt}}/a)Z^{0.3}/a^{0.7}$ versus E with associated error bars giving the RMS deviations from the function $4 + 0.44Z^{0.5} + 0.104E^{0.872}$, for the 41 elemental materials of Tanuma, Powell and Penn.^[13] The solid line shows the function $7.1 + 0.104E^{0.872}$ (i.e. near the middle of $4 + 0.44Z^{0.5} + 0.104E^{0.872}$ with $Z=50$). The RMS deviation is 8.5%.

the $\lambda(E)$ curve at low kinetic energies requires a slightly more complex function (P in Eqn (8) becomes energy dependent), and so here we only consider data for $E \geq 100$ eV. Kinetic energies below 100 eV are rarely relevant in XPS and, in AES, are usually for core-valence-valence transitions whose intensities, on the rapidly rising secondary electron emission background, are not well defined and whose shape depends markedly on the mix of the elements in the combined layer (through changes in the valence band density of states) making practical intensity measurement more uncertain.

Thus, for elements, the IMFP in nm is given by

$$\lambda = (7.1 + 0.104E^{0.872}) a^{1.7}/Z^{0.3} \quad (11)$$

for $E \geq 100$ eV to an average RMS deviation for all elements of 10.1%. This is close to the RMS deviation of 12.0% for TPP-2M with the same set of data and the same energy range from 100 to 30 keV (Note that the RMS deviations are calculated from the deviation of the ratio of the computed result to the value from the optical data, λ_{Opt} , away from unity. Note also that the average RMS deviation of the values for each element averaged over energy is always smaller than the RMS deviation for the whole data set as an entity. The former is the expression of scatter adopted by Tanuma, Powell and Penn and is used here for consistency). Eqn (11) is, of course, much simpler than Eqns (1)–(7) and only involves Z and a .

A small improvement may be made to Eqn (11) by observing that the coefficient P is dependent on Z to give the IMFP in nm:

$$\lambda = (4 + 0.44Z^{0.5} + 0.104E^{0.872}) a^{1.7}/Z^{0.3} \quad (12)$$

with an RMS deviation from the optical data of 8.5%.

That the energy dependence of Eqn (12) is useful can be seen from the scatter of the average ratio of $(\lambda_{\text{Opt}}/\lambda)$ over all 41 elemental materials at each of the 57 energy values for the range 100–30 000 eV. The standard deviation of these 57 average ratios is only 0.8%. This scatter is insignificant compared with the overall accuracies and shows that Eqn (12) describes the energy dependence of λ_{Opt} accurately from 100 to 30 000 eV.

Next, we consider the organic materials. It is not easy to repeat Fig. 2 without some guidance to use the effective values of Z and a . For the materials studied by Tanuma, Powell and Penn,^[15] the average values of Z and a , $Z_{\text{Av org}}$ and $a_{\text{Av org}}$, calculated from the densities and molecular formulae, were close to 4 and 0.25 nm, respectively. Figure 3 shows the results for $(\lambda_{\text{Opt}}/a_{\text{Av org}})Z_{\text{Av org}}^{0.3}/a_{\text{Av org}}^{0.7}$ versus E for Eqn (12) where $Z_{\text{Av org}}$

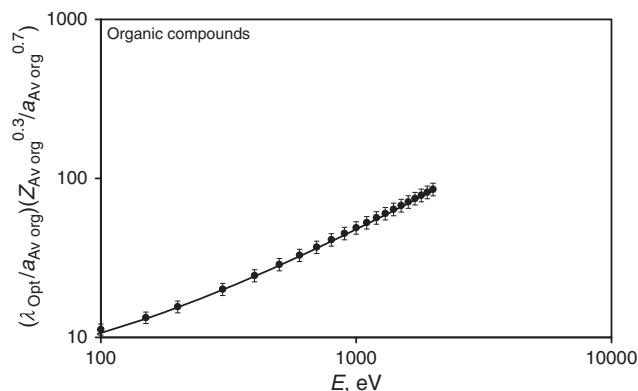


Figure 3. Plot of $(\lambda_{\text{Opt}}/a_{\text{Av org}})Z_{\text{Av org}}^{0.3}/a_{\text{Av org}}^{0.7}$ versus E for the 14 organic materials as in Fig. 2. The RMS deviation is 7.9%.

and $a_{\text{Av org}}$ have been set at 4 and 0.25 nm, respectively, for all of the organic materials. Individual Z and a values may be assigned but average values are more useful to study as they may have to be used for unknown organic layers anyway. All other numbers are as for the elements. The RMS deviation here is 7.9% for $E \geq 100$ eV, very close to the 6.9% for TPP-2M but, of course, with significantly fewer parameters, i.e. only E .

Finally, we should consider the inorganic materials. Here, the scatter between the IMFPs calculated from optical data and from TPP-2M was significantly poorer^[14] than for the elements^[12,13] or the organic materials^[15] and it may be that the IMFPs calculated from optical data are less accurate. Indeed, in their publication,^[14] Tanuma, Powell and Penn suggest that, for calculating the IMFPs in compounds, the generic equation TPP-2 (TPP-2 was the forerunner of TPP-2M) is generally better than the value calculated from the optical data. They attribute the poor correlation to excessive sum rule errors in the optical data for calculating the IMFP rather than shortcomings of TPP-2. However here, it is inappropriate to follow this guidance and use TPP-2M if we wish to find a simpler, and not significantly poorer, equation than TPP-2M itself.

We note the correlation, shown by Tanuma, Powell and Penn,^[14] of the average of the f-sum and KK-sum rule errors with the difference between the IMFPs calculated from the optical data and the generic equation TPP-2 then used. This indicates that a negative error in the sum rule leads to a weakening of the scattering and hence a lengthening of the calculated IMFP. The f-sum rule errors were generally lower than the KK-sum rule errors. However, Tanuma, Powell and Penn^[14] note that the f-sum integration is influenced appreciably by the optical data in the 50–10 000 eV range, whilst that for the KK-sum is influenced by the data in the 2–50 eV range. The IMFP calculation is based on an integration for which the main contributions come from roughly 5 to 200 eV. Figure 4 shows a plot of the divergence from unity of the ratio of $\lambda_{\text{Opt}}/\lambda_{\text{Eqn (12)}}$ averaged over the electron energy from 100 to 2000 eV plotted versus the KK-sum rule errors. It is clear that the increased error reduces λ_{Opt} here on a 1:1 basis and that, at a KK-sum rule error of 0, Eqn (12) is within a few per cent of the correct value. It is not clear, in individual cases, the precise energy range of the error in the optical data and, therefore, the extent of each error. The sum rule simply indicates the direction of the error and its seriousness. However, on average, the sum rule error may simply scale the IMFP. The

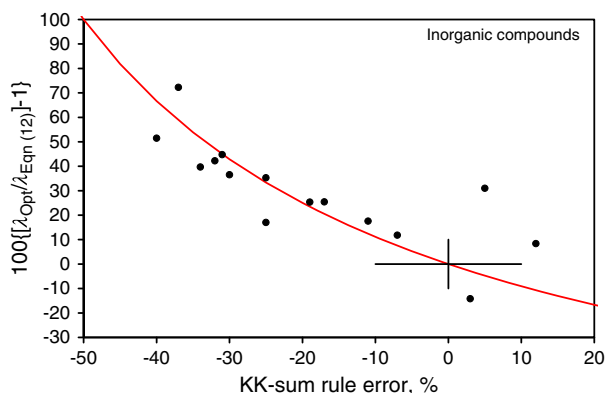


Figure 4. (colour online) Plot of the average percentage divergence of λ_{Opt} away from the values from Eqn (12) versus the KK-sum rule error, for the 15 inorganic materials. The curve shows a simple prediction described in the text and passing through the origin (shown by the vertical and horizontal lines).

curve drawn in Fig. 4 is the prediction for a sum rule error that, for instance, halving the oscillator strength present leads to λ_{Opt} increasing by a factor of 2. The effect is not the same as that for N_v in TPP-2M because the optical data will obtain the value of E_p more or less right. Figure 4 indicates that Eqn (12) may improve on the original λ_{Opt} values by avoiding the sum rule errors. We therefore 'correct' the calculated IMFPs for the inorganic materials by allowing for the tabulated errors in the f-sum and KK-sum rules, using the average s of the two values shown in Table 2 of Tanuma, Powell and Penn^[14] or the higher value if the lower has a '>' sign. The new values λ^* are simply $\lambda_{\text{Opt}}(1+s)$ where s is generally negative.

It is not clear what Z value should be used for inorganic compounds. The most simple approach used here is to calculate an average Z from the molecular formula, if it is known, and shown as follows:

$$Z = \frac{gZ_G + hZ_H}{(g+h)} \quad (13)$$

If the molecular formula is not known, it may be estimated from the AES or XPS analysis itself.

The a value is given by Eqn (9). Figure 5 shows the data for these 'corrected' IMFP values λ^* plotted as before as $(\lambda^*/a)Z^{0.3}/a^{0.7}$ versus E with the curve for Eqn (11). The result here shows the scatters for the 15 inorganic compounds and the fit with an RMS deviation of 10.5% for Eqn (12). We could plot a narrow fan of curves in Fig. 5 for the full range of the parameter P but this may be confusing. We show this later in Fig. 6. Figure 5 looks very good but its validity depends on the validity of our 'correction' to the calculated IMFPs. If we ignore the 'correction' for the sum rule errors, the RMS deviation from unity for the ratio of λ from Eqn (12) and λ_{Opt} for $E \geq 100$ eV is 20%, compared with 17.5% for TPP-2M calculated in the same way.

The importance of expressing λ for the inorganic materials using the same equation as for elements is that, of course, in a real analytical situation, layers tend to be of more than one element and the transition from, say, a Ti layer to one of Si via $\text{Ti}_{1-x}\text{Si}_x$, through Ti_5Si_3 , TiSi and TiSi_2 or similarly from Fe to Fe_2O_3 or to FeCO_3 needs to be treated as continua analytically and not as a transition to a separate class with separate coefficients because, in general systems, the precise compound may not be known or be stoichiometric.

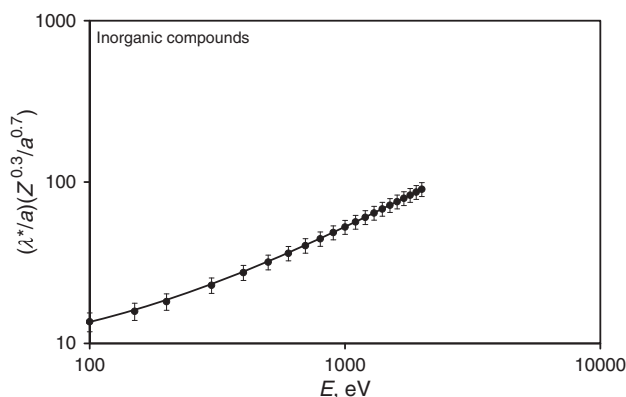


Figure 5. Plot of $(\lambda^*/a)Z^{0.3}/a^{0.7}$ versus E with associated error bars giving the RMS deviations from the function $4 + 0.44Z^{0.5} + 0.104E^{0.872}$, for the 15 compounds of Tanuma, Powell and Penn.^[14] The solid line shows the function $7.1 + 0.104E^{0.872}$. The RMS deviation is 8.3%.

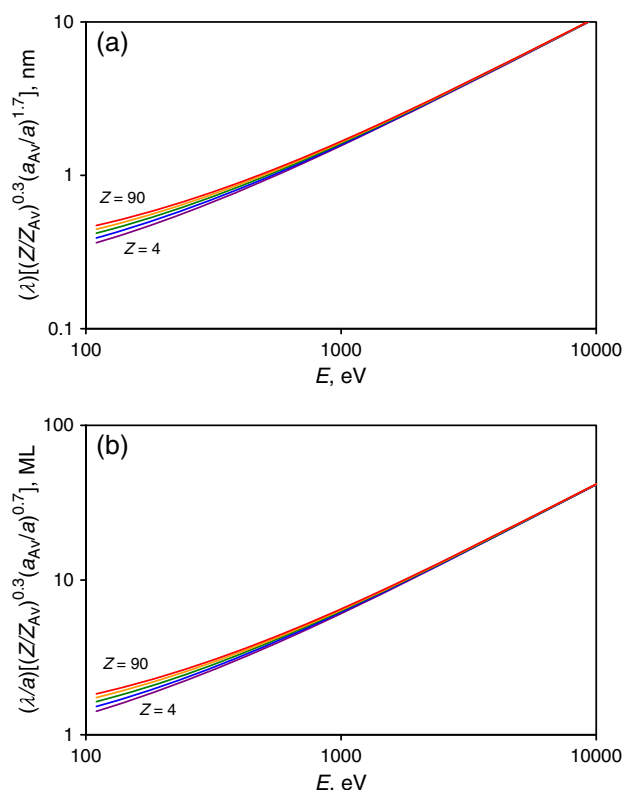


Figure 6. (colour online) Universal plots using Eqn (12) for (a) $\lambda[(Z/Z_{Av})^{0.3}(a_{Av}/a)^{1.7}]$ in nm and (b) $\lambda/a[(Z/Z_{Av})^{0.3}(a_{Av}/a)^{0.7}]$ in monolayers (ML) versus E for Z values of 4, 15, 35, 60 and 90 with the latter as the highest curve to show the curves that are omitted from Figs. 2, 3 and 5.

One may expect the band gap to be significant in the electron-loss mechanism. However, there is only a weak correlation between E_g and the ratio of λ_{Opt} to the values from Eqn (12) so we initially ignore its effect. This may seem surprising but it occurs through the band gap increasing as the bond formation energy rises and this, in turn, causes the atomic density to rise. Thus, the effect of E_g is partly incorporated in the fitting to a . This is a rather more important point than may at first appear. In using TPP-2M, one may be tempted, when applying it to materials other than those listed (which is not recommended by Tanuma, Powell and Penn^[14]), to guessing values from the nearest equivalent materials if the value is unknown, or to interpolate the parameters from, say, the elemental data. In doing this, it is necessary to allow for the underlying physics in that a density increase at a fixed composition usually requires a stronger bonding and a consequent concomitant change in band gap.

We may add a small effect for E_g but values for E_g are generally unavailable and so it is not a very helpful parameter. Rather more widely tabulated are the heats of formation H .^[23] Fortunately, empirically $E_g \approx 3.15H$ where E_g is in electronvolts and H is in electronvolts per atom for the 15 inorganic materials of Tanuma, Powell and Penn,^[14] similar to the result of Di Quarto *et al.*^[24] This effect is added into Eqn (12), through a term W where $W = 0.06H$ or $0.02E_g$, and H and E_g have the units given previously, to give the IMFP in nm:

$$\lambda = (4 + 0.44Z^{0.5} + 0.104E^{0.872}) a^{1.7} / [Z^{0.3}(1 - W)] \quad (14)$$

S1, IMFP in nm

Here, as far as possible, very simple rounded numbers have been used for the fitting parameters. For later reference, this

equation is called 'S1'. The RMS deviation of the inorganic compounds is now 8.3% using either H or E_g . The heat of formation only has a small effect and is generally only significant for alkali halides containing F and Cl and for oxides. Values of H for the 15 inorganic compounds are from 0 to 4.5 eV/atom.

We have not included W in the data for organics because adequate results are already obtained. The effect is present in exactly the same way as in Eqn (14), but to utilise the improved accuracy, the value for the average Z needs to be increased slightly. The RMS deviation between Eqn (14) and λ_{Opt} then falls from 7.9% to 7.2%. The range of W for the organics is smaller than for the inorganic compounds and so W is ignored for the organics in Eqn (14). The use of W is only recommended, or needed, for inorganic materials.

Discussion

So, after 23 years,^[11] maybe the quest for a universal curve is closer. Figure 6 shows how the low-energy region of Eqn (14) depends on Z . In Fig. 6(a) the result is in nm and (b) in monolayers. To bring the plots to a more understandable scale for analysts, here we plot λ in nm, scaled by $(Z/Z_{Av})^{0.3}(a_{Av}/a)^{1.7}$ and λ/a in monolayers, scaled by $(Z/Z_{Av})^{0.3}(a_{Av}/a)^{0.7}$ where for convenience, $Z_{Av} = 40$ and $a_{Av} = 0.25$ nm, respectively. Surprisingly, Eqn (14) appears to be at least as good as TPP-2M for the elements, inorganic compounds and organic compounds studied with an overall RMS deviation compared with the optical calculations of 8.7% if the heats of formation H are ignored, falling to 8.4% if H is included and the values for inorganic compounds are 'corrected' for the sum rule errors. Clearly, for the IMFPs of elements, and similarly for the 14 organic compounds, if there are theoretical values calculated from reliable optical data, one would use those values rather than Eqn (14). For the inorganic compounds, Tanuma *et al.*^[14] recommend the use of the generic equations rather than the theoretical values as they are more likely to be accurate. For studying the influence of parameters such as the density ρ on the IMFP, it may or may not be that the TPP-2M equation is helpful, because one needs to know the influence of ρ on E_g , etc., whereas Eqn (14) does not really separate individual influences.

In practical analysis, one often has a surface layer that is unknown and is the objective of the analysis. One may have no data on the band gap or the mass density. However, the analysis itself will provide the average atomic number of the overlayer and so in Eqn (14) only the average atomic volume relevant to the layer needs to be estimated and, for the IMFP in ML, this influence is weakened by the power being less than unity – indeed, compared with the bulk density importance in Eqns (1) and (2), the atomic density is now at a power below 0.25. As a last resort, the average value of $a_{Av} = 0.25$ nm may be used giving an RMS deviation for λ/a , i.e. the IMFP in ML for the 41 elemental materials, of an acceptable 11.5%. In this case, λ/a in ML is given by

$$\lambda/a = (1.52 + 0.167Z^{0.5} + 0.0394E^{0.872}) / Z^{0.3} \quad (15)$$

S2, IMFP in ML, Z dependence only

as shown in Fig. 7. In Eqn (15), the value of a used on the left is, of course, the true a rather than a_{Av} . The value of $(a_{Av})^{0.7}$ has been used in the term on the right of Eqn (14).

If the IMFP is required in nm, $a_{Av} = 0.25$ nm may be used again, giving an RMS deviation for λ , i.e. the IMFP in nm for 35 of the 41 elemental materials, excluding the large alkali metals and the

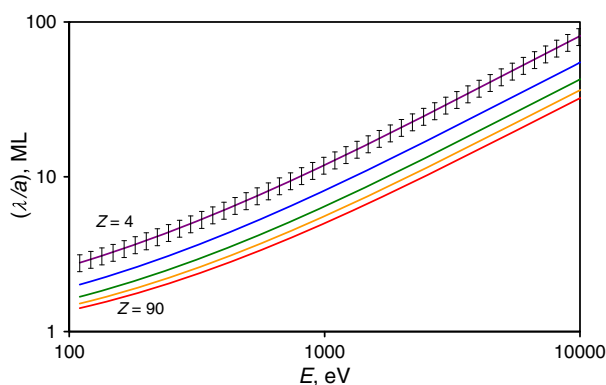


Figure 7. (colour online) Universal plot for λ/a in monolayers (ML) for all materials using Eqn (15) with Z set at 4, 15, 35, 60 and 90 with error bars shown only on the $Z=4$ curve, set at 11.5%.

small graphite and diamond, of a still acceptable 15.0%. In this case, λ in nm is given by Eqn (14) where $a^{1.7}$ has the numerical value 0.095. Simplifying further and removing the $0.44Z^{0.5}$ term and with re-optimization give

$$\lambda = (0.73 + 0.0095E^{0.872})/Z^{0.3} \quad (16)$$

IMFP in nm, Z dependence only

with the RMS deviation of 15.0% only degraded to 15.9%.

Moving outside the range of materials studied by Tanuma, Powell and Penn, we may evaluate a values for a range of inorganic materials from the formulae and densities in Table 3.2 of Kaye and Laby.^[25] For 87 oxides, 29 sulfides and 23 sulfates, the a values average 0.25 ± 0.03 nm, such that the RMS deviation incurred in using Eqn (15) instead of Eqn (14) for λ/a adds only a further 7.4%, implying an overall RMS of Eqn (15) of 12% for such material categories.

It is instructive to check if Eqn (14) and TPP-2M scatter randomly about the values from the optical calculations λ_{Opt} or if they both diverge the same way for each substance. In Fig. 8, we plot the ratio of the results for TPP-2M $\lambda_{\text{TPP-2M}}$ to those of the original optical calculations λ_{Opt} versus the similar results for Eqn (14) $\lambda_{\text{Eqn (14)}}$ also to λ_{Opt} . For the inorganic materials, we use the corrections described previously. These results do not vary significantly with energy and so the plotted points are for the average for energies above 100 eV. In Fig. 8, the dashed lines show the RMS deviation values for the ratios on each axis. Although the results from Eqn (14) give a lower RMS deviation than that for TPP-2M, this is probably not all that significant and it is concluded that the two formulae are equally valid for $100 \leq E \leq 30\,000$ eV.

If the λ_{Opt} values for the inorganic materials are not corrected for the sum rule errors, the relevant data points in Fig. 7 move radially towards the origin and the error bars move slightly. Both Eqn (14) and TPP-2M are still equally valid for $100 \leq E \leq 30\,000$ eV.

The greatest mean divergence for $\lambda_{\text{TPP-2M}}/\lambda_{\text{Opt}}$ is for LiF where $\lambda_{\text{TPP-2M}}/\lambda_{\text{Opt}} = 1.73$. This is the poorest description of λ_{Opt} by TPP-2M as noted in Table 8 of reference^[15] but surprisingly in the earlier equation TPP-2 of Tanuma, Powell and Penn,^[14] LiF was not an outlier. With Eqn (14), LiF is not an outlier either. The transition from TPP-2 to TPP-2M^[15] was made to describe the lower density organic materials and, in the fitting process, the inorganic materials were excluded because those values of λ_{Opt} were based on much less reliable data than for the other two groups of materials. Thus, the transition from TPP-2

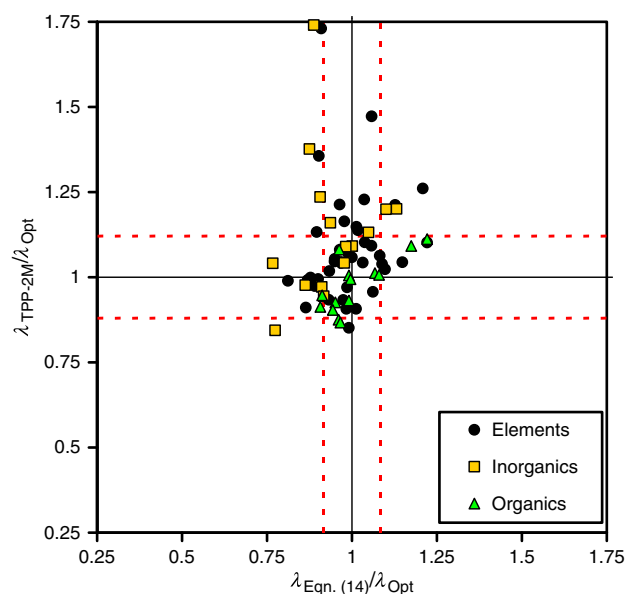


Figure 8. (colour online) Plot of $\lambda_{\text{TPP-2M}}/\lambda_{\text{Opt}}$ versus $\lambda_{\text{Eqn (14)}}/\lambda_{\text{Opt}}$ to show the relative divergences of $\lambda_{\text{TPP-2M}}$ and $\lambda_{\text{Eqn (14)}}$ from λ_{Opt} for the three classes of materials. The solid lines show the unity values and the dashed lines the RMS deviations about unity for the whole set of elemental, inorganic and organic data on each axis as 12.0% for TPP-2M and 8.4% for Eqn (14).

to TPP-2M did significantly more than accommodate the lower density organic materials although this change is not investigated here.

It is clear that there is good overall consistency between the present empirical relations and the original calculations of the IMFPs from the optical data and that this also gives greater credibility to the original data that they form part of a simple behaviour from material to material. From time-to-time, experiments appear in which data for individual materials are compared with λ_{Opt} or $\lambda_{\text{TPP-2M}}$ and where there are significant differences (maybe up to a factor of 2). It seems increasingly likely that, in these cases, it may be that the differences indicate a need to reconsider the basis of the experimental data rather than the accuracy of the theoretical calculations.

Conclusion

A simple universal curve for IMFPs in nm or monolayers is developed as the S1 equation Eqn (14), involving only the average atomic number and average atomic size for the material involved and, for alkali halides and oxides, the heat of formation. This has an overall RMS deviation of 8.4% compared with the calculated values from optical data for elements, organic compounds and inorganic compounds with the latter 'corrected' here for sum rule errors. The individual RMS deviation values of 8.5%, 8.3% and 7.9% for elements, inorganic materials and organic materials, respectively, are all very consistent. This simple relationship should be useful for estimating IMFP values generally and especially in films for which values of IMFPs calculated from optical data are unavailable or for which optical data are uncertain. If the atomic size is unknown, a value of 0.25 nm may be used for elemental and inorganic layers as the average found in the present calculations. The heat of formation may then be ignored. This gives a result that is only dependent on the average atomic number Z ,

as given in the S2 equation Eqn (15). The RMS value of 8.5%, given previously for the 41 elemental materials, then degrades to 11.5%. For organic materials, average values of Z and a are taken as 4 and 0.25 nm, respectively.

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