CHAPTER ONE: MATHEMATICS

March 8, 2018

[DRAFT 16]

This is expected to be the penultimate version.

Contents

Chapter One: Mathematics

1.1 Introduction, Nomenclature and Conventions

Introduction

The approach taken here is that of applied mathematics: detailed proofs are eschewed in favor of describing tools that are useful to scientists and engineers. As noted by Kyrala [1] "Scientists and engineers are not usually interested in presentations which devote 90% of the space to enlarging the class of admissible functions by 1%". Derivations are however given when these provide physical insight and/or connections to other material. The coverage probably exceeds that needed for most current relaxation applications but is given (i) as background for the derivation of some results that are relevant to relaxation phenomena; (ii) to satisfy basic intellectual curiosity; (iii) to present mathematics that are currently not common but might be in the future. The style of writing has been influenced by that used by Pais in his history of particle physics [2] and his authorative biography of Einstein [3], and also by the advice for clear communication given by the late TV News anchor in the USA in the 1970's, Walter Cronkite: he said approximately "avoid as much as possible qualifying adverbs and adjectives such as 'somewhat', 'very', 'extremely'". I also eschew the subjunctive as much as possible.

Most of the references are not recent, for three reasons: (i) the mathematics has not changed in the last several hundred years; (ii) recent text books dilute the material far too much for them to be useful references as opposed to good teaching aids; (iii) the classic texts can be downloaded for free or purchased at low cost online for those who wish to delve deeply into the mathematics.

Nomenclature

Exponential functions with argument *A* are written as exp (*A*). Natural logarithms are used throughout (with a few exceptions) and are written as ln (base 10 logarithms are denoted by log). Algebraic powers are written explicitly; for example square roots are written as fractional $\frac{1}{2}$ exponents rather than $\sqrt{\ }$. Averages are denoted by angular brackets, <...>, and sets of variables or other mathematical objects are enclosed in braces, {…}. Vectors are denoted by boldface arrowed fonts (e.g. $\vec{\mathbf{F}}$), tensors by boldface fonts without arrows (e.g. **F**), matrices by curved brackets (…), and determinants by straight braces $|...|$. Angles are expressed in radians. Complex functions are denoted by an asterisk F^* and complex conjugates are denoted by a dagger $F^{\dagger}$. Real parts of a complex function are denoted by a prime and the imaginary components by a double prime, for example $P^*(iz) = P'(x,y) + iP''(x,y)$. The types of argument(s) for named functions are indicated by *x* or *y* for real arguments and *iz* for complex ones.

Many additional properties of the mathematical functions discussed here are given in tabulations such as those in Abramowitz and Stegun [4]. Several books devoted to physical applications of mathematics or to special mathematical topics such as complex functions give more detailed expositions [6-9]. There are also a large number of websites that can be found by search engines.

Conventions

The mathematics and applications of complex numbers have an inherent ambiguity associated with the positive and negative signs of the square root of (–1). In the phenomenological world of classical relaxation the sign of the square root determines the physically irrelevant direction of rotation in the complex plane and the ambiguity is resolved by a sign convention. Unfortunately, electrical engineers use a different convention than everybody else, namely a positive sign for the argument of the complex exponential, exp($j\omega t$). Scientists and mathematicians use the convention that ensures that the charge on a capacitor lags behind the applied voltage that in turn implies that the imaginary component of the complex refractive index is negative (see Chapter 2 for details). This in turn enforces a negative sign for the argument of the complex exponential, exp($-i\omega t$), in order that exponential attenuation occurs in an absorbing medium. This is the convention adopted here. These conventions are distinguished by electrical engineers writing $\left|(-1)^{1/2}\right|$ as j and everyone else writing it as i. An excellent discussion of the merits of using i is given in [5].

1.2 Elementary Results

1.2.1 Solution of a Quadratic Equation

For

$$z^2 + a_1 z + a_0 = 0 \tag{1.1}$$

the solutions are

$$z = \frac{-a_1 \pm \left(a_1^2 - 4aa_0\right)^{1/2}}{2}. \tag{1.2}$$

There are two real solutions for $\left(a_1^2 - 4aa_0\right) > 0$ and two complex conjugate roots for $\left(a_1^2 - 4a_0 a_2\right) < 0$.

1.2.2 Solution of a Cubic Equation

For

$$z^3 + a_2 z^2 + a_1 z + a_0 = 0 \tag{1.3}$$

define

$$\begin{aligned} q &\equiv a_1/3 - a_2^2/9, \\ r &\equiv \left(a_1 a_2 - 3a_0\right)/6 - a_2^2/9, \\ s_1 &\equiv \left[r + \left(q^3 - r^2\right)^{1/2}\right]^{1/2}, \\ s_2 &= \left[r - \left(q^3 - r^2\right)^{1/2}\right]^{1/2}. \end{aligned} \tag{1.4}$$

The three solutions are then

$$z_1 = (s_1 + s_2) - a_2/3,$$
$$z_2 = -\tfrac{1}{2}(s_1 + s_2) - a_2/3 + i\left(3^{1/2}/2\right)(s_1 - s_2), . \tag{1.5}$$
$$z_2 = -\tfrac{1}{2}(s_1 + s_2) - a_2/3 - i\left(3^{1/2}/2\right)(s_1 - s_2).$$

The three roots are related by

$$z_1 + z_2 + z_3 = -a_2,$$
$$z_1 z_2 + z_1 z_3 + z_2 z_3 = a_1, \tag{1.6}$$
$$z_1 z_2 z_3 = -a_0.$$

The types of roots are:

$$q^3 + r^2 > 0 \qquad \text{(one real and a pair of complex conjugates)},$$
$$q^3 + r^2 = 0 \qquad \text{(all real of which at least two are equal)}, \tag{1.7}$$
$$q^3 + r^2 < 0 \qquad \text{(all real)}.$$

1.2.3 Arithmetic and Geometric Series

Arithmetic Series:

$$\sum_{k=1}^{n} k = \frac{n(n+1)}{2}. \tag{1.8}$$

Geometric Series:

$$\sum_{n=0}^{N-1} x^n = \frac{1 - x^N}{1 - x} \ \left(|x| < 1\right). \tag{1.9}$$

Special cases:

$$\sum_{n=m}^{\infty} x^n = \frac{x^m}{1 - x} \quad \left(|x| < 1\right), \tag{1.10}$$

$$\sum_{n=1}^{\infty} x^n = \frac{x}{1 - x} \quad \left(|x| < 1\right), \tag{1.11}$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1 - x} \quad \left(|x| < 1\right). \tag{1.12}$$

1.2.4 Full and Partial Derivatives

The relation between the full differential and partial differential of a function *f*(*x*,*y*) is

$$\frac{df}{dx}=\left(\frac{\partial f}{\partial x}\right)_y+\left(\frac{\partial f}{\partial y}\right)_x\left(\frac{dy}{dx}\right) \tag{1.13}$$

or

$$df=\left(\frac{\partial f}{\partial x}\right)_y dx+\left(\frac{\partial f}{\partial y}\right)_x dy\ , \tag{1.14}$$

from which

$$\left(\frac{\partial y}{\partial x}\right)_f=\frac{-\left(\partial f/\partial x\right)_y}{\left(\partial f/\partial y\right)_x}=\left(\frac{\partial x}{\partial y}\right)_f^{-1}\ . \tag{1.15}$$

Also,

$$\left(\frac{\partial f}{\partial x}\right)_y=\left(\frac{\partial f}{\partial w}\right)_y\left(\frac{\partial w}{\partial x}\right)_y \tag{1.16}$$

and

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x=\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\ . \tag{1.17}$$

1.2.5 Differentiation of Definite Integrals

Liebnitz's theorem

$$\frac{d}{dy}\int_{a(y)}^{b(y)} f\left(x,y\right)dx=\int_{a(y)}^{b(y)}\frac{\partial f\left(x,y\right)}{\partial y}dx+f\left(b,y\right)\frac{db}{dy}-f\left(a,y\right)\frac{da}{dy}\ . \tag{1.18}$$

1.2.6 Integration by Parts

Integration of

$$d\left[F\left(x\right)G\left(x\right)\right]=FdG+GdF \tag{1.19}$$

yields

$$F(x)G(x) = \int F\left(\frac{dG}{dx}\right)dx + \int G\left(\frac{dF}{dx}\right)dx\,, \tag{1.20}$$

so that

$$\int F\left(\frac{dG}{dx}\right)dx = F(x)G(x) - \int G\left(\frac{dF}{dx}\right)dx\,. \tag{1.21}$$

1.2.7 Binomial Expansions

The coefficients of $c^{n-m}x^m$ in the expansion of $(x \pm c)^n$ are given by

$$(\pm 1)^m \binom{n}{m} = \frac{(\pm 1)^m n!}{m!(n-m)!}; \qquad \binom{n}{m} \equiv \frac{n!}{m!(n-m)!}, \tag{1.22}$$

where (!) signifies the factorial function (see §1.3.1). For example the binomial expansion of $(x\text{-}1)^4$ is $x^4 - 4x^3 + 6x^2 - 4x + 1$.

1.2.8 Partial Fractions

For the generic function $1/\Pi_i\left(x - x_i\right)$ the coefficient of $(x - x_j)^{-1}$ is $1/\Pi_{i \neq j}\left(x_j - x_i\right)$ so that

$$\frac{f(x)}{\left[\Pi_i\left(x - x_i\right)\right]} = \sum_j \left[\frac{f\left(x_j\right)}{\Pi_{i \neq j}\left(x_j - x_i\right)\left(x - x_i\right)}\right], \tag{1.23}$$

provided the denominator does not have repeated roots. For example

$$\begin{aligned}\frac{x + a}{\left(x - x_1\right)\left(x - x_2\right)} &= \frac{x_1 + a}{\left(x - x_1\right)\left(x_1 - x_2\right)} + \frac{x_2 + a}{\left(x_2 - x_1\right)\left(x - x_2\right)} \\ &= \frac{1}{\left(x_1 - x_2\right)}\left[\frac{x_1 + a}{\left(x - x_1\right)} - \frac{x_2 + a}{\left(x - x_2\right)}\right]\end{aligned}\,. \tag{1.24}$$

For repeated roots

$$\frac{1}{(x - d)^n} = \sum_{m=1}^{n} \frac{A_m x^{m-1}}{(x - d)^m}\,. \tag{1.25}$$

The coefficients A_m are all proportional to $[x^{n-1}(x\text{-}d)]^{-1}$ and the numerical coefficients of x^{m-1} are those for the binomial expansion of $(x\text{-}1)^{n-1}$. For example

$$\frac{1}{(x-d)^4}=\left[\frac{1}{d^3(x-d)}\right]\left[1-\frac{3x}{(x-d)}+\frac{3x^2}{(x-d)^2}-\frac{x^3}{(x-d)^3}\right]. \tag{1.26}$$

1.2.9 Coordinate Systems in Three Dimensions

The location of a point in three dimensional space can be specified in several ways, according to the coordinate system chosen. Examples:

Cartesian Coordinates {x,y,z}

These are mutually orthogonal linear axes and are sometimes denoted by {x_1,x_2,x_3} or similar. The direction of the z–axis is defined by the right hand rule for right handed Cartesian coordinates: if rotation of the x-axis towards the y–axis is seen as counterclockwise then the z axis points towards the viewer.

Cylindrical Coordinates {r,φ,z}

Retain the Cartesian z–axis but specify the location in the x–y plane in terms of circular coordinates r and φ:

$$\begin{aligned} r^2 &= x^2+y^2,\\ x &= r\cos\varphi,\\ y &= r\sin\varphi, \end{aligned} \tag{1.27}$$

where φ is the angle between the positive x-axis and the radius joining the origin with the projection of the point onto the x–y plane.

Spherical Coordinates {r,φ,θ}

Retain r and φ from the cylindrical system but specify the z position by the angle θ between the line in the x–y plane joining the origin with the projected point, and the line joining the origin with the point itself:

$$\begin{aligned} r^2 &= x^2+y^2+z^3,\\ x &= r\sin\theta\cos\varphi,\\ y &= r\sin\theta\sin\varphi,\\ z &= r\cos\theta. \end{aligned} \tag{1.28}$$

1.3 Advanced Functions

Note: some of the material in this section refers to, or depends on, results that are discussed in section §1.8 on complex variables.

1.3.1 Gamma and Related Functions

The *gamma function* $\Gamma(z)$ is a generalization of the factorial function $(x–1)!$ to complex variables, to which it reduces when z is a positive real integer x:

$$\Gamma(z) = \int_0^\infty t^{z-1} \exp(-t)\, dt \qquad [\mathrm{Re}(z) > 0]. \tag{1.29}$$

For real *x*

$$\Gamma(x) = (x-1)!. \tag{1.30}$$

$\Gamma(z)$ has the same recurrence formula as the factorial, $\Gamma(z+1) = z\Gamma(z)$, and has singularities at negative real integers [$1/\Gamma(x)$ is oscillatory about zero for $x<0$]. A special value is obtained from $\Gamma(x)\Gamma(1-x)=\pi/\sin(\pi x)$: $\Gamma(1/2) = (-1/2)! = \pi^{1/2}$. For large z $\Gamma(z)$ is given by *Stirling's approximation*:

$$\lim_{z\to\infty} \Gamma(z) = (2\pi)^{1/2} z^{z-1/2} \exp(-z) \qquad |\arg(z)| < \pi\,. \tag{1.31}$$

The *beta function* $B(z,w)$ is

$$\begin{aligned} B(z,w) \equiv \frac{\Gamma(z)\Gamma(w)}{\Gamma(z+w)} &= \int_0^1 z^{z-1}(1-t)^{w-1} dt = \int_0^\infty t^{z-1}(1+t)^{-z-w}\, dt \\ &= 2\int_0^{\pi/2} [\sin(t)]^{2z-1} [\cos(t)]^{2w-1}\, dt, \qquad [\mathrm{Re}(z), \mathrm{Re}(w) > 0], \end{aligned} \tag{1.32}$$

and the *Psi or Digamma function* is [4]

$$\begin{aligned} \psi(z) = \frac{d \ln\Gamma(z)}{dz} = \frac{1}{\Gamma(z)}\frac{d\Gamma(z)}{dz} &= \int_0^\infty \left[\frac{\exp(-t)}{t} - \frac{\exp(-zt)}{1-\exp(-t)}\right] dt \qquad [\mathrm{Re}(z) > 0] \\ &= \int_0^\infty \left[\exp(-t) - \frac{1}{(1+t)^z}\right] \frac{dt}{t}. \end{aligned} \tag{1.33}$$

The *incomplete gamma function* is defined for real variables *x* and *a* as

$$G(x,a) = \frac{1}{\Gamma(x)} \int_0^a t^{x-1} \exp(-t)\, dt\,. \tag{1.34}$$

1.3.2 Error Function

The *error function* erf(z) is an integral of the Gaussian function discussed in §1.4.1:

$$\mathrm{erf}(z) = \frac{2}{\pi^{1/2}} \int_0^z \exp(-t^2)\, dt\,. \tag{1.35}$$

The *complementary error function* erfc(z) is

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = \frac{2}{\pi^{1/2}} \int_z^{\infty} \exp\left(-t^2\right) dt\,. \tag{1.36}$$

The functions erf and erfc commonly occur in diffusion problems. An occasionally encountered but apparently unnamed function is

$$\begin{aligned} w(z) \equiv \exp\left(-z^2\right)\operatorname{erfc}(-iz) &= \frac{i}{\pi}\int_{-\infty}^{+\infty} \frac{\exp\left(-t^2\right)}{z-t}\,dt = \frac{i}{\pi}\int_0^{\infty} \frac{\exp\left(-t^2\right)}{z^2-t^2}\,dt \\ &= \exp\left(-z^2\right)\left[1+\frac{2i}{\pi^{1/2}}\right]\int_0^z \exp\left(t^2\right) dt. \end{aligned} \tag{1.37}$$

1.3.3 Exponential Integrals

The *exponential integrals* $E_n(z)$ and $Ei(z)$ are (n an integer)

$$E_n(z) = \int_1^{\infty} \frac{\exp(-zt)}{t^n}\,dt\,, \tag{1.38}$$

$$Ei(x) = -P\int_{-x}^{+\infty} \frac{\exp(-t)}{t}\,dt = P\int_{-\infty}^{+x} \frac{\exp(-t)}{t}\,dt\,, \tag{1.39}$$

where P denotes the Cauchy principal value (see §1.8.4).

1.3.4 Hypergeometric Function

This function $F(a,b,c,z)$ is the solution to the differential equation

$$\left\{z(1-z)d_z^2 + \left[c-(a+b+1)z\right]d_z - ab\right\}F(z) = 0\,, \tag{1.40}$$

where d_z^n denotes the n^{th} derivative (the superscript is omitted for n=1). Its series expansion is

$$\frac{\Gamma(a)\Gamma(b)}{\Gamma(c)}F(a,b,c,z) = \sum_{k=0}^{\infty}\left[\frac{\Gamma(a+k)\Gamma(b+k)}{k!\,\Gamma(c+k)}\right]z^k \quad |z|<1. \tag{1.41}$$

Its *Barnes Integral* definition is

$$\frac{\Gamma(a)\Gamma(b)}{\Gamma(c)}F(a,b,c,z)=\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty}\left[\frac{\Gamma(a+s)\Gamma(b+s)\Gamma(-s)}{\Gamma(c+s)}\right](-z^{s})\,ds\,, \tag{1.42}$$

where the path of integration passes to the left around the poles of Γ(–*s*) and to the right of the poles of Γ(*a*+*s*)Γ(*b*+*s*). The integral definition of *F*(*a*,*b*,*c*,*z*) is preferred over the series expansion because the former is analytic and free of singularities in the *z*-plane cut from *z* = 0 to *z* = +∞ along the non-negative real axis, whereas the series expansion is restricted to $|z|<1$. The hypergeometric function has three regular singularities at *z* = 0, *z* = 1, and *z* = +∞. Since solutions to most second order linear homogeneous differential equations used in science rarely have more than three regular singularities, most named functions are special cases of *F*(*a*,*b*,*c*,*z*). Examples:

$$(1-z)^{-a}=F(a,b,b,z)\,, \tag{1.43}$$

$$-(1/z)\ln(1-z)=F(1,1,2,z)\,, \tag{1.44}$$

$$\exp(z)=\lim_{a\to\infty}F(a,b,b,z/a)\,. \tag{1.45}$$

1.3.5 Confluent Hypergeometric Function

This function *F*(*a*,*c*,*z*) is obtained by replacing *z* with *z/b* in *F*(*a*,*b*,*c*,*z*) so that the singularity at *z* = 1 is replaced by one at *z* = *b*. For *b*→∞ *F*(*a*,*c*,*z*) acquires an irregular singularity at *z* = ∞ formed from the confluence of the regular singularities at *z* = *b* and *z* = ∞, so that

$$F(a,c,z)=\lim_{b\to\infty}(a,b,c,z/b)\,. \tag{1.46}$$

The function *F*(*a*,*c*,*z*) is also seen to be a solution to [cf. eq. (1.40)]

$$\left[zd_z^2+(c-z)d_z-a\right]F(z)=0 \tag{1.47}$$

and the Barnes integral representation is

$$\frac{\Gamma(a)}{\Gamma(c)}F(a,c,z)=\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty}\left[\frac{\Gamma(a+s)\Gamma(-s)}{\Gamma(c+s)}\right](-z)^{s}\,ds\,, \tag{1.48}$$

that can be shown to be equivalent to

$$\frac{\Gamma(c-a)\Gamma(a)}{\Gamma(c)}F(c-a,c,-z)=\int_0^1\exp(-zt)\,t^{c-a-1}(1-t)^{a-1}\,dt\,, \tag{1.49}$$

where $F(c-a,c,-z)=\exp(-z)F(a,c,z)$.

1.3.6 Williams-Watt Function

This function probably holds the record for its number of names: Williams-Watt (WW), Kohlrausch-Williams-Watt (KWW), fractional exponential, stretched exponential, and probably others (WilliamsWatt is used here). The function is

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad (0 < \beta \le 1). \tag{1.50}$$

It is the same as the Weibull reliability distribution described below [eq. (1.91)] but with different values of β. The distribution of relaxation (or retardation) times $g(\tau)$ used in relaxation applications is defined by

$$\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] = \int_{-\infty}^{+\infty} g(\ln\tau)\exp\left(-\frac{t}{\tau}\right) d\ln\tau\,, \tag{1.51}$$

but cannot be expressed in closed form. The mathematical properties of the WW function have been discussed in detail by Montrose and Bendler [11], and of the many properties described there just one is singled out here: in the limit $\beta \to 0$ the distribution $g_{WW}(\ln\tau)$ approaches the log-gaussian form

$$\lim_{\beta\to 0} g(\ln\tau) = \left\{1/\left[(2\pi)^{1/2}\sigma\right]\right\}\exp\left\{-\left[\ln\left(\tau/\langle\tau\rangle\right)\right]^2/\sigma^2\right\} \qquad (\beta = 1/\sigma). \tag{1.52}$$

1.3.7 Bessel Functions

Bessel functions are solutions to the differential equation

$$\left[z\partial_z\left(z\partial_z\right) + \left(z^2 - \nu^2\right)\right]y = \left[z^2\partial_z^2 + z\partial_z + \left(z^2 - \nu^2\right)\right]y = 0\,, \tag{1.53}$$

where v is a constant corresponding to the v^{th} order Bessel function solution, and there are Bessel functions of the 1st, 2nd and 3rd kinds for each order. This multiplicity of forms makes Bessel functions appear more intimidating than they are, and to make matters worse several authors have used their own definitions and nomenclature (see ref [4] for example). Bessel functions frequently arise in problems that have cylindrical symmetry because in cylindrical coordinates $\{r,\varphi,z\}$ Laplace's partial differential equation $\nabla^2 f = 0$ (see §1.7) is

$$\left[\frac{1}{r}\partial_r\left(r\partial_r\right) + \left(\frac{1}{r^2}\partial_\theta^2\right) + \partial_z^2\right]y = 0\,. \tag{1.54}$$

If a solution to eq. (1.54) of the form $f=R(r)\Phi(\theta)Z(z)$ is assumed (separation of variables) then the ordinary differential equation for R becomes

$$\left[rd_r\left(rd_r\right)\right]R + \left(kr^2 - \nu^2\right) = 0\,, \tag{1.55}$$

that is seen to be the same as eq. (1.53). The constant k usually depends on the boundary conditions of a problem and can sometimes depend on the zeros of the Bessel function J_ν (see below). Bessel functions of the 1st kind and of order ν are written as $J_\nu(x)$ and Bessel functions of the 2nd kind are written as $J_{-\nu}(x)$. When ν is not an integer $J_\nu(x)$ and $J(x)_{-\nu}$ are independent solutions and the general solution is a linear combination of them:

$$Y_\nu(x) = \frac{\cos(\nu\pi) J_\nu(x) - J_{-\nu}(x)}{\sin(\nu\pi)} \qquad (\text{noninteger}\, \nu), \tag{1.56}$$

where the trigonometric terms are chosen to ensure consistency with the solutions for integer $\nu = n$ for which $J_\nu(x)$ and $J_{-\nu}(x)$ are not independent:

$$J_{-n}(x) = (-1)^n J_n(x). \tag{1.57}$$

Also

$$J_{n-1} + J_{n+1} = \left(\frac{2n}{x}\right) J_n. \tag{1.58}$$

Bessel functions $H_\nu(x)$ of the 3rd kind are defined as

$$\begin{aligned} H_\nu^1(x) &= J_\nu(x) + iY_\nu(x), \\ H_\nu^2(x) &= J_\nu(x) - iY_\nu(x), \end{aligned} \tag{1.59}$$

and are sometimes called Hankel functions.

Bessel functions are oscillatory and in the limit $x\to\infty$ are equal to circular trigonometric functions. This is apparent from eq. (1.53) for the real variable x after it has been divided through by x^2 to give $\left[\partial_x^2 + (1/x)\partial_x + (1 - \nu^2/x^2)\right] y = 0$ - for $x\to\infty$ this becomes $\left[\partial_x^2 + 1\right] y = 0$ whose solution is [$a\sin(x)$ + $b\cos(x)$].

1.3.8 Orthogonal Polynomials

Polynomials $P_p(x)$ characterized by a parameter p are orthogonal within an interval (a,b) if

$$\int_a^b P_m(x) P_n(x)\, dx = \delta_{mn} \equiv \begin{cases} 1(m = n) \\ 0(m \neq n) \end{cases}, \tag{1.60}$$

where δ_{mn} is the Kronecker delta. Examples of such orthogonal polynomials are:

1.3.8.1 Legendre

Legendre polynomials $P_\ell(x)$ for real arguments are solutions to the differential equation

$$\left[\left(1-x^2\right)d_x^2-2xd_x+\ell\left(\ell+1\right)\right]y=0 \quad \left(\ell \text{ a positive integer}\right), \tag{1.61}$$

and often occur as solutions to problems with spherical symmetry for which the coordinates of choice are clearly the spherical ones $\{r,\varphi,\theta\}$. Orthogonality is ensured only if $0<|x|\le 1$. The simplest way to derive the first few Legendre coefficients is to apply the Rogrigues generating function

$$P_\ell\left(x\right)=\frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}\left(x^2-1\right)^\ell, \tag{1.62}$$

that becomes tedious for high values of ℓ although this rarely occurs for physical applications. The first four Legendre polynomials are (for $x\le 1$) $P_0=1$; $P_1=1$; $P_2=(3x^2–1)/2$, and $P_3=(5x^3–3x)/2$.

Associated Legendre polynomials $P_\ell^m\left(x\right)$ are solutions to the differential equation

$$\left[\left(1-x^2\right)d_x^2-2xd_x+\left\{\ell\left(\ell+1\right)-\frac{m^2}{1-x^2}\right\}\right]y=0 \quad \left(\ell \text{ a positive integer, } m^2\le\ell^2\right), \tag{1.63}$$

and are related to $P_\ell\left(x\right)$ by

$$P_\ell^m\left(x\right)=\left(1-x^2\right)^{m/2}d_x^m P_\ell\left(x\right). \tag{1.64}$$

The parameter m takes on values $-\ell,-\ell+1,...0,...\ell-1,\ell$.

Spherical harmonics $U(\varphi,\theta)$ are defined by

$$U\left(\varphi,\theta\right)=P_\ell^m\left(\cos\theta\right).\begin{cases}\sin\left(m\varphi\right)\\ \cos\left(m\varphi\right)\end{cases}, \tag{1.65}$$

where $|x|\le 1$ is automatic and orthogonality is ensured. The most important equation in physics for which spherical harmonics are solutions is probably the Schrodinger equation for the hydrogen atom. Indeed the mathematical structure of the periodic table of the elements is essentially that of spherical harmonics, the most significant difference between the two being that the first transition series occurs in the 4th row rather than in the 3rd. Other deviations occur at the bottom of the periodic table because of relativistic effects.

1.3.8.2 Laguerre

Laguerre polynomials $L_n(x)$ are solutions to

$$\left[xd_x^2+\left(1-x\right)d_x+n\right]y=0, \tag{1.66}$$

and have the generating function

$$L_n(x) = \left(\frac{1}{n!}\right)\exp(x)\left\{d_x^n\left[x^n \exp(x)\right]\right\} \tag{1.67}$$

and recursion relations

$$\begin{aligned}
&\frac{dL_{n+1}}{dx} - \frac{dL_n}{dx} + L_n = 0, \\
&x\left(\frac{dL_n}{dx}\right) - nL_n + nL_{n-1} = 0, \\
&(n+1)L_{n+1} - (2n+1-x)L_n + nL_{n-1} = 0.
\end{aligned} \tag{1.68}$$

The first three Laguerre polynomials are $L_0=1$; $L_1=1–x$; $L_2=1–2x+x^2/2$.

1.3.8.3 Hermite

Hermite polynomials $H_n(x)$ are solutions to the equation

$$\left[d_x^2 - x^2 d_x + (2n+1)\right]H_n = 0 \tag{1.69}$$

and have the recursion relations

$$\begin{aligned}
&\frac{dH_n}{dx} - 2nH_{n-1} = 0, \\
&H_{n+1} - 2xH_n + 2nH_{n-1} = 0.
\end{aligned} \tag{1.70}$$

$H_n(r)$ functions are proportional to the derivatives of the error function:

$$H_n(x) = (-1)^n \left(\frac{\pi^{1/2}}{2}\right)\exp\left(x^2\right)\left[\frac{\partial^{n+1}}{\partial x^{n+1}}\operatorname{erf}(x)\right], \tag{1.71}$$

and are solutions to the radial component of the Schroedinger equation for the hydrogen atom. Also $H_n(-x) = (-1)^n H_n(x)$. The first five Hermite polynomials are $H_0 = 1$; $H_1 = 2x$; $H_2 = 4x^2–2$; $H_3=8x^3 – 12x$; $H_4=16x^4–48x^2+12$.

1.3.9 Sinc Function

The *sinc function* is

$$\operatorname{sinc}(x) \equiv \frac{\sin(x)}{x}. \tag{1.72}$$

The value of $\operatorname{sinc}(0) = 1 \neq \infty$ arises from $\lim_{x\to 0}\left[\sin(x)\right] = x$. The sinc function is proportional to the Fourier transform of the rectangle function

$$\begin{aligned}\mathrm{Rect}(x) &= 0 && (x < -\tfrac{1}{2})\\ &= 1 && (-\tfrac{1}{2} \le x \le \tfrac{1}{2})\\ &= 0 && (x > \tfrac{1}{2}),\end{aligned} \tag{1.73}$$

and arises in the study of optical effects of rectangular apertures. The function $\mathrm{sinc}^2(x)$ is proportional to the Fourier transform of the triangular function

$$\begin{aligned}\mathrm{Triang}(x) &= 0 && (x < -\tfrac{1}{2})\\ &= 1 + 2x && (-\tfrac{1}{2} \le x \le 0)\\ &= 1 - 2x && (0 \le x \le +\tfrac{1}{2})\\ &= 0 && (x > +\tfrac{1}{2}).\end{aligned} \tag{1.74}$$

Relations between the parameters defining the width and height of the Rect and Triang functions and the parameters of the sinc and sinc^2 functions are given in [5].

1.3.10 Airy Function

The *Airy function* $\mathrm{Ai}(x)$ is defined in terms of the Bessel function $J_1(x)$ as

$$\mathrm{Ai}(x) \equiv \left[\left(\frac{2J_1(x)}{x}\right)\right]^2, \tag{1.75}$$

that is the circular aperture analog of $\mathrm{sinc}^2(x)$. Its properties are used to define the Rayleigh criterion for optical resolution for circular apertures. The relation between the parameters of the Airy function and the diameter of the circular aperture is also given in [5].

1.3.11 Struve Function

The *Struve function* $H_\nu(z)$ is part of the solution to the equation

$$\left[z^2 d_z^2 + z d_z + \left(z^2 - \nu^2\right)\right] f = \frac{4(z/2)^{\nu+1}}{\pi^{1/2}\Gamma(\nu + \tfrac{1}{2})}\ , \tag{1.76}$$

where $f(z) = aJ_\nu(z) + bY_\nu(z) + H_\nu(z)$. Its recurrence relations are

$$\begin{aligned}H_{\nu-1} + H_{\nu+1} &= \left(\frac{2\nu}{z}\right) H_\nu + \frac{(z/2)^{\nu+1}}{\pi^{1/2}\Gamma(\nu + \tfrac{3}{2})},\\ H_{\nu-1} - H_{\nu+1} &= 2\frac{dH_\nu}{dz} - \frac{(z/2)^{\nu+1}}{\pi^{1/2}\Gamma(\nu + \tfrac{3}{2})}.\end{aligned} \tag{1.77}$$

For positive integer values of $v = n$ and real arguments the functions $H_n(x)$ are oscillatory with amplititudes that decrease with increasing x [4], as expected from their relation to the Bessel function $J_{n+1/2}(x)$ for positive integer n:

$$H_{-(n+1/2)}(x) = (-1)^n J_{n+1/2}(x). \tag{1.78}$$

1.4 Elementary Statistics

Much of the following material is distilled from reference [10] that gives an excellent account of statistics at the basic level discussed here.

1.4.1 Probability Distribution Functions

1.4.1.1 Gaussian

The *Gaussian* or *Normal* distribution $N(x)$ is

$$N(x) = \frac{1}{(2\pi)^{1/2}\sigma}\exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]. \tag{1.79}$$

The name Normal distribution is used because $N(x)$ specifies the probability of measuring a randomly (normally) scattered variable x with a *mean* (average) μ and a breadth of scatter parameterized by the standard deviation σ. The n^{th} moments or averages of the n^{th} powers of x are

$$\langle x^n \rangle = \frac{1}{(2\pi)^{1/2}\sigma}\int_{-\infty}^{+\infty} x^n \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]dx. \tag{1.80}$$

It is easily verified that $\langle x \rangle = \mu$ by first changing the variable from x to $y = x - \mu$ and then recognizing that $\int_{-\infty}^{+\infty} y^n \exp(-a^2 y^2)\,dy$ is zero for odd values of n. Corrections are applied to the idealized formula eq. (1.80) for a finite number n of observations. The estimate for σ, traditionally given the symbol s, is

$$s^2 = \frac{\sum_{i=1}^{n}\left(x_i - \langle x \rangle\right)^2}{n-1}, \tag{1.81}$$

compared with

$$\sigma^2 = \lim_{n\to\infty}\left[\frac{\sum_{i=1}^{n}(x_i-\mu)^2}{n}\right], \tag{1.82}$$

where the square of the standard deviation σ^2 is the *variance*. The probability p of finding a variable between $\mu \pm a$ is

$$p = \operatorname{erf}\left(\frac{a}{\sigma 2^{1/2}}\right) = \operatorname{erf}\left(\frac{q}{2^{1/2}}\right). \tag{1.83}$$

Thus the probabilities of observing values within $\pm\sigma$, $\pm 2\sigma$ and $\pm 3\sigma$ of the mean are 68.0%, 95.4% and 99.9% respectively. The distribution in s^2 for repeated sets of observations is the χ^2 or "chi-squared" distribution discussed below.

If a limited number of observations of data that have an underlying distribution with variance σ^2 produce an estimate $\bar{x}$ of the mean, and these sets of observations are repeated n times, then it can be proved that the distribution in $\bar{x}$ is normal and that the standard deviation of the distribution of measured mean values is $\sigma n^{-1/2}$. The quantity $\sigma n^{-1/2}$ is often called the standard error in x to distinguish it from the standard deviation σ of the distribution in x. The inverse proportionality to $n^{1/2}$ is a quantification of the intuitive idea that more precise means result when the number of repetitions n increases.

For a function $F(x_i)$ of multiple variables $\{x_i\}$, each of which is normally distributed and for which the standard deviations σ_i (or their estimates s_i) are known, the variance in $F(x_i)$ is given by

$$\sigma_F^2 = \sum_i \left(\frac{\partial F}{\partial x_i}\right)^2 \sigma_i^2 \approx \sum_i \left(\frac{\partial F}{\partial x_i}\right)^2 s_i^2 . \tag{1.84}$$

If F is a linear function of the variables $F = \sum_i a_i x_i$ then σ_F^2 is the a_i weighted sum of the individual variances. If F is the product of functions with variables x_i and then

$$\left(\frac{\sigma_F}{\langle F\rangle}\right)^2 = \sum_i \left(\frac{\sigma_i}{\langle x_i\rangle}\right)^2 . \tag{1.85}$$

Distributions other than the Gaussian also arise but the *central limit theorm* asserts that in the limit $n\to\infty$ the distribution in sample averages obtained from *any* underlying distribution of individual data is Gaussian.

1.4.1.2 Binomial

The *binomial distribution* $B(r)$ expresses the probability of obtaining r successes in n trials given that the individual probability for success is p:

$$B(r)=\left(\frac{n!}{r!(n-r)!}\right)p^r(1-p)^{n-r}. \quad (1.86)$$

For large n the function $B(r)$ approximates the Gaussian function $N(x)$ providing p is not too close to 0 or 1 [10]. For example the approximation is good for $n > 20$ if $0.3 < p < 0.7$.

1.4.1.3 Poisson

The *Poisson distribution* $P(x)$ is defined as

$$P(x)=\left(\frac{\mu^x\exp(-\mu)}{x!}\right)\quad(\mu>0). \quad (1.87)$$

The mean and the variance of the Poisson distribution are both equal to μ so that the standard deviation is $\mu^{1/2}$. The Poisson distribution is useful for describing the number of events per unit time and is therefore relevant to relaxation phenomena. If the average number of events per unit time is v then in a time interval t there will be vt events on average and the number x of events ocurring in time t follows the Poisson distribution with $\mu = vt$:

$$P(x,t)=\left(\frac{(vt^x)\exp(-vt)}{x!}\right). \quad (1.88)$$

1.4.1.4 Exponential

The *Exponential distribution* $E(x)$ is

$$E(x)=\begin{cases}\lambda\exp(-\lambda x) & x>0\\ 0 & x\le 0\end{cases}. \quad (1.89)$$

1.4.1.5 Weibull

The *Weibull distribution* $W(t)$ is

$$W(t)=m\lambda t^{m-1}\exp(-\lambda t^m)\qquad(m>1). \quad (1.90)$$

The Weibull reliability function $R(t)$ is

$$R(t)=\int_0^t W(t')dt'=\exp(-\lambda t^m), \quad (1.91)$$

where $R(t)$ is often used for probabilities of failure. The similarity to the WW function (§1.3.6) is evident.

1.4.1.6 Chi-Squared

For repeated sets of n observations from an underlying distribution with variance σ^2 the variance estimates s^2 obtained from each set will exhibit a scatter that follows the χ^2 distribution (see also §1.4.1.1). The quantity χ^2 is actually a variable rather than a function,

$$\chi^2 \equiv \frac{(n-1)s^2}{\sigma^2}. \tag{1.92}$$

The nomenclature χ^2 rather than χ is used to emphasize that χ^2 is positive definite because $(n–1)$, s^2 and σ^2 are all positive definite. Note that very small or very large values of χ^2 correspond to large differences between s and σ, indicating that the probability of them being equal is small.

The χ^2 distribution is referred to here as $P_v\left(\chi^2\right)$ and is defined by [4]

$$P_\nu\left(\chi^2\right) \equiv \left(\frac{1}{2^{\nu/2}\Gamma(\nu/2)}\right)\int_0^{\chi^2} t^{(\nu/2-1)} \exp\left(\frac{-t}{2}\right) dt, \tag{1.93}$$

where ν is the number of degrees of freedom The term outside the integral in eq. (1.93) ensures that these probabilities integrate to unity in the limit $\chi^2 \to \infty$. Equations (1.34) and (1.93) indicate that $P_v\left(\chi^2\right)$ is equivalent to the incomplete gamma function $G(x,a)$ [4]. $P_\nu(\chi^2)$ is the probability that s^2 is less than χ^2 when there are n degrees of freedom; it is also referred to as a confidence limit α so that $(1–\alpha)$ is the probability that s^2 is greater than χ^2. The integral in eq. (1.93) has been tabulated but software packages often include either it or the equivalent incomplete gamma function. Tables list values of χ^2 corresponding to specified values of α and n and are written as $\chi^2_{\alpha,\nu}$ in this book. Thus if an observed value of χ^2 is less than a hypothesized value at the lower confidence limit α, or exceeds a hypothesized value at the upper confidence limit $(1–\alpha)$, then the hypothesis is inconsistent with experiment.

The chi-squared distribution is also useful for assessing the uncertainty in a variance σ^2 (i.e. the uncertainty in an uncertainty!), as well as assessing any agreement between two sets of observations or between experimental and theoretical data sets. For example suppose that a theory predicts a measurement to be within a range of $\mu \pm 20$ at a 95% confidence level $(\pm 2\sigma)$ so that $\sigma = 10$ and $\sigma^2 = 100$, and that 10 experimental measurements produce a mean and variance of $\bar{x} = 312$ and $s^2 = 195$ respectively. Is the theory consistent with experiment? Since $s^2 > \sigma^2$ the qualitative answer is no but this does not specify the confidence limits for this conclusion. Answering the question quantitatively requires that the theoretical value of χ^2 at some confidence level be outside the experimental range. If it is then the theory can be rejected at that 95% confidence level. The first step is to compute $\chi^2_{\text{theory}} = (n-1)s^2/\sigma^2 = (9)(195)/(100) = 17.55$. The second step is to find from tables that $\chi^2_{calc} = 16.9$ for $P_v\left(\chi^2\right) = 5\% = 0.05$ and 9 degrees of freedom, and since this is less than 17.55 it lies outside the theoretical range and the theory is rejected. In this example the mean $\bar{x}$ is not needed.

1.4.1.7 *F*

If two sets of observations, of sizes n_1 and n_2 and variances s_1^2 and s_2^2 that each follow the χ^2 distribution, are repeated then the ratio $F = s_1^2 / s_2^2$ follows the *F*-distribution:

$$F \equiv \frac{x_1/(n_1-1)}{x_2/(n_2-1)} = \frac{\left[(n_1-1)s_1^2/\sigma^2\right]/(n_1-1)}{\left[(n_2-1)s_2^2/\sigma^2\right]/(n_2-1)} = \frac{s_1^2}{s_2^2}, \tag{1.94}$$

Thus if *F* » 1 or *F* « 1 then there is a low probability that s_1^2 and s_2^2 are estimates of the same σ^2 and the two sets can be regarded as sampling different distributions. The *F* distribution quantifies the probability that two sets of observations are consistent, for example sets of theoretical and experimental data. As an example consider the analysis of enthalpy relaxation data for polystyrene described by Hodge and Huvard [12]. The standard deviations for five sets of best fits to experimental data were computed individually, as well as that for a set computed from the averages of the five. The latter was assumed to represent the population and an *F*-test was used to identify any data set as unrepresentative of this population at the 95% confidence level. The *F* statistic was 1.37 so that $1/1.37 = 0.73 \le s^2/\sigma^2 \le 1.37$. The values of s^2 for two data sets were found to be outside this range and were rejected as unrepresentative and further analyses were restricted to the three remaining sets.

1.4.1.8 Student *t*

This distribution $S(t)$ is defined as

$$S(t) = \frac{\left(1+t^2/n\right)^{-1/2(n+1)} \Gamma\left[(n+1)/2\right]}{(n\pi)^{1/2}\,\Gamma(n/2)}, \tag{1.95}$$

where

$$t = \frac{X}{(Y/n)^{1/2}} \tag{1.96}$$

and *X* is a sample from a normal distribution with mean 0 and variance 1 and *Y* follows a χ^2 distribution with *n* degrees of freedom. An important special case is when *X* is the mean μ and *Y* is the estimated standard deviation *s* of a repeatedly sampled normal distribution (μ and *s* are statistically independent even though they are properties of the same distribution):

$$t = \frac{\bar{x} - \mu}{\left(sn^{-1/2}\right)}, \tag{1.97}$$

where *n* is the number of degrees of freedom that is often one less than the number of observations used to determine $\bar{x}$.

1.4.2 Student *t*–Test

The Student *t*–test is useful for testing the statistical significance of an observed result compared with a desired or known result. The test is analogous to the confidence level that a measurement lies within some fraction of the standard deviation from the mean of a normal distribution. The specific problem the *t*-test addresses is that for a small number of observations the sample estimate s of the true standard deviation σ is not a good one and this uncertainty in s must be taken into account. Thus the *t*–distribution is broader than the normal distribution but narrows to approach it as the number of observations increases. Consider as an example ten measurements that produce a mean of 11.5 and a standard deviation of 0.50. Does the sample mean differ "significantly" from that of another data set with a different mean, μ = 12.2 for example. The averages differ by (12.2-11.5)/0.5 = 1.40 standard deviations. This corresponds to a 85% probability that a *single* measurement will lie within $\pm 1.40\sigma$ but this is not very useful for deciding whether the difference between the *means* is statistically significant. The t statistic [eq. (1.97)] is $\left(\bar{x}-\mu\right)/\left(s/n^{1/2}\right)$ = (11.5-12.2)/(0.5/3) = 4.2, compared with the *t*–statistics confidence levels 2.5%, 1% and 0.1% for nine degrees of freedom: 2.26, 2.82 and 4.3 respectively (obtained from Tables and software packages). This indicates that there is only a $2\times 0.1 = 0.2\%$ probability that the two means are statistically indistinguishable, or equivalently a 99.8% probability that the two means are different and that the two means are from different distributions. For the common problem of comparing two means from distributions that do not have the same variances, and of making sensible statements about the liklihood of them being statistically distinguishable or not, the only additional data needed are the estimated variances of each set. If the number of observations and standard deviation of each set are $\{n_1,s_1\}$ and $\{n_2,s_2\}$, the t-statistic is characterized by n_1+n_2-2 degrees of freedom and a variance of

$$s^2 = \frac{(n_1-1)s_1^2+(n_2-1)s_2^2}{n_1+n_2-2} = \frac{\sum\left(x_i-\bar{x}_1\right)^2+\sum\left(x_i-\bar{x}_2\right)^2}{n_1+n_2-2}. \qquad (1.98)$$

1.4.3 Regression Fits

A particularly good account of regressions is given in Chatfield [10], to which the reader is referred to for more details than are given here. Amongst other niceties this book is replete with worked examples. Two frequently used criteria for optimization of an equation to a set of data $\{x_i,y_i\}$ are minimization of the regression coefficient r discussed below [eq. (1.109)], and of the sum of squares of the differences between observed and calculated data. The sum of squares for the quantity y is:

$$\Xi_y^2 = \sum_{i=1}^{n}\left(y_i^{oberved} - y_i^{calculated}\right)^2. \qquad (1.99)$$

Minimization of Ξ_y^2 for y being a linear function of independent variables $\{x\}$ is achieved when the differentials of Ξ_y^2 with respect to the parameters of the linear equation are zero. For the linear function $y=a_0+a_1x$ for example,

$$\begin{aligned}\Xi_y^2 &= \sum_{i=1}^{n}\left(y_i - a_0 - a_1x_i\right)^2 = \sum_{i=1}^{n}\left(y_i^2 + a_0^2 + a_i^2x_i^2 - 2a_0y_i + 2a_0a_1x_i - 2a_1x_iy_i\right) \\ &= Sy^2 + na_0^2 + a_i^2Sx^2 - 2a_0Sy + 2a_0a_1Sx - 2a_1Sxy,\end{aligned} \qquad (1.100)$$

where the notation $S=\sum_{i=1}^{n}$ has been used. Equating the differentials of Ξ_y^2 with respect to a_0 and a_1 to zero yields respectively

$$\frac{d\Xi_y^2}{da_0}=0\Rightarrow na_0-Sy+a_1Sx=0 \tag{1.101}$$

and

$$\frac{d\Xi_y^2}{da_1}=0\Rightarrow a_0Sx-Sxy+a_1Sx^2=0\,. \tag{1.102}$$

The solutions are

$$a_0=\frac{Sx^2Sy-SxySx}{nSx^2-\left(Sx\right)^2} \tag{1.103}$$

and

$$a_1=\frac{nSxy-SxSy}{nSx^2-\left(Sx\right)^2}\,. \tag{1.104}$$

The uncertainties in a_0 and a_1 are

$$s_{a_0}^2=\left(\frac{s_{y|x}^2}{n}\right)\left[1+\frac{n\left(\overline{x}\right)^2}{\sum\left(x_i-\overline{x}\right)^2}\right] \tag{1.105}$$

and

$$s_{a_1}^2=\frac{s_{y|x}^2}{\sum\left(x_i-\overline{x}\right)^2}\,, \tag{1.106}$$

where

$$s_{y|x}^2=\frac{Sy^2-a_0Sy-a_1Sxy}{\left(n-2\right)}\,. \tag{1.107}$$

The quantity (n–2) in the denominator of eq. (1.107) reflects the loss of 2 degrees of freedom by the determinations of a_0 and a_1. For N+1 variables x_n, that can be powers of a single variable x if desired, eqs (1.101) and (1.102) generalize to

$$\sum_{n=0}^{N} a_n S x^{n+m} = S\left(x^{N+m-2} y\right) \qquad m = 0:N\,, \tag{1.108}$$

that constitute N+1 equations in N+1 unknowns that can be solved using Cramers Rule [eq. (1.119)]. For minimization of the sum of squares Ξ_x^2 in x the coefficients in $x = a'_0 + a'_1 y$ are obtained by simply exchanging x and y in eqs. (1.99) - (1.108).

To minimize the scatter around any functional relation between x and y the maximum value of the correlation coefficient r, defined by eq. (1.109) below, needs to be found:

$$\begin{aligned} r &\equiv \frac{\sum_i \left(y_{calc,i} - \bar{y}_{calc}\right)\left(y_{obs,i} - \bar{y}_{obs}\right)}{\left\{\left[\sum_i \left(y_{calc,i} - \bar{y}_{calc}\right)^2\right]\left[\sum_i \left(y_{obs,i} - \bar{y}_{obs}\right)^2\right]\right\}^{1/2}}, \\ &= \frac{n^2 S\left(y_{calc} y_{obs}\right) + (1-2n) S y_{calc} S y_{obs}}{\left\{\left[n^2 S y_{calc}^2 + (1-2n)\left(S y_{calc}\right)^2\right]\left[n^2 S y_{obs}^2 + (1-2n)\left(S y_{obs}\right)^2\right]\right\}^{1/2}}, \end{aligned} \tag{1.109}$$

where $\left\{y_{calc,i}\right\}$ are the calculated values of y obtained from the experimental $\left\{x_i\right\}$ data using the equation to be best fitted, and $\left\{y_{obs,i}\right\}$ are the observed values of $\left\{y_i\right\}$. Note that $\left\{y_{calc,i}\right\}$ and $\left\{y_{obs,i}\right\}$ are interchangeable in eq. (1.109).

The variable set $\{x_n\}$ can be chosen in many ways, in addition to the powers of a single variable already mentioned. For an exponential fit for example they can be exp(x) or ln(x), and they can also be chosen to be functions of x and y and other variables. A simple example is fitting (T,Y) data to the modified Arrhenius function

$$Y = A T^{-3/2} \exp\left(\frac{B}{T}\right), \tag{1.110}$$

that is linearized using $1/T$ as the independent variable and $\ln(YT^{3/2})$ as the dependent variable.

It often happens that an equation contains one or more parameters that cannot be obtained directly by linear regression. In this case (essentially practical for only one additional parameter) computer code can be written that finds a minimum in r as a function of the extra parameter. Consider for example the Fulcher temperature dependence for many dynamic quantities (typically an average relaxation or retardation time):

$$\tau = A_F \exp\left(\frac{B_F}{T - T_0}\right). \tag{1.111}$$

Once linearized as $\ln\tau = \ln A_F + B_F / \left(T - T_0\right)$ this equation can be least squares fitted to {T,τ} data using the independent variable $(T - T_0)^{-1}$ with trial values of T_0. This technique allows the uncertainties in A and B to be computed from eqs. (1.105) and (1.106) but the uncertainty in T_0 must be found by trial and error.

Software algorithms are the only practical option when more than 3 best fit parameters need to be found from an equation or a system of equations. These algorithms find the extrema of a user defined objective function Φ (typically the maximum in the correlation coefficient r) as a function of the desired parameters. Algorithms for this include the methods of *Newton-Raphson*, *Steepest Descent*, *Levenberg-Marquardt* (that combines the methods of Steepest Descent and Newton-Raphson), *Simplex*, and *Conjugate Gradient*. The Simplex algorithm is probably the best if computation speed is not an issue (usually the case these days) because it has a small (smallest?) tendency to get trapped in a local minimum rather than the global minimum.

1.5 Matrices and Determinants

A determinant is a square two dimensional array that can be reduced to a single number according to a specific procedure. The procedure for a second rank determinant is

$$\det\mathbf{Z} = \begin{vmatrix} z_{11} & z_{12} \\ z_{21} & z_{22} \end{vmatrix} = z_{11}z_{22} - z_{21}z_{12}\,. \tag{1.112}$$

For example the determinant $\mathbf{A} = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = \left(1*4 - 2*3\right) = -2$.

Third rank determinants are defined as

$$\det Z = \begin{vmatrix} z_{11} & z_{12} & z_{13} \\ z_{21} & z_{22} & z_{23} \\ z_{31} & z_{32} & z_{33} \end{vmatrix} = z_{11}\begin{vmatrix} z_{22} & z_{23} \\ z_{32} & z_{33} \end{vmatrix} - z_{12}\begin{vmatrix} z_{21} & z_{23} \\ z_{31} & z_{33} \end{vmatrix} + z_{13}\begin{vmatrix} z_{21} & z_{22} \\ z_{31} & z_{32} \end{vmatrix}\,, \tag{1.113}$$

where the 2×2 determinants are the *cofactors* of the elements they multply. The general expression for an $n\times n$ determinant is simplified by denoting the cofactor of z_{ij} by $\mathbf{Z}_{ij}$,

$$\det\mathbf{Z} = \sum_{j=1}^{n}\left(-1\right)^{i+j} z_{ij}\mathbf{Z}_{ij} = \sum_{i=1}^{n}\left(-1\right)^{i+j} z_{ij}\mathbf{Z}_{ij}\,, \tag{1.114}$$

where a theorem that asserts the equivalence of expansions in terms of rows or columns is used. The transpose of a determinant is obtained by exchanging rows and columns and is denoted by a superscripted t. Some properties of determinants are:

(i) det$\mathbf{Z}$ = det$\mathbf{Z}^t$. This is just a restatement that expansions across rows and columns are equivalent.

(ii) Exchanging two rows or two columns reverses the sign of the determinant. This implies that if two rows (or two columns) are identical then the determinant is zero.

(iii) If the elements in a row or column are multiplied by k then the determinant is multiplied by k.

(iv) A determinant is unchanged if k times the elements of one row (or column) are added to the corresponding elements of another row (or column). Extension of this result to multiple rows or columns, in combination with property (iii), yields the important result that a determinant is zero if two or more rows or columns are linear combinations of other rows or columns.

A matrix is essentially a type of number that is expressed as a (most commonly two dimensional) array of numbers. An example of an $m \times n$ matrix is

$$\mathbf{Z} = \begin{pmatrix} z_{11} & z_{12} & \cdots & z_{1n} \\ z_{21} & z_{22} & \cdots & z_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ z_{m1} & z_{m2} & \cdots & z_{mn} \end{pmatrix}, \tag{1.115}$$

where by convention the first integer *m* is the number of rows and the second integer *n* is the number of columns. Matrices can be added, subtracted, multiplied, and divided. Addition and subtraction is defined by adding or subtracting the individual elements and is obviously meaningful only for matrices with the same values of *m* and *n*. Multiplication is defined in terms of the elements z_{mn} of the product matrix **Z** being expressed as a sum of products of the elements x_{mi} and y_{in} of the two matrix multiplicands **X** and **Y**:

$$\mathbf{Z} = \mathbf{X} \otimes \mathbf{Y} \Rightarrow z_{mn} = \sum_i x_{mi} y_{in} . \tag{1.116}$$

For example $\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} = \begin{pmatrix} a+3b & 2a+4b \\ c+3d & 2c+4d \end{pmatrix}$. Matrix multiplication is generally not commutative, i.e. $\mathbf{X} \otimes \mathbf{Y} \neq \mathbf{Y} \otimes \mathbf{X}$. For example $\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} a+2c & b+2d \\ 3a+4c & 3b+4d \end{pmatrix} \neq \begin{pmatrix} A & B \\ C & D \end{pmatrix}$. The transpose of a square *n* = *m* matrix $\mathbf{Z}^t$ is defined by exchanging rows and columns, i.e. by a reflection through the principal diagonal (that which runs from the top left to bottom right). The unit matrix **U** is defined by all the principal diagonal elements u_{mm} being unity and all off-diagonal elements being zero. It is easily found that $\mathbf{U} \otimes \mathbf{X} = \mathbf{X} \otimes \mathbf{U} = \mathbf{X}$ for all **X**.

The inverse matrix $\mathbf{Z}^{-1}$ defined by $\mathbf{Z}^{-1}\mathbf{Z}=\mathbf{Z}\mathbf{Z}^{-1}=\mathbf{U}$ is needed for matrix division and is given by

$$\mathbf{Z}^{-1} = \left[\frac{(-1)^{i+j} \det \mathbf{Z}^t{}_{ij}}{\det \mathbf{Z}} \right], \tag{1.117}$$

where $\mathbf{Z}^t{}_{ij}$ is the transpose of the cofactor. The method is illustrated by the following table for the inverse of the matrix $\mathbf{A} = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$:

i	j	$(-1)^{i+j}$	$\mathbf{Z}^t{}_{ij}$	numerator	$\mathbf{A}^{-1}_{ij}$

1	1	+1	4	+4	−2
1	2	−1	2	−2	+1
2	1	−1	3	−3	+3/2
2	2	+1	1	+1	−1/2

Thus the inverse matrix $\mathbf{A}^{-1}$ is $\begin{pmatrix} -2 & +1 \\ +3/2 & -1/2 \end{pmatrix}$. Matrix inversion algorithms are included in most (all?) software packages.

Determinants provide a convenient method for solving N equations in N unknowns $\{x_i\}$,

$$\sum_{i=1}^{N} A_{ji} x_i = C_j, \qquad j = 1:N, \tag{1.118}$$

where A_{ij} and C_j are constants. The solutions for $\{x_i\}$ are obtained from *Cramer's Rule*:

$$x_i = \frac{\begin{vmatrix} A_{11} & C_1 & A_{1n} \\ \cdots & \cdots & \cdots \\ A_{n1} & C_n & A_{nn} \end{vmatrix}}{\begin{vmatrix} A_{11} & A_{1i} & A_{1n} \\ \cdots & \cdots & \cdots \\ A_{n1} & A_{ni} & A_{nn} \end{vmatrix}} = \frac{\begin{vmatrix} A_{11} & C_1 & A_{1n} \\ \cdots & \cdots & \cdots \\ A_{n1} & C_n & A_{nn} \end{vmatrix}}{\det \mathbf{A}}. \tag{1.119}$$

If det$\mathbf{A}$ = 0 then by property (iv) above at least two of its rows are linearly related and there is therefore no unique solution.

1.6 Jacobeans

Changing a single variable in an integral, from x to y for example, is accomplished using the derivative dx/dy:

$$\int f(x)\,dx = \int f\left[x(y)\right]\left(\frac{dx}{dy}\right)dy. \tag{1.120}$$

For a change in more than one variable in a multiple integral, $\{x,y\}$ to $\{u,v\}$ for example, the integral transformation

$$\int\left[x(u,v), y(u,v)\right]dx\,dy \rightarrow \int f(u,v)\,du\,dv \tag{1.121}$$

requires that du and dv be expressed in terms of *dx* and *dy* using eq. (1.14):

$$dxdy = \left[\left(\frac{\partial x}{\partial u}\right)du + \left(\frac{\partial x}{\partial v}\right)dv\right]\left[\left(\frac{\partial y}{\partial u}\right)du + \left(\frac{\partial y}{\partial v}\right)dv\right] . \tag{1.122}$$

For consistency with established results it is necessary to adopt the definitions *dudu* = *dvdv* = 0, *dudv* = –*dvdu*, and $\partial x\partial y/\partial u^2 = \partial x\partial y/\partial v^2 = 0$. Equation (1.122) then becomes

$$dxdy = \left[\left(\frac{\partial x}{\partial u}\right)\left(\frac{\partial y}{\partial v}\right) - \left(\frac{\partial x}{\partial v}\right)\left(\frac{\partial y}{\partial u}\right)dudv\right] = \det\begin{vmatrix}\left(\frac{\partial x}{\partial u}\right) & \left(\frac{\partial x}{\partial v}\right)\\ \left(\frac{\partial y}{\partial u}\right) & \left(\frac{\partial y}{\partial v}\right)\end{vmatrix} \equiv \left[\frac{\partial(x,y)}{\partial(u,v)}\right] , \tag{1.123}$$

and

$$\int f(x,y)\,dx\,dy \to \int f\left[x(u,v),y(u,v)\right]\left[\frac{\partial(x,y)}{\partial(u,v)}\right]du\,dv . \tag{1.124}$$

The determinant in eq. (1.123) is called the *Jacobean* and is readily extended to any number of variables:

$$\det\begin{vmatrix}\left(\frac{\partial x_1}{\partial v_1}\right) & \ldots & \left(\frac{\partial x_1}{\partial v_n}\right)\\ \ldots & \ldots & \ldots\\ \left(\frac{\partial x_n}{\partial v_1}\right) & \ldots & \left(\frac{\partial x_n}{\partial v_n}\right)\end{vmatrix} \equiv \left[\frac{\partial(x_1 \ldots x_i \ldots x_n)}{\partial(v_1 \ldots v_i \ldots v_n)}\right] \equiv \frac{\partial \vec{\mathbf{X}}}{\partial \vec{\mathbf{V}}}, \tag{1.125}$$

where the variables $\{x_{i=1:n}\}$ and $\{v_{i=1:n}\}$ have been subsumed into the *n*-vectors $\vec{\mathbf{X}}$ and $\vec{\mathbf{V}}$ respectively. The condition that $\vec{\mathbf{X}}(\vec{\mathbf{V}})$ can be found when $\vec{\mathbf{V}}(\vec{\mathbf{X}})$ is given is that the Jacobean is nonzero. In this case the general expression for a change of variables is

$$\int f(\vec{\mathbf{X}})d\vec{\mathbf{X}} = \int f\left[\vec{\mathbf{X}}(\vec{\mathbf{V}})\right]\left(\frac{\partial x_1 \ldots x_n}{\partial v_1 \ldots v_n}\right)d\vec{\mathbf{V}} = \int f\left[\vec{\mathbf{X}}(\vec{\mathbf{V}})\right]\left(\frac{d\vec{\mathbf{X}}}{d\vec{\mathbf{V}}}\right)d\vec{\mathbf{V}} . \tag{1.126}$$

As a specific example of these formulae consider the transformation from Cartesian to spherical coordinates:

$$\begin{aligned} x(r,\varphi,\theta) &= r\sin\varphi\cos\theta,\\ y(r,\varphi,\theta) &= r\sin\varphi\sin\theta,\\ z(r,\varphi,\theta) &= r\cos\varphi, \end{aligned} \tag{1.127}$$

for which the Jacobean is

$$\begin{vmatrix} \sin\varphi\cos\theta & r\cos\varphi\cos\theta & r\sin\varphi\sin\theta \\ \sin\varphi\sin\theta & r\cos\varphi\sin\theta & -r\sin\varphi\cos\theta \\ \cos\varphi & -r\sin\varphi & 0 \end{vmatrix} = r^2\sin\varphi\,, \tag{1.128}$$

so that

$$\iiint f\left(x,y,z\right)dx\,dy\,dz = \iiint f\left(r,\varphi,\theta\right)\left[r^2\sin\varphi\right]dr\,d\varphi\,d\theta\,. \tag{1.129}$$

1.7 Vectors

Vectors are quantities having both magnitude and direction, the latter being specified in terms of a set of coordinates that are almost always orthogonal for relaxation applications (such as those specified in §1.2.7). In two dimensions the point $(x,y) = (r\cos\varphi, r\sin\varphi)$ can be interpreted as a vector that connects the origin to the point: its magnitude is r and its direction is defined by the angle φ relative to the positive x-axis: $\varphi = \arctan(y/x)$. A vector in n dimensions requires n components for its specification that are normally written as a $\left(1\times n\right)$ matrix (column vector) or $\left(n\times 1\right)$ matrix (row vector). The *magnitude* or *amplitude* r is a single number and is a *scalar*. Vectors are written here in bold face with an arrow and magnitudes are written in italics: a vector $\vec{\mathbf{A}}$ has a magnitude A. Addition of two vectors with components (x_1, y_1, z_1) and (x_2, y_2, z_2) is defined as $(x_1+x_2, y_1+y_2, z_1+z_2)$, corresponding to placing the origin of the added vector at the terminus of the original and joining the origin of the first to the end of the second ("nose to tail"). Multiplication of a vector by a scalar yields a vector in the same direction with only the magnitude multiplied. For example the direction of the diagonal of a cube relative to the sides of a cube is independent of the size of the cube.

It is convenient to specify vectors in terms of unit length vectors $\mathbf{i}$, $\hat{\mathbf{j}}$ and $\mathbf{k}$ in the directions of orthogonal Cartesian coordinates $\{x,y,z\}$. A vector $\vec{\mathbf{A}}$ with components A_x, A_y, and A_z is then defined by

$$\vec{\mathbf{A}} = \hat{\mathbf{i}}A_x + \hat{\mathbf{j}}A_y + \mathbf{k}A_z\,. \tag{1.130}$$

The direction of the $\mathbf{k}$ vector relative to the $\mathbf{i}$ and $\hat{\mathbf{j}}$ vectors is therefore determined by the same right hand rule convention as that for the z-axis relative to the x and y axes (§1.2.7). Orthogonality of these unit vectors is demonstrated by the relations

$$\hat{\mathbf{i}}\times\hat{\mathbf{i}} = \hat{\mathbf{j}}\times\hat{\mathbf{j}} = \mathbf{k}\times\mathbf{k} = 0\,, \tag{1.131}$$

and

$$\begin{aligned} \hat{\mathbf{i}}\times\hat{\mathbf{j}} &= -\hat{\mathbf{j}}\times\hat{\mathbf{i}} = \mathbf{k} \\ \hat{\mathbf{j}}\times\mathbf{k} &= -\mathbf{k}\times\hat{\mathbf{j}} = \hat{\mathbf{i}}\;. \\ \mathbf{k}\times\hat{\mathbf{i}} &= -\hat{\mathbf{i}}\times\mathbf{k} = \hat{\mathbf{j}} \end{aligned} \tag{1.132}$$

where $\times$ denotes the vector or cross product defined below.

There are two forms of vector multiplication. The *scalar product* is defined as the product of the magnitudes and the cosine of the angle θ between the vectors:

$$\vec{\mathbf{A}}\bullet\vec{\mathbf{B}} = AB\cos\theta . \tag{1.133}$$

This product is denoted by a dot and is often referred to as the dot product. Since $B\cos\theta$ is the projection of the vector $\vec{\mathbf{B}}$ onto the direction of $\vec{\mathbf{A}}$ and vice versa the scalar product can be regarded as the product of the magnitude of one vector and the projection of the other upon it. If $\theta = \pi/2$ the scalar product is zero even if A and/or B are nonzero, and the scalar product changes sign as θ increases through $\pi/2$. If $\vec{\mathbf{A}}$ and $\vec{\mathbf{B}}$ are defined by eq. (1.130), then

$$\vec{\mathbf{A}}\bullet\vec{\mathbf{B}} = A_x B_x + A_y B_y + A_z B_z \ . \tag{1.134}$$

The *vector product*, denoted by $\vec{\mathbf{A}}\times\vec{\mathbf{B}}$ and often referred to as the cross product, is defined by a vector of magnitude $AB\sin\theta$ that is perpendicular to the plane defined by $\vec{\mathbf{A}}$ and $\vec{\mathbf{B}}$. The sign of $\vec{\mathbf{C}} = \vec{\mathbf{A}}\times\vec{\mathbf{B}}$ is again defined by the right hand rule for right handed coordinates: when viewed along $\vec{\mathbf{C}}$ the shorter rotation from $\vec{\mathbf{A}}$ to $\vec{\mathbf{B}}$ is clockwise or, analogous to the definition of a right hand coordinate system, when the index finger of the right hand is bent from $\vec{\mathbf{A}}$ to $\vec{\mathbf{B}}$ the thumb points in the direction of $\vec{\mathbf{C}}$. Reversal of the order of multiplication of $\vec{\mathbf{A}}$ and $\vec{\mathbf{B}}$ therefore changes the sign of $\vec{\mathbf{C}}$. The definition of the cross product is

$$\vec{\mathbf{A}}\times\vec{\mathbf{B}} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix} = \hat{\mathbf{i}}\left(A_y B_z - A_z B_y\right) - \hat{\mathbf{j}}\left(A_x B_z - A_z B_x\right) + \hat{\mathbf{k}}\left(A_x B_y - A_y B_x\right). \tag{1.135}$$

Thus changing the order of multiplication corresponds to exchanging two rows of the determinant, thereby reversing the sign of the determinant as required (§1.5).

Combining scalar and vector products yields:

$$\vec{\mathbf{A}}\bullet\left(\vec{\mathbf{B}}\times\vec{\mathbf{C}}\right) = \left(\vec{\mathbf{A}}\times\vec{\mathbf{B}}\right)\bullet\vec{\mathbf{C}} = \vec{\mathbf{B}}\bullet\left(\vec{\mathbf{C}}\times\vec{\mathbf{A}}\right) = \begin{vmatrix} A_x & A_y & A_z \\ B_x & B_y & B_z \\ C_x & C_y & C_z \end{vmatrix} , \tag{1.136}$$

that is the volume enclosed by the vectors $\vec{\mathbf{A}}$, $\vec{\mathbf{B}}$, $\vec{\mathbf{C}}$. Also,

$$\vec{\mathbf{A}}\times\left(\vec{\mathbf{B}}\times\vec{\mathbf{C}}\right) = \left(\vec{\mathbf{A}}\bullet\vec{\mathbf{C}}\right)\vec{\mathbf{B}} - \left(\vec{\mathbf{A}}\bullet\vec{\mathbf{B}}\right)\vec{\mathbf{C}} \neq \left(\vec{\mathbf{A}}\times\vec{\mathbf{B}}\right)\times\vec{\mathbf{C}} = -\vec{\mathbf{C}}\times\left(\vec{\mathbf{A}}\times\vec{\mathbf{B}}\right) = \left(\vec{\mathbf{C}}\bullet\vec{\mathbf{A}}\right)\vec{\mathbf{B}} - \left(\vec{\mathbf{C}}\bullet\vec{\mathbf{B}}\right)\vec{\mathbf{A}} \tag{1.137}$$

and

$$\left(\vec{\mathbf{A}}\times\vec{\mathbf{B}}\right)\bullet\left(\vec{\mathbf{C}}\times\vec{\mathbf{D}}\right) = \left(\vec{\mathbf{A}}\bullet\vec{\mathbf{C}}\right)\left(\vec{\mathbf{B}}\bullet\vec{\mathbf{D}}\right) - \left(\vec{\mathbf{B}}\bullet\vec{\mathbf{C}}\right)\left(\vec{\mathbf{A}}\bullet\vec{\mathbf{D}}\right). \tag{1.138}$$

The contravariant unit vectors for nonorthogonal axes (corresponding to $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, $\hat{\mathbf{k}}$) are often written as $\hat{\mathbf{e}}^1$, $\hat{\mathbf{e}}^2$ and $\hat{\mathbf{e}}^3$ (up to $\hat{\mathbf{e}}^n$ for *n* dimensions), and the *reciprocal unit vectors* $\hat{\mathbf{e}}_n$ are defined (in three dimensions) by

$$\hat{\mathbf{e}}_{\mathbf{1}} = \frac{\hat{\mathbf{e}}^{\mathbf{2}} \times \hat{\mathbf{e}}^{\mathbf{3}}}{\hat{\mathbf{e}}^1 \bullet \hat{\mathbf{e}}^2 \times \hat{\mathbf{e}}^3}; \hat{\mathbf{e}}_2 = \frac{\hat{\mathbf{e}}^3 \times \hat{\mathbf{e}}^1}{\hat{\mathbf{e}}^1 \bullet \hat{\mathbf{e}}^2 \times \hat{\mathbf{e}}^3}; \hat{\mathbf{e}}_3 = \frac{\hat{\mathbf{e}}^1 \times \hat{\mathbf{e}}^2}{\hat{\mathbf{e}}^1 \bullet \hat{\mathbf{e}}^2 \times \hat{\mathbf{e}}^3} . \tag{1.139}$$

Note that $\hat{\mathbf{e}}_i \bullet \hat{\mathbf{e}}^i = 1 \left(i = 1, 2, 3 \right)$. The reciprocal lattice vectors used in solid state physics are examples of covariant vectors corresponding to contravariant real lattice vectors. The *contravariant components* A^i of a vector $\vec{\mathbf{A}}$ are then defined by

$$\vec{\mathbf{A}} = \sum_i A^i \hat{\mathbf{e}}^i \ , \tag{1.140}$$

and the *covariant components* A_i are

$$\vec{\mathbf{A}} = \sum_i A_i \hat{\mathbf{e}}_i \ . \tag{1.141}$$

The area and orientation of an infinitesimal plane segment is defined by a differential area vector $d\vec{\mathbf{a}}$ that is perpendicular to the plane. The sign of $d\vec{\mathbf{a}}$ for a closed surface is defined to be positive when it points outwards from the surface. For open surfaces the direction of $d\vec{\mathbf{a}}$ is defined by convention and must be separately specified. If $\left\{ \vec{\mathbf{a}}^i \right\}$ define the area vectors of the faces of a closed polyhedron it can be shown that

$$\sum_i \vec{\mathbf{a}}^i = 0. \tag{1.142}$$

This result is obvious for a cube and an octahedron but it is instructive to demonstrate it explicitly for a tetrahedron. Let $\vec{\mathbf{A}}$, $\vec{\mathbf{B}}$ and $\vec{\mathbf{C}}$ define the edges of a tetrahedron that radiate out from a vertex. The three faces defined by these edges are $\vec{\mathbf{A}} \times \vec{\mathbf{B}}$, $\vec{\mathbf{B}} \times \vec{\mathbf{C}}$, and $\vec{\mathbf{C}} \times \vec{\mathbf{A}}$. The three edges forming the faces opposite the vertex are $\vec{\mathbf{B}} - \vec{\mathbf{A}}$, $\vec{\mathbf{C}} - \vec{\mathbf{B}}$, and $\vec{\mathbf{A}} - \vec{\mathbf{C}}$ (adding to zero as must be), and the face enclosed by these edges is $\left(\vec{\mathbf{A}} - \vec{\mathbf{C}} \right) \times \left(\vec{\mathbf{C}} - \vec{\mathbf{B}} \right)$. Expansion of the last result yields $\left(\vec{\mathbf{B}} \times \vec{\mathbf{A}} \right) + \left(\vec{\mathbf{C}} \times \vec{\mathbf{B}} \right) + \left(\vec{\mathbf{A}} \times \vec{\mathbf{C}} \right)$ (after noting that $\left(\vec{\mathbf{C}} \times \vec{\mathbf{C}} \right) = 0$) and this exactly cancels the contributions from the other three faces.

Differentiation of vectors with respect to scalars follows the same rules as differentiation of scalars. For example,

$$\frac{d\left(\vec{\mathbf{A}} \bullet \vec{\mathbf{B}} \right)}{dw} = \vec{\mathbf{A}} \bullet \left(\frac{d\vec{\mathbf{B}}}{dw} \right) + \left(\frac{d\vec{\mathbf{A}}}{dw} \right) \bullet \vec{\mathbf{B}} \tag{1.143}$$

and

$$\frac{d\left(\vec{\mathbf{A}}\times\vec{\mathbf{B}}\right)}{dw}=\vec{\mathbf{A}}\times\left(\frac{d\vec{\mathbf{B}}}{dw}\right)+\left(\frac{d\vec{\mathbf{A}}}{dw}\right)\times\vec{\mathbf{B}}=\vec{\mathbf{A}}\times\left(\frac{d\vec{\mathbf{B}}}{dw}\right)-\vec{\mathbf{B}}\times\left(\frac{d\vec{\mathbf{A}}}{dw}\right) . \qquad (1.144)$$

The derivatives of a scalar (e.g. *w*) in the directions of $\mathbf{i}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ yield the *gradient vector* grad*(w)* or $\vec{\nabla}w$, defined as

$$\vec{\nabla}w=\mathrm{grad}\,w=\hat{\mathbf{i}}\left(\frac{\partial w}{\partial x}\right)+\hat{\mathbf{j}}\left(\frac{\partial w}{\partial y}\right)+\hat{\mathbf{k}}\left(\frac{\partial w}{\partial z}\right), \qquad (1.145)$$

where

$$\vec{\nabla}\equiv\hat{\mathbf{i}}\frac{\partial}{\partial x}+\hat{\mathbf{j}}\frac{\partial}{\partial y}+\hat{\mathbf{k}}\frac{\partial}{\partial z} \qquad (1.146)$$

is termed *del* or *nabla* and the products of the operators $\partial/\partial x^i$ with *w* are interpreted as $\partial w/\partial x^i$.

The scalar product of $\vec{\nabla}$ with a vector $\vec{\mathbf{A}}$ is the *divergence*, $\mathrm{div}\vec{\mathbf{A}}$ or $\vec{\nabla}\bullet\vec{\mathbf{A}}$:

$$\vec{\nabla}\bullet\vec{\mathbf{A}}=\left(\frac{\partial A_x}{\partial x}\right)+\left(\frac{\partial A_y}{\partial y}\right)+\left(\frac{\partial A_z}{\partial z}\right). \qquad (1.147)$$

The scalar product of $\vec{\nabla}$ with itself is the *Laplacian*

$$\vec{\nabla}\bullet\vec{\nabla}=\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}. \qquad (1.148)$$

The differential of an arbitrary displacement $d\vec{\mathbf{s}}$ is

$$d\vec{\mathbf{s}}=\hat{\mathbf{i}}\,dx+\hat{\mathbf{j}}\,dy+\mathbf{k}\,dz. \qquad (1.149)$$

Recalling the differential of a scalar function [eq. (1.14)],

$$dw=\left(\frac{\partial w}{\partial x}\right)dx+\left(\frac{\partial w}{\partial y}\right)dy+\left(\frac{\partial w}{\partial z}\right)dz, \qquad (1.150)$$

it follows from eqs. (1.145) and (1.149) that *dw* can be defined as the scalar product of $d\vec{\mathbf{s}}$ and $\vec{\nabla}w$:

$$dw=d\vec{\mathbf{s}}\bullet\vec{\nabla}w. \qquad (1.151)$$

Any two dimensional surface defined by constant *w* implies

$$dw = 0 = d\vec{\mathbf{s}}_0 \bullet \vec{\nabla} w, \tag{1.152}$$

where $d\vec{\mathbf{s}}_0$ lies within the surface. Since $d\vec{\mathbf{s}}_0$ and $\vec{\nabla} w$ are in general not zero $\vec{\nabla} w$ must be perpendicular to $d\vec{\mathbf{s}}_0$, i.e. normal to the surface at that point. Conversely *dw* is greatest when $d\vec{\mathbf{s}}$ and $\vec{\nabla} w$ lie in the same direction [eq. (1.151)], so that $\vec{\nabla} w$ defines the direction of maximum change in *w* to be perpendicular to the surface of constant *w* and this maximum has the value *dw*/*ds*.

The vector product of $\vec{\nabla}$ with $\vec{\mathbf{A}}$ is the *curl* of $\vec{\mathbf{A}}$:

$$\mathrm{curl}\vec{\mathbf{A}} \equiv \vec{\nabla} \times \vec{\mathbf{A}} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix}. \tag{1.153}$$

Straightforward algebraic manipulation of this definitions reveals that

$$\vec{\nabla} \bullet \left(\vec{\nabla} \times \vec{\mathbf{A}} \right) = 0 \ , \tag{1.154}$$

$$\vec{\nabla} \times \left(\vec{\nabla} \bullet \vec{\mathbf{A}} \right) = 0 \ , \tag{1.155}$$

and (tediously)

$$\vec{\nabla} \times \vec{\nabla} \times \vec{\mathbf{A}} = \vec{\nabla} \left(\vec{\nabla} \bullet \vec{\mathbf{A}} \right) - \nabla^2 \vec{\mathbf{A}}, \tag{1.156}$$

where the commutative properties $\partial^2 / \partial x \partial y = \partial^2 / \partial y \partial x$ etc. are used.

As a physical example of some of these formulae consider an electrical current density $\vec{\mathbf{J}}$ that represents the amount of electric charge flowing per second per unit area through a closed surface $\vec{\mathbf{S}}$ enclosing a volume *V***.** Then the charge per second (current) flowing through an area $d\vec{\mathbf{s}}$ (not necessarily perpendicular to $\vec{\mathbf{J}}$) is given by the scalar product $\vec{\mathbf{J}} \bullet d\vec{\mathbf{S}}$. The currents flowing into and out of *V* have opposite signs so that if *V* contains no sources or sinks of charge then the surface integral is zero, i.e. $\oint \vec{\mathbf{J}} \bullet d\vec{\mathbf{s}} = 0$. If sources or sinks of charge exist within the volume then the integral yields a measure of the charge within the volume. In particular the cumulative current can be shown to be $\oint \vec{\nabla} \bullet \vec{\mathbf{J}} dV$ and *Gauss's theorem* results:

$$\oint \vec{\mathbf{J}} \bullet d\vec{\mathbf{S}} = \int \vec{\nabla} \bullet \vec{\mathbf{J}} dV = \iiint \vec{\nabla} \bullet \vec{\mathbf{J}} dx dy dz \, . \tag{1.157}$$

Two other useful integral theorems are
Green's Theorem in the Plane:

$$\oint_C \left(Pdx + Qdy \right) = \iint \left(\frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y} \right), \tag{1.158}$$

where P and Q are functions of x and y within an area A. The left hand side of eq. (1.158) is a line integral along a closed contour C that encloses the area A and the right hand side is a double integral over the enclosed area (see §1.9.3.2 for details about line integrals).

Stokes' Theorem

This theorem equates a surface integral of a vector $\vec{\mathbf{V}}$ over an open three dimensional surface to a line integral of the vector around a curve that defines the edges of the open surface. Let the line element be $d\vec{\mathbf{s}}$, and the vector area be $\vec{\mathbf{A}} = A\hat{\mathbf{n}}$ where $\hat{\mathbf{n}}$ is the unit vector perpendicular to the plane of the surface. Stoke's theorem is then

$$\oint \vec{\mathbf{V}} \bullet d\vec{\mathbf{s}} = \iint_A \left(\vec{\nabla} \times \vec{\mathbf{V}} \right) \bullet d\vec{\mathbf{A}} = \iint_A \left(\vec{\nabla} \times \vec{\mathbf{V}} \right) \bullet \hat{\mathbf{n}} dA. \tag{1.159}$$

A simple example illustrates this theorem. Consider a butterfly net surface that has a roughly conical mesh attached to a hoop (not necessarily circular). Stoke's theorem asserts that for the vector field $\vec{\mathbf{V}}$ (for example air passing through the net) the area vector integral of the mesh equals the line integral around the hoop *regardless of the shape of the mesh*. Thus a boundary condition on the function $\vec{\mathbf{V}}$ is all that is needed to determine the surface integral for any surface whatsoever.

1.8 Complex Variables

This is the most important section in this book. Several books on complex functions are recommended. An excellent introduction is Kyrala's "*Applied Functions of a Complex Variable*" [1] (sadly long out of print and not (yet?) a Dover reprint), that has many excellent worked examples. The classic texts by Copson [7] and Titchmarsh [13,14] are recommended for more complete and rigorous treatments.

1.8.1 Complex Numbers

A *complex number*, *z*, is a number pair whose components are termed (for a historical reason) *real* (x) and *imaginary* (y):

$$z = x + iy \qquad i \equiv +\left(-1\right)^{1/2}. \tag{1.160}$$

For example,

$$z^2 = \left(x^2 - y^2 \right) + 2ixy\,. \tag{1.161}$$

Two complex numbers z_1 and z_2 are equal if, and only if, their real and imaginary components are both equal. The related functions obtained by replacing i with $-i$ are referred to as *complex conjugates*. In the physical literature of relaxation phenomenology the asterisk is usually used to define functions in the complex frequency domain [e.g. $f^*(i\omega)$], to distinguish them from the corresponding time domain functions $f(t)$, and this nomenclature is followed here. Complex conjugation is denoted in this book by the superscripted dagger $\dagger$:

$$z^{\dagger} = x - iy. \tag{1.162}$$

The reciprocal of z^* is then

$$\frac{1}{z^*} = \frac{1}{x+iy} = \frac{x-iy}{x^2+y^2} = \frac{z^{\dagger}}{x^2+y^2} = \frac{z^{\dagger}}{|z|^2}, \tag{1.163}$$

where $|z|$ is the (positive) *complex modulus* equal to the real number defined by $|z| \equiv +\left(z^* z^{\dagger}\right)^{1/2}$. The mathematical term "modulus" should not be confused with that used in the relaxation literature (for example electric modulus). Confusion is averted by preceding the word "modulus" in relaxation applications with the appropriate adjective ("electric modulus"), and in mathematical contexts by "complex modulus".

Quaternions are a mathematically interesting generalization of complex numbers (although rarely (if ever) used in relaxation phenomenology) that are characterized by a real component and three “imaginary” numbers I, J, K defined by:,

$$\begin{aligned} I^2 &= J^2 = K^2 = -1, \\ I &= JK = -KJ, \\ J &= KI = -IK, \\ K &= IJ = -JI. \end{aligned} \tag{1.164}$$

A quaternion is then given by $x_0 + Ix_1 + Jx_2 + Kx_3$ and its conjugate is $x_0 - Ix_1 - Jx_2 - Kx_3$. Quaternions can also be expressed as 2×2 matrices:

$$\begin{aligned} I &= \begin{pmatrix} 0 & +1 \\ -1 & 0 \end{pmatrix}, \\ J &= \begin{pmatrix} 0 & +i \\ +i & 0 \end{pmatrix}, \\ K &= \begin{pmatrix} +i & 0 \\ 0 & -i \end{pmatrix}. \end{aligned} \tag{1.165}$$

They are used to describe rotations in three dimensions. The noncommuting properties exhibited in eqs. (1.164) reflect the fact that changing the order of rotation axes in three dimensional space results in different final directions.

1.8.2 Complex Functions

A *complex function* of one or more variables is separable into real and imaginary components, for example

$$f^*(z) = f^*(x,y) = u(x,y) + iv(x,y). \tag{1.166}$$

It is customary in the physical literature to denote the real component of a complex function with a prime and the imaginary component with a double prime so that $u(x,y) = f'(x,y)$ and $v(x,y) = f''(x,y)$:

$$f^*(z) = f'(x,y) + if''(x,y). \tag{1.167}$$

The real and imaginary components of a complex function are also commonly denoted by Re and Im respectively: $f' = \mathrm{Re}\left[f(z)\right]$ and $f'' = \mathrm{Im}\left[f(z)\right]$.
For $f^*(z) = 1/g^*(z)$ [cf. eq. (1.163)]

$$f' + if'' = \frac{1}{g' + ig''} = \frac{g' - ig''}{g'^2 + g''^2} = \frac{g^\dagger}{|g|^2}, \tag{1.168}$$

and

$$g' + ig'' = \frac{1}{f' + if''} = \frac{f' - if''}{f'^2 + f''^2} = \frac{f^\dagger}{|f|^2} \tag{1.169}$$

so that

$$\begin{aligned} g' &= \frac{f'}{f'^2 + f''^2}, \\ g'' &= \frac{-f''}{f'^2 + f''^2}. \end{aligned} \tag{1.170}$$

Of the large number of possible functions of a complex variable only *analytical functions* are useful for describing relaxation phenomena (and all other physical phenomena for that matter because they ensure causality, see below). They are defined as being uniquely differentiable, meaning that the derivatives are continuous and that (importantly) differentiation with respect to z does not depend on the direction of differentiation in the complex plane [7,13]. Thus differentiation of an analytical function $f^*(z) = u(x,y) + iv(x,y)$ parallel to the x-axis $\partial/\partial x$ produces the same result as differentiation parallel to the y-axis $\partial/\partial y$, resulting in the real and imaginary parts of an analytical function being related to one another. All of the material below refers to analytical functions.

Complex analytical functions can be expressed as an infinite sum of powers of z or $(z - a)$ (a = constant), that must of course converge in order to be useful. Convergence may be restricted to values of $|z|$ less than some number R (often unity). Because the conditions for convergence are defined in terms of differentials [7,13], that for analytical functions depend only on $r = |z|$ and not on the phase angle θ [see §1.8.3 and eq. (1.180) below], the real number R is referred to as the *radius of convergence*. Details about the conditions needed for convergence and associated issues are found in mathematics texts. The most general series expansion is the *Laurent series*

$$f(z) = \sum_{n=-\infty}^{n=+\infty} f_n (z-a)^n , \tag{1.171}$$

where f_n and a are in general complex and n is a real integer. If $f_n = 0$ for $n < 0$ the series is a *Taylor series*:

$$f(z) = \sum_{n=0}^{n=+\infty} f_n (z-a)^n , \tag{1.172}$$

and if in addition $a = 0$ the series is a *MacLaurin series*:

$$f(z) = \sum_{n=0}^{n=+\infty} f_n z^n \ . \tag{1.173}$$

The coefficients f_n are defined by the complex derivatives of $f^*(z)$:

$$f_n = \frac{1}{n!}\left(\frac{d^n f}{dz^n}\right), \tag{1.174}$$

so that the Taylor series expansion becomes

$$f^*(z) = \sum_{n=0}^{n=\infty} \frac{1}{n!}\left(\frac{d^n f}{dz^n}\right)(z-a)^n \ . \tag{1.175}$$

A function that is central to the application of complex numbers to relaxation phenomena is the *complex exponential*,

$$\begin{aligned} \exp(z^*) &= \exp(x+iy) \\ &= \exp(x)\exp(iy) \\ &= \exp(x)\left[\cos(y) + i\sin(y)\right], \end{aligned} \tag{1.176}$$

where the *Euler relation*

$$\exp(iy) = \cos(y) + i\sin(y) \tag{1.177}$$

has been invoked. The Euler relation implies that the cosine of the real variable y can be written as

$$\cos(y) = \mathrm{Re}\left[\exp(iy)\right] \tag{1.178}$$

and the sine function as

$$\sin(y) = \mathrm{Re}\left[i\exp(-iy)\right] = \mathrm{Re}\left[-i\exp(iy)\right] \ . \tag{1.179}$$

Since the sine and cosine functions differ only by the phase angle $\pi/2$ eqs. (1.178) and (1.179) indicate that i shifts the phase angle by $\pi/2$. The usefulness of complex numbers in describing physical properties measured with sinusoidally varying excitations derives from this property of i.

Since multiplication of z^* by (–1) turns $+x$ into $-x$ and y into $-y$, a rotation of $\pm\pi/2$ can be interpreted as multiplication by $i = \pm(-1)^{1/2}$. By convention positive angles are defined by counterclockwise rotation so that multiplication by i yields $+x\to+y$ and $+y\to-x$. The complex number $z = x + iy$ can be regarded as a point in a Cartesian (x,iy) plane, with the x axis representing the real component and the y axis the imaginary component. The (x,iy) plane is referred to as the *complex plane* and sometimes as the Argand *plane*. The Cartesian coordinates of z^* in this plane can also be expressed in terms of the circular coordinates r (the always positive radius of the circle centered at the origin and passing through the point), and the *phase angle* θ between the $+x$ axis and the radial line joining the point (x,iy) with the origin:

$$z = r\exp(i\theta), \tag{1.180}$$

so that

$$x = r\cos\theta \tag{1.181}$$

and

$$y = r\sin\theta . \tag{1.182}$$

[cf. eqs. (1.27)]. As noted above the radius r is always real and positive:

$$r = |z| . \tag{1.183}$$

The limit $z\to\infty$ is defined by $r\to\infty$ independent of θ and is therefore unique.

The inverse exponential is the *complex logarithm* Ln(z^*), that is multi-valued since trigonometric functions are periodic with period 2π:

$$\begin{aligned} &z^* = x + iy = r\exp(i\theta) = r\exp\left[i(\theta + 2n\pi)\right] \Rightarrow \\ &\mathrm{Ln}(z^*) = \ln(r) + i(\theta + 2n\pi). \end{aligned} \tag{1.184}$$

The *principal logarithm* is defined by $n = 0$ and $-\pi \le \theta \le +\pi$ and is usually implied by the term "logarithm"; it is indicated by a lower case Ln→ln so that $\mathrm{Ln}(z) = \ln(r)+iy$. From $x = \cos\theta$ and $y = \sin\theta$ and $r = 1$ two special cases are $\ln(i) = i\pi/2$ and $\ln(-1) = i\pi$.

The Cartesian construction provides a simple proof of the Euler relation since the function $f = \cos\theta + i\sin\theta$ is unity for $\theta = 0$ and satisfies

$$\frac{df}{d\theta} = -\sin\theta + i\cos\theta = i\left[\cos\theta + i\sin\theta\right] = if \ , \tag{1.185}$$

that is the differential equation for the exponential function $f = \exp(i\theta)$ since only the exponential function is proportional to its derivative and is unity at the origin.

Rotation by $\pi/2$ can also be described by two equivalent 2×2 matrices:

$$\begin{pmatrix} 0 & -1 \\ +1 & 0 \end{pmatrix}, \tag{1.186}$$

$$\begin{pmatrix} 0 & +1 \\ -1 & 0 \end{pmatrix}, \tag{1.187}$$

that describe clockwise or counter-clockwise rotations respectively by $\pi/2$ when pre-multiplying a vector (the direction of rotation reverses when the matrices post-multipy the vector). The matrices of eq. (1.186) and (1.187) are therefore matrix equivalents of $\pm i$. Their product is unity, corresponding to $(+i)(-i) = +1$, and their squares are also easily shown to be (–1). The complex number $z = x + iy$ can then be expressed as

$$z = \begin{pmatrix} +x & +y \\ -y & +x \end{pmatrix}, \tag{1.188}$$

and eq. (1.161) becomes

$$z = \begin{pmatrix} +x & +y \\ -y & +x \end{pmatrix} \otimes \begin{pmatrix} +x & +y \\ -y & +x \end{pmatrix} = \begin{pmatrix} x^2 - y^2 & +2xy \\ -2xy & x^2 - y^2 \end{pmatrix}. \tag{1.189}$$

The Euler relation enables simple derivations of trigonometric identities. For example:

$$\begin{aligned} \exp\left[i(x+y)\right] &= \cos(x+y) + i\sin(x+y) \\ &= \exp(ix)\exp(iy) \\ &= \left[\cos(x) + i\sin(x)\right]\left[\cos(y) + i\sin(y)\right] \\ &= \left[\cos(x)\cos(y) - \sin(x)\sin(y)\right] + i\left[\cos(x)\sin(y) + \sin(x)\cos(y)\right], \end{aligned} \tag{1.190}$$

so that equating the real and imaginary components yields

$$\cos(x+y) = \cos(x)\cos(y) - \sin(x)\sin(y) \tag{1.191}$$

and

$$\sin(x+y) = \sin(x)\cos(y) + \sin(y)\cos(x). \tag{1.192}$$

The Euler relation eq. (1.177) implies that trigonometric (*circular*) functions can be expressed in terms of complex exponentials. Changing the variable y to the angle θ then reveals that

$$\sin\theta = \frac{\exp(i\theta) - \exp(-i\theta)}{2i} \tag{1.193}$$

and

$$\cos\theta = \frac{\exp(i\theta) + \exp(-i\theta)}{2} . \tag{1.194}$$

The symmetry properties sin(–θ) = –sinθ and cos(–θ) = cosθ are evident from these relations. The circular functions are so named because the parametric equations $x = R\cos\theta$ and $y = R\sin\theta$ generate the equation of a circle, $x^2+y^2 = R^2$.

Equations (1.193) and (1.194) provide a convenient introduction to the *hyperbolic functions*, denoted by adding an "h" to the trigonometric function names that are defined by replacing $i\theta$ with θ:

$$\sinh\theta = \frac{\exp(\theta) - \exp(-\theta)}{2} , \tag{1.195}$$

$$\cosh\theta = \frac{\exp(\theta) + \exp(-\theta)}{2} , \tag{1.196}$$

so that

$$\cos(i\theta) = \cosh(\theta) , \tag{1.197}$$

$$\sin(i\theta) = i\sinh(\theta) , \tag{1.198}$$

$$\tan(i\theta) = i\tanh(\theta) , \tag{1.199}$$

$$\sinh^2(\theta) - \cosh^2(\theta) = 1 . \tag{1.200}$$

For complex arguments $z = x + iy$:

$$\sin(z) = \sin(x)\cosh(y) + i\cos(x)\sinh(y) \tag{1.201}$$

and

$$\cos(z) = \cos(x)\cosh(y) - i\sin(x)\sinh(y) . \tag{1.202}$$

The functions are named hyperbolic because the parametric equations $x=k\cosh(\theta)$ and $y=k\sinh(\theta)$ generate the hyperbolic equation $x^2 - y^2 = k^2$.

The inverse hyperbolic functions are multi-valued because of the multi-valuedness of the complex logarithm:

$$\mathrm{Arcsinh}(z) = (-1)^{1/2}\,\mathrm{arcsinh}(z) + n\pi i , \tag{1.203}$$

$$\mathrm{Arccosh}(z) = \pm\mathrm{arccosh}(z) + 2n\pi i , \tag{1.204}$$

$$\text{Arctanh}(z) = \text{arctanh}(z) + n\pi i \;, \tag{1.205}$$

in which n is a real integer. As with the complex logarithm it is customary to use uppercase first letters to denote the full multi-valued function and lowercase first letters to denote the principal values for which $n = 0$. For real arguments the principal functions have the logarithmic forms

$$\text{arcsinh}(x) = \ln\left[x + \left(x^2+1\right)^{1/2}\right], \tag{1.206}$$

$$\text{arccosh}(x) = \ln\left[x + \left(x^2-1\right)^{1/2}\right], \qquad x \geq 1 \tag{1.207}$$

$$\text{arctanh}(x) = \ln\left[\frac{1+x}{1-x}\right]^{1/2}, \qquad 0 \leq x^2 < 1 \tag{1.208}$$

$$\text{arcsech}(x) = \ln\left[\frac{1}{x} + \left(\frac{1}{x^2}-1\right)^{1/2}\right], \qquad 0 < x \leq 1 \tag{1.209}$$

$$\text{arccosech}(x) = \ln\left[\frac{1}{x} + \left(\frac{1}{x^2}+1\right)^{1/2}\right], \qquad x \neq 0 \tag{1.210}$$

$$\text{arccoth}(x) = \ln\left[\frac{x+1}{x-1}\right]^{1/2}. \qquad x^2 > 1 \tag{1.211}$$

1.8.2.1 Cauchy Riemann Conditions

The relationship between the real and imaginary components of an analytical function is given by the *Cauchy-Riemann conditions*, obtained from forcing the differential ratio $\lim\limits_{\delta\to 0}\left\{\left[f(z+\delta) - f(z)\right]/\delta\right\}$ to be independent of the direction in the complex plane of $\delta = \alpha + i\beta$. It is instructive to derive these conditions by equating the limits $\alpha(\beta = 0)\to 0$ and $\beta(\alpha = 0)\to 0$. These two derivatives are

$$\frac{df}{dx} = \lim_{\alpha\to 0}\left\{\frac{u(x+\alpha,y) + iv(x+\alpha,y) - u(x,y) - iv(x,y)}{\alpha}\right\} = \frac{\partial u}{\partial x} + i\frac{\partial v}{\partial x} \tag{1.212}$$

and

$$\begin{aligned}\frac{df}{dy} &= \lim_{\beta\to 0}\left\{\frac{u(x,y+\beta) + iv(x,y+\beta) - u(x,y) - iv(x,y)}{i\beta}\right\} \\ &= \lim_{\beta\to 0}\left\{\frac{-iu(x,y+\beta) + v(x,y+\beta) + iu(x,y) - v(x,y)}{\beta}\right\} = \frac{\partial v}{\partial y} - i\frac{\partial u}{\partial y}.\end{aligned} \tag{1.213}$$

Equating the real and imaginary parts of eqs. (1.212) and (1.213) produces the *Cauchy-Riemann* conditions

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \tag{1.214}$$

and

$$\frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x}. \tag{1.215}$$

The functions u and v are harmonic because they obey the Laplace equations $\left(\partial_x^2 + \partial_y^2\right)u = 0$ and $\left(\partial_x^2 + \partial_y^2\right)v = 0$.

Functions that are analytical except for isolated singularities (poles) where the functions are infinite are also useful in relaxation phenomenology. For example a singularity at the origin corresponds to a pathology at zero frequency, which although immeasurable by ac techniques will nevertheless influence the function at low frequencies. The word "analytical" is often used incorrectly in the physical literature to denote a function that does not have to be evaluated numerically. We refer to such functions as *closed form functions* in this book. Some closed form analytic functions have not yet been given specific names [$w(z)$ in eq. (1.37) for example].

1.8.2.2 Complex Integration and Cauchy Formulae

It is convenient to first consider integration of a real function of a real variable (say x) in which the integration interval includes a singularity. The integral may still exist (i.e. not be be infinite) but must be evaluated as a *Cauchy principal value*, which is denoted by P in front of the integral (often omitted and assumed if necessary). For an integrand with a singularity at the origin, for example,

$$P\int_{-a}^{+a} f(x)\,dx = \lim_{\varepsilon \to 0}\left[\int_{-a}^{-\varepsilon} f(x)\,dx + \int_{+\varepsilon}^{+a} f(x)\,dx\right]. \tag{1.216}$$

It is essential that the limit be taken symmetrically on each side of the singularity.

Complex integration corresponds to contour integration in the complex plane. The value of such a complex contour integral of an analytical function is independent of the contour. Thus the integral for a closed contour is zero and the *Cauchy Theorem* results:

$$\oint f(z)\,dz = 0. \tag{1.217}$$

Application of the Cauchy Theorem to the derivative of an analytical function gives the *Cauchy Integral Theorem*: The derivative

$$\frac{df(z)}{dz} = \lim_{z \to w}\left[\frac{f(z) - f(w)}{z - w}\right] \tag{1.218}$$

implies

$$\oint\left[\frac{f(z)-f(w)}{z-w}\right]=\oint\frac{df}{dz}=0 \qquad \text{(from eq. (1.217))}, \tag{1.219}$$

so that

$$\begin{aligned}\oint\left[\frac{f(z)}{z-w}\right]&=\oint\left[\frac{f(w)}{z-w}\right]\\ &=f(w)\oint d\ln(z-w)=f(w)\oint d\left\{\ln|z-w|+i\theta\right\}\\ &=f(w)[i\theta]\Big|_0^{2\pi}=f(w)[2\pi i],\end{aligned} \tag{1.220}$$

where eq. (1.184) for the complex logarithm has been invoked and the closed contour integral of the real function $\ln(|z-w|)$ is zero by the Cauchy theorem. This produces the *Cauchy integral theorem*:

$$f(w)=\frac{1}{2\pi i}\oint\left[\frac{f(z)}{z-w}\right]. \tag{1.221}$$

An important factor to consider when analyzing eq. (1.221) is that the range of integration includes the singularity at $z = w$ that cannot be simply handled using the Cauchy principal value alone because this essentially excises a segment from the contour integral. The (almost literal) work around is to add to the contour a semicircular bypass around the singularity with radius ρ and then taking the limit $\rho \to 0$.

1.8.2.3 Residue Theorem

Application of the Cauchy Integral Theorem to a closed annulus enclosing the circle $r=|z-a|$ with concentric radii b and c such that $b\le|z-a|\le c$ yields

$$2\pi i f(w)=\oint_{|z-a|=b}\frac{f(z)}{z-w}-\oint_{|z-a|=c}\frac{f(z)}{z-w}. \tag{1.222}$$

Placing $(z-w)=(z-a)-(w-a)$ and expanding $(z-w)^{-1}$ as a geometric series [eq. (1.10)] gives

$$\frac{1}{(z-a)-(w-a)}=\frac{1}{(z-a)}\sum_{n=0}^{\infty}\left[\frac{(w-a)}{(z-a)}\right]^n \qquad \left(c=|z-a|>|w-a|\right) \tag{1.223}$$

and

$$\frac{1}{(z-a)-(w-a)}=\frac{-1}{(w-a)}\sum_{n=0}^{\infty}\left[\frac{(z-a)}{(w-a)}\right]^n \qquad \left(b=|z-a|>|w-a|\right) \tag{1.224}$$

Inserting eqs. (1.223) and (1.224) into eq. (1.222) yields

$$\begin{aligned} f(w) &= \frac{1}{2\pi i}\left[\oint \frac{f(z)}{z-w}\right]\sum_{n=0}^{\infty}\left[\frac{(w-a)}{(z-a)}\right]^n + \frac{1}{2\pi i}\left[\oint \frac{f(z)}{z-w}\right]\sum_{n=0}^{\infty}\left[\frac{(z-a)}{(w-a)}\right]^n \\ &= \frac{1}{2\pi i}\sum_{n=0}^{\infty}\left[\oint \frac{f(z)}{(z-a)^{n+1}}\right](w-a)^n + \frac{1}{2\pi i}\sum_{n=0}^{\infty}\left[\oint \frac{f(z)}{(w-a)^{n+1}}\right](z-a)^n. \end{aligned} \tag{1.225}$$

Equation (1.225) is a Laurent series $\sum_{-\infty}^{+\infty} c_n (w-a)^n$ with

$$c_n = \frac{1}{2\pi i}\left[\oint \frac{f(z)}{(z-a)^{n+1}}\right] \qquad n \geq 0 \tag{1.226}$$

$$c_n = \frac{1}{2\pi i}\left[\oint f(z)(z-a)^{n+1}\right] \qquad n < 0 \tag{1.227}$$

The n = –1 term in eq. (1.227) is important because $(z-a)^{n+1}$ is then unity for all values of $(z-a)$ so that

$$\oint f(z) = 2\pi i \sum_k c_{-1,k}\ , \tag{1.228}$$

in which $c_{-1,k}$ is called the residue at the k^{th} pole because it is the only term that survives the closed contour integration. If $f(z)$ is entirely analytical within the contour (i.e. there are no singularities so that $c_{n,k} = 0$ for $n < 0$ and $f(z)$ becomes a Taylor series) then the contour integral is zero and the Cauchy Theorem is recovered. The coefficients $c_{-1,k}$ can be evaluated even if the Laurent expansion of $f(z)$ is not known, by taking the n^{th} derivative of $f(z)$ for a singularity of order n [7,13]:

$$c_{-1} = \frac{1}{(n-1)!}\left\{\frac{d^{n-1}\left[(z-a)^n\right]f(z)}{dz^{n-1}}\right\}\Bigg|_{z=a}. \tag{1.229}$$

For n = 1 this simplifies to

$$c_{-1} = \lim_{z\to a}\left[(z-a)\,f(z)\right], \tag{1.230}$$

and for $f(z) = g(z)/h(z)$ with $g(z)$ having no singularites at $z = a$ and $h(a) = 0 \neq (dh/dz)\big|_{z=a}$ then

$$c_{-1} = \lim_{z\to a}\left[\frac{(z-a)^n g(z)}{h(z)-h(a)}\right] = \frac{g(a)}{\left(dh/dz\right)\big|_{z=a}}. \tag{1.231}$$

1.8.2.4 Hilbert Transforms, Crossing Relations, and Kronig-Kramer Relations

The Hilbert transforms are obtained by applying the Cauchy theorem to a contour comprising a segment of the real-axis and a semicircle joining its ends. In the limit that the segment is infinitely long so that integration is performed from $x = -\infty$ to $x = +\infty$ the contribution from the semicircle vanishes if the function has the (physically necessary) property that it vanishes as $z\to\infty$. Application of the Cauchy theorem to this contour for $f(w) = u(w) + iv(w)$ then gives

$$f(w) = \frac{1}{2\pi i}\int_{-\infty}^{+\infty}\frac{f(x)\,dx}{x-w}. \tag{1.232}$$

When the semicircular bypass around the singularity is included (§1.8.3.2) eq. (1.232) becomes

$$f(w) = \frac{1}{2\pi i}\left\{\lim_{\rho\to 0}\left[\int_{-\infty}^{x-\rho}\frac{f(x)\,dx}{x-w} + \int_{x+\rho}^{+\infty}\frac{f(x)\,dx}{x-w}\right] + \oint_{\sim\rho}\frac{f(x)\,dx}{x-w}\right\}, \tag{1.233}$$

where $\oint_{\sim\rho}$ denotes an open semicircular arc of radius ρ rather than a closed contour. The semicircular contour integral is evaluated using the Residue Theorem (RT) taking into account symmetry so that only half the RT value is attained. Equation (1.228) then becomes (with k = 1)

$$\oint f(z) = \pi i c_{-1} \tag{1.234}$$

and eq. (1.230) becomes

$$c_{-1} = (x-w)\,f(w) \tag{1.235}$$

so that

$$\oint f(x) = \pi i (x-w)\,f(w). \tag{1.236}$$

Equation (1.236) yields $f(w)/2$ for the third term in eq. (1.233) so that

$$f(w) = \frac{1}{\pi i}\int_{-\infty}^{+\infty}\frac{f(x)\,dx}{x-w}$$
$$= \frac{1}{\pi i}\int_{-\infty}^{+\infty}\frac{\left[u(x)+iv(x)\right]dx}{x-w} = \frac{-i}{\pi}\int_{-\infty}^{+\infty}\frac{u(x)\,dx}{x-w} + \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{v(x)\,dx}{x-w} \tag{1.237}$$
$$= u(w) + iv(w).$$

Note that the limit $\rho\to 0$ in eq. (1.233) is needed only for evaluating the Cauchy principal value because the radius of the semi-circular half-closed contour is irrelevant for the residue theorem. Equation (1.237) yields the *Hilbert Transforms*

$$u(w) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{v(x)\,dx}{x-w} \tag{1.238}$$

and

$$v(w) = \frac{-1}{\pi}\int_{-\infty}^{+\infty}\frac{u(x)\,dx}{x-w}. \tag{1.239}$$

Note that $u(x)$ or $v(x)$ must be known everywhere on the real axis in order that $v(w)$ or $u(w)$ can be evaluated at a single point. In physical applications this often means assuming a specific function with which to extrapolate $x\to\pm\infty$. The form of this extrapolation function is unimportant if the extrapolated part of the integral is a sufficiently small fraction of the total.

A special result is that for $v(w)$ = constant = C

$$\frac{du}{dw} = \frac{C}{\pi}\int_{-\infty}^{+\infty}\frac{dx}{(x-w)^2} = \frac{2C}{\pi}\int_{0}^{+\infty}\frac{dx}{(x-w)^2} = \frac{2C}{\pi}\left(\frac{-1}{x-w}\right)\Bigg|_0^{\infty} = \frac{-2C}{\pi w}, \tag{1.240}$$

so that

$$C = \left(\frac{-\pi}{2}\right)\frac{du(w)}{d\ln(w)}. \tag{1.241}$$

The *crossing relations* derive from the important physical requirement that the *Fourier transforms* of many physically relevant functions $f(\omega)$ be real (these transforms are discussed in 1.8.4.2 below). Real Fourier transforms (see §1.7.9) imply

$$f(x) = u(x) + iv(x) = f^{\dagger}(-x) = u(-x) - iv(-x), \tag{1.242}$$

that in turn implies the crossing relations

$$u(x) = u(-x) \tag{1.243}$$

and

$$v(x) = -v(-x). \tag{1.244}$$

Applying these crossing relations to the Hilbert transforms removes integration over negative values of *x* and yields the *Kronig-Kramers relations*

$$u(x) = \frac{2}{\pi}\int_0^{+\infty} \frac{\omega v(\omega)\,d\omega}{\omega^2 - x^2} \tag{1.245}$$

and

$$v(x) = \frac{-2x}{\pi}\int_0^{+\infty} \frac{u(\omega)\,d\omega}{x^2 - \omega^2}. \tag{1.246}$$

They were first derived by Kronig and Kramers in the context of elementary particle theory in 1926 and are also known as *dispersion relations*. For large values of *x* the Kronig-Kramers relations yield the *sum rules*:

$$\lim_{x\to\infty} u(x) = \frac{-2}{\pi x^2}\int_0^{+\infty} \omega v(\omega)\,d\omega; \qquad \lim_{x\to\infty} v(x) = \frac{2}{\pi x}\int_0^{+\infty} u(\omega)\,d\omega. \tag{1.247}$$

For small values of *x*

$$\lim_{x\to 0} v(x) = \frac{-2x}{\pi}\int_0^{+\infty} \frac{u(\omega)}{\omega^2}\,d\omega. \tag{1.248}$$

1.8.2.5 Plemelj Formulae

The multivalued character of the complex logarithm [eq. (1.184)] leads to the curious result that some functions can attain different values at the same point depending on the direction of approach to the point (i.e. they are discontinuous at the point). Such functions are *sectionally analytic*. Consider a line *L* (not necessarily straight or closed) and a circle of radius ρ centered at a point τ lying on *L*. Call the segment of *L* that lies within the circle λ and the rest as Λ, and consider the following function as it approaches τ from each end of *L*:

$$F(z)=\frac{1}{2\pi i}\int_L \frac{f(t)\,dt}{t-z}=\frac{1}{2\pi i}\int_\Lambda \frac{f(t)\,dt}{t-z}+\frac{1}{2\pi i}\int_\lambda \frac{f(t)\,dt}{t-z} \tag{1.249}$$

$$=\frac{1}{2\pi i}\int_\Lambda \frac{f(t)\,dt}{t-z}+\frac{1}{2\pi i}\int_\lambda \frac{\left[f(t)-f(\tau)\right]dt}{t-z}+\frac{f(\tau)}{2\pi i}\int_\lambda \frac{dt}{t-z}. \tag{1.250}$$

The second integral of eq. (1.250) approaches zero as (i) $z\to\tau$ from each side of L and (ii) $\rho\to 0$ (it is important that the second limit be taken after the first). The third integral is the change in $\ln(t-z)$ as t varies across λ and this is where the peculiarity originates. The magnitude $\ln\left(\left|t-z\right|\right)$ has the same value $\ln(\rho)$ at each end, but the angle subtended at z by the line segment λ has a different sign as z approaches L from each side, because the directions of rotation of the vector $(t-z)$ are opposite as t moves along λ [1]. This angle contributes $\pm\pi i$ to the complex logarithm as $z\to\tau$ from each side and yields the *Plemelj formulae*:

$$F^+(\tau)=\frac{1}{2\pi i}\int_L \frac{f(t)\,dt}{t-\tau}+\frac{f(\tau)}{2}\neq F^-(\tau)=\frac{1}{2\pi i}\int_L \frac{f(t)\,dt}{t-\tau}-\frac{f(\tau)}{2}\ . \tag{1.251}$$

If L is a closed loop, the Plemelj formulae become

$$\begin{aligned}F^+(\tau)&=\frac{1}{2\pi i}\int_L \frac{\left[f(t)-f(\tau)\right]dt}{t-\tau}+f(\tau),\\ F^-(\tau)&=\frac{1}{2\pi i}\int_L \frac{\left[f(t)-f(\tau)\right]dt}{t-\tau},\end{aligned}\ . \tag{1.252}$$

so that a discontinuity of magnitude $f(\tau)$ occurs. Examples of $\{f(t),F(z)\}$ pairs are (a and b denote the ends of L):

$$f(t)=t^{-1}\qquad\Leftrightarrow\qquad F(z)=z^{-1}\ln\left[\frac{a(z-b)}{b(z-a)}\right] \tag{1.253}$$

and

$$f(t)=t^{n}\qquad\Leftrightarrow\qquad F(z)=\sum_{\ell+k=1-n}\left(\frac{b^{\ell+1}-a^{\ell+1}}{\ell+1}\right)z^k+z^n\ln\left[\frac{(z-b)}{(z-a)}\right] \tag{1.254}$$

from which

$$f(t)=1\qquad\Leftrightarrow\qquad F(z)=\ln\left[\frac{(z-b)}{(z-a)}\right], \tag{1.255}$$

$$f(t)=t \qquad \Leftrightarrow \qquad F(z)=(b-a)+z\ln\left[\frac{(z-b)}{(z-a)}\right]. \tag{1.256}$$

1.8.2.6 Analytical Continuation

The radius of convergence R of a series expansion of a function $f(z-z_0)$ about a point z_0 is determined by the nearest singularity. It is often possible to move z_0 to another location inside R and find another radius of convergence (that may or may not be determined by the same singularity) and thereby define a larger part of the complex plane within which the expansion converges and the function is analytic. This process is known as analytical continuation, and by repeated application the entire complex plane can often be covered apart from isolated singularities (that may be infinite in number, however). An important application of this principle is extending a function defined by a real argument to the entire complex plane. The Laplace and Fourier transforms discussed below are examples of such a continuation and using the residue theorem to evaluate a real integral is another.

1.8.2.7 Conformal Mapping

A complex function $f(z) = u(x,y)+iv(x,y)$ can be regarded as *mapping* the points z in the complex z plane onto points $f(z)$ in the complex f plane. Changes in z produce changes in $f(z)$ with a magnification factor given by df/dz. Since the derivative of an analytical function is independent of the direction of differentiation this magnification is isotropic and depends only on the radial separation of any two points in the z plane; such a mapping is said to be *conformal*. An important mapping function is the complex exponential $f(z) = \exp(-z)$.

1.8.3 Transforms

1.8.3.1 Laplace

The Laplace transform and its inverse are the most important transforms in relaxation phenomenology. It arises from mapping of the complex function $z = \exp(-s)$ from the complex s-plane onto the complex z-plane (the change in variables from those used above is made to introduce the traditional Laplace variable s). The exponential function maps the inside of the circle of convergence $|z|<R$ onto the half plane defined by $\mathrm{Re}(s) > -\ln(R)$ [a result of $s=-\ln(z)=-\ln\left[R-i(\theta+2n\pi)\right]$. Thus an analytical function $G(z)$ defined by the MacLaurin series

$$G(z)=\sum_{n=0}^{\infty} g_n z^n \tag{1.257}$$

transforms to

$$G(s)=\sum_{n=0}^{\infty} g_n \exp(-ns), \tag{1.258}$$

that is generalized to an integral by replacing the integer variable n with a continuous variable t:

$$G(s)=\int_0^\infty g(t)\exp(-st)\,dt\,. \tag{1.259}$$

The function $G(s)$ in eq. (1.259) is the *Laplace transform* of $g(t)$. It is an analytical function if the integral converges for sufficiently large values of s (specified below), that will always occur if $g(t)$ does not become infinite too rapidly as $t\to\infty$ (recall that this is the same condition used to derive the Hilbert transforms from the Cauchy Integral Theorem). The edge of the area of convergence for eq. (1.259) is a line defined by $\mathrm{Re}(s) = \rho$ where ρ is now the abscissa of convergence corresponding to the condition $\mathrm{Re}(s) > -\ln(R)$ in the MacLaurin expansion.

The *inverse Laplace transform* is as important as the Laplace transform itself. It is derived by considering the Cauchy integral theorem with variables s and z:

$$G(s)=\frac{1}{2\pi i}\oint\frac{G(z)\,dz}{s-z}\,, \tag{1.260}$$

in which the closed contour comprises a straight line parallel to the imaginary axis defined by $x = \sigma > \rho$ and a semicircle in the complex half plane. If the radius of the semicircle becomes infinite its contribution to the contour integration will be zero if $G(z)$ approaches zero faster than $(s–z)^{-1}$. In this case the Cauchy integral becomes

$$G(s)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{G(z)\,dz}{s-z}\,, \tag{1.261}$$

where the direction of contour integration is clockwise. The factor $(s–z)^{-1}$ can be expressed as

$$(s-z)^{-1}=\int_0^\infty \exp\left[-(s-z)t\right]dt=\int_0^\infty \exp(-st)\exp(zt)\,dt\,, \tag{1.262}$$

insertion of which into eq. (1.261) and reversing the order of integration yields

$$G(s)=\int_0^\infty \exp(-st)\left[\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\exp(zt)G(z)\right]dt\,. \tag{1.263}$$

Comparing eq. (1.259) with eq. (1.263) reveals that

$$g(t)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\exp(+st)G(s)\,ds\,, \tag{1.264}$$

that is therefore the *inverse Laplace transform* of $G(s)$. The path of integration of this inverse Laplace transform can also be considered to be part of a closed semi-circular contour in the s – plane. For $t > 0$ the semicircle must pass through the negative half plane of $\mathrm{Re}(s)$ to ensure exponential attenuation. Since this half plane lies outside the region of convergence defined by $\sigma > \rho$ this semicircular contour must enclose at least one singularity, and the integral (1.264) is nonzero by the residue theorem and can be evaluated using it. For $t < 0$ the semicircular part of the closed contour must pass through the positive half plane of Re(s) to ensure exponential attenuation, but since this contour lies totally within the area of convergence the integral is identically zero by eq. (1.217). Thus

$$\begin{aligned} g(t) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \exp(+st)G(s)\,ds \qquad && t \geq 0 \\ &= 0 && t < 0. \end{aligned} \tag{1.265}$$

Equation (1.265) ensures the *causality condition* that a response cannot precede the excitation at time zero. This is the principle reason for Laplace transforms being so important to relaxation phenomenology. The derivation of eq. (1.265) indicates that causality and analyticity are closely linked, and indeed it can be shown that analyticity compels causality and vice versa.

The value of the abscissa of convergence σ can sometimes be determined by inspection, especially if the function to be transformed includes an exponential factor. Consider for example the function $g(t) = t^n \sinh(mt)$ for which the long time limit is $\tfrac{1}{2}t^n \exp(mt)$. The integrand of the LT is then $\tfrac{1}{2}t^n \exp(mt)\exp(-st) = \tfrac{1}{2}t^n \exp\left[-(s-m)t\right]$ that is integrable if $s > m$ so that $\rho = m$.

The product of two Laplace transforms is not the Laplace transform of the product of the functions. For $R(s) = P(s)Q(s)$ the inverse Laplace transform $r(t)$ is the *convolution integral*

$$r(t) = \int_0^t p(\tau)q(t-\tau)\,d\tau\,, \tag{1.266}$$

that often arises in relaxation phenomenology because it expresses the *Boltzmann superposition* of responses to time dependent excitations (§1.14).

The *bilateral Laplace transform* is defined as

$$F(ds) = \int_{-\infty}^{+\infty} \exp(-st)\, f(t)\,dt\,, \tag{1.267}$$

that can clearly be separated into two unilateral transforms

$$F(s) = \int_0^{+\infty} \exp(-st)\, f(t)\,dt + \int_0^{+\infty} \exp(+st)\, f(-t)\,dt\,. \tag{1.268}$$

The first of these transforms diverges for large negative real values of s and the second diverges for large positive real values of s so that convergence becomes restricted to a strip running parallel to the imaginary s axis. Equation (1.267) is not necessarily a Fourier transform (see below) because the complex variable s can have a real component whereas the Fourier variable is purely imaginary.

Laplace transforms are also mathematically useful because they transform differential equations (for example in time) into simple polynomials (in frequency). This is readily shown using integration by parts (§1.2.5) of the Laplace transform (LT) of the n^{th} derivative of the function $f(t)$:

$$LT\left(\frac{d^n f}{dt^n}\right) = s^n F(s) - \sum_{k=0}^{n-1}\left(\frac{d^k f(0)}{dt^k}\right) s^{n-k-1} \quad (1.269)$$

(the equation for this given in [1] is incorrect). For $n=1(k=0)$ eq. (1.269) yields

$$LT\left(\frac{df}{dt}\right) = sF(s) - f(0). \quad (1.270)$$

Because $t\to 0$ corresponds to $\omega\to\infty$ eq. (1.270) can also be written as

$$LT\left(\frac{df}{dt}\right) = sF(s) - F(\infty). \quad (1.271)$$

Other Laplace transforms are exhibited in Appendix A. Practically useful functions often have dimensionless variables, such as t/τ_0 and $s = i\omega\tau_0$ for example, and these introduce additional numerical factors into the formulae. For example, eq. (1.270) becomes

$$LT\left[\frac{df(t/\tau_0)}{dt}\right] = i\omega\tau_0 F(i\omega\tau_0) - f(0). \quad (1.272)$$

The *Laplace-Stieltjes integral* is a generalized Laplace transform where the integral is with respect to a function of *t* rather than *t* itself:

$$\int_0^\infty \exp(-st)\, d\phi(t). \quad (1.273)$$

1.8.3.2 Fourier

Consider again the Laurent expansion for an analytical function *f*(*z*), eq. (1.171). As with the Laplace transform the annulus of convergence for this series gets mapped by the exponential function onto a strip parallel to the imaginary axis, but now negative values of the summation index are included and the exponential mapping is confined to purely imaginary arguments to avoid exponential amplification for negative real arguments. Then, in analogy with eq. (1.258),

$$G(\omega) = \sum_{n=-\infty}^{+\infty} g_n \exp(-in\omega). \quad (1.274)$$

Continuing the analogy with the Laplace transform derivation, eq. (1.274) can also be expressed in terms of the continuous variable, *t*:

$$G(\omega) = \int_{-\infty}^{+\infty} g(t)\exp(-i\omega t)\, dt. \quad (1.275)$$

$G(\omega)$ is the *Fourier transform* (*FT*) of $g(t)$ and is in general complex. The similarity of the Fourier and Laplace transforms can be exploited to derive the inverse Fourier transform. Recall the inverse Laplace transform eq. (1.264):

$$g(t)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}G(z)\exp(+zt)\,dz\,. \tag{1.276}$$

Putting $z = \sigma+i\omega$ where σ is a constant so that $dz = id\omega$ yields

$$\exp(-\sigma t)g(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}G(\sigma+i\omega)\exp(+i\omega t)\,d\omega\ . \tag{1.277}$$

Now define

$$f(t)=\exp(-\sigma t)g(t) \tag{1.278}$$

and

$$F(\omega)=G(\sigma+i\omega)\,. \tag{1.279}$$

Equation (1.277) then becomes

$$f(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}F(\omega)\exp(+i\omega t)\,d\omega\,, \tag{1.280}$$

and eq. (1.275) is essentially unchanged:

$$F(\omega)=\int_{-\infty}^{+\infty}f(t)\exp(-i\omega t)\,dt\,. \tag{1.281}$$

Equations (1.280) and (1.281) comprise the *Fourier inversion* formulae. They are more symmetric than the Laplace formulae because the Fourier transform includes both positive and negative arguments. To emphasize this symmetry $f(t)$ is sometimes multