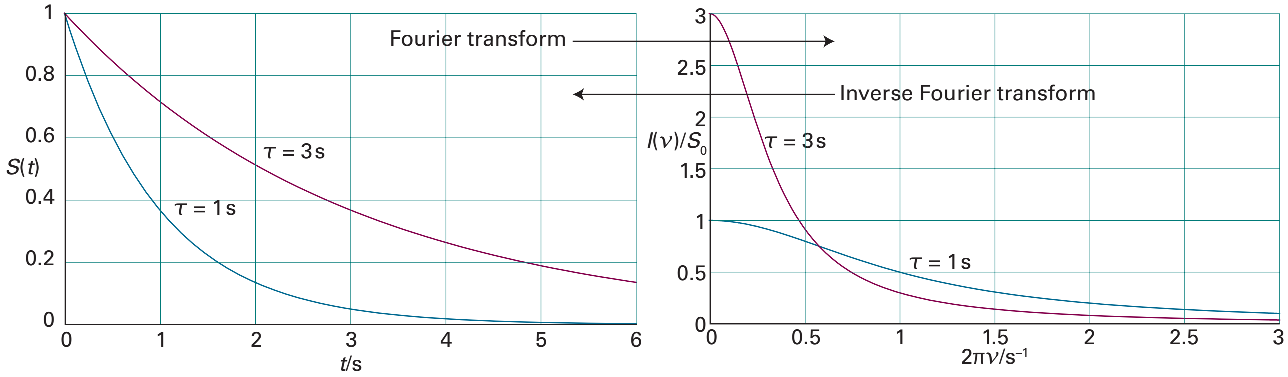
THE CHEMIST'S TOOLKIT 28 The Fourier transform



Sketch 28.1

A **Fourier transform** expresses any waveform as a superposition of harmonic (sine and cosine) waves. If the waveform is $S(t)$, then the contribution $I(\nu)$ of the oscillating function $\cos(2\pi\nu t)$ is given by the integral

$$I(\nu)=\int_0^\infty S(t)\cos(2\pi\nu t)\mathrm{d}t \qquad (28.1)$$

If the signal varies slowly, then the greatest contribution comes from low-frequency waves; rapidly changing features in the signal are reproduced by high-frequency contributions. If the signal is a simple exponential decay of the form $S(t) = S_0 e^{-t/\tau}$, the contribution of the wave of frequency ν is

$$I(\nu)=S_0\int_0^\infty e^{-t/\tau}\cos(2\pi\nu t)\mathrm{d}t=\frac{S_0\tau}{1+(2\pi\nu\tau)^2} \qquad (28.2)$$

Sketch 28.1 shows a fast and slow decay and the corresponding frequency contributions: note that a slow decay has predominantly low-frequency contributions and a fast decay has many high-frequency contributions.

If an experimental procedure results in the function $I(\nu)$ itself, then the corresponding signal can be reconstructed by forming the **inverse Fourier transform**:

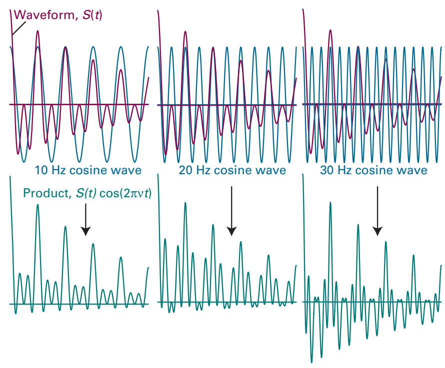
$$S(t)=\frac{2}{\pi}\int_0^\infty I(\nu)\cos(2\pi\nu t)\mathrm{d}\nu \qquad (28.3)$$

There are complex versions of these cosine transforms, as described below.

Fourier transforms are applicable to spatial functions too. Their interpretation is similar but it is more appropriate to think in terms of the wavelengths of the contributing waves. Thus, if the function varies only slowly with distance, then its Fourier transform has mainly long-wavelength contributions. If the features vary quickly with distance (as in the electron density in a crystal), then short-wavelength contributions feature.

Further information

Some insight into the physical significance of taking a Fourier transform can be obtained by considering the process for analysing a wave of general form, like that at the top of each part of Sketch 28.2. According to eqn 28.1, the procedure involves forming the product of the waveform and a cosine wave with frequency ν, and then determining the area under the product.



Sketch 28.2

When S(t) is multiplied by a cosine wave with frequency 10 Hz, the oscillations in the two functions largely coincide, with the result that the product $S(t)\cos(2\pi\nu t)$ has more positive peaks than negative peaks, and therefore a non-zero area. The wave of frequency 10 Hz, therefore makes a significant contribution. When the procedure is repeated with a cosine function oscillating at 20 Hz, the product also results in a non-zero area, so a cosine function oscillating at this frequency also makes a significant contribution to the original waveform. However, if the frequency of the cosine function is 30 Hz, the product has as many positive and negative peaks and the area is essentially zero. A cosine function at this frequency makes a negligible contribution to the waveform.

The most general formulation of a Fourier transform is to express the function $f(t)$ as a superposition of cosine and sine functions, not just cosine functions. The two types of functions can be handled simultaneously by using de Moivre's relation $e^{ix} = \cos x + i\sin x$ and writing

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{f}(\nu)e^{2\pi i\nu}\,d\nu \qquad (28.4a)$$

where $\tilde{f}(\nu)$ is the Fourier transform of $f(t)$, and can be interpreted as the amplitude of the contribution of the cosine and sine waves in the superposition that recreates the function $f(t)$. The inverse relation is

$$\tilde{f}(\nu) = \int_{-\infty}^{\infty} f(t)e^{-2\pi i\nu t}\,dt \qquad (28.4b)$$

The cosine contribution is given by the real part of $\tilde{f}(\nu)$ and the sine contribution is given by the imaginary part.

Brief illustration 28.1: The Fourier transform of an oscillating, exponentially decaying wave

The introductory part of this Toolkit illustrated the result of a cosine Fourier transformation of an exponential decay. It is instructive to consider the complex version of that calculation and to generalize it to a function that oscillates with a frequency ν_0 as it decays. To avoid the repetition of many factors of 2π, henceforth, write $2\pi\nu = \omega$. Then the (complex) function in the time domain is

$$f(t) = \begin{cases} f_0 \underbrace{e^{i\omega_0 t}}_{\text{Oscillating component}} \underbrace{e^{-t/\tau}}_{\text{Decaying exponential}} & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{cases}$$

The observed signal is the real part of $f(t)$, bearing in mind that $\text{Re}\, e^{ix} = \cos x$. See Sketch 28.3 (which also displays the Fourier transform, as explained below). The Fourier transform of this function is

$$\tilde{f}(\nu) = \int_0^{\infty} f_0 e^{i\omega_0 t}e^{-t/\tau}e^{-i\omega t}\,dt = f_0\int_0^{\infty} e^{\{i(\omega_0-\omega)-1/\tau\}t}\,dt \qquad (28.5)$$

$$= f_0 \left.\frac{e^{\{i(\omega_0-\omega)-1/\tau\}t}}{i(\omega_0-\omega)-1/\tau}\right|_0^{\infty} = f_0\frac{-1}{i(\omega_0-\omega)-1/\tau} \qquad (28.6)$$

The fraction of the right has both real an imaginary parts; they can be extracted by multiplying the numerator and denominator by the complex conjugate of the denominator

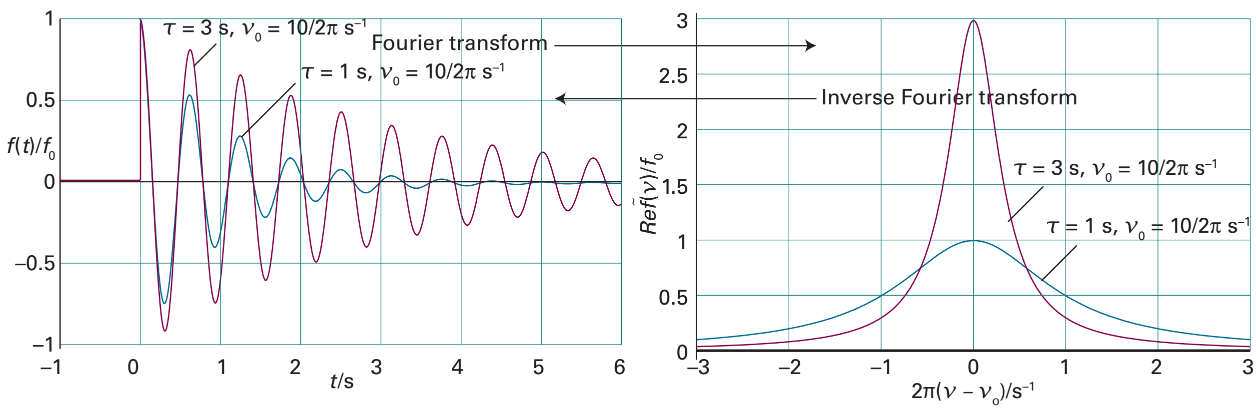
$$\tilde{f}(\nu) = f_0\frac{-1}{i(\omega_0-\omega)-1/\tau}\times\frac{-i(\omega_0-\omega)-1/\tau}{-i(\omega_0-\omega)-1/\tau}$$

$$= f_0\frac{i(\omega_0-\omega)+1/\tau}{(\omega_0-\omega)^2+1/\tau^2} \qquad (28.7)$$

The real part of $\tilde{f}(\nu)$ is therefore

$$\text{Re}\,\tilde{f}(\nu) = \frac{f_0/\tau}{(\omega_0-\omega)^2+1/\tau^2} = \frac{f_0\tau}{(\omega_0-\omega)^2\tau^2+1} \qquad (28.8)$$

which is essentially the same as in eqn 28.2 with the exception that the frequency $2\pi\nu = \omega$ has been replaced by $\omega_0 - \omega$.



Sketch 28.3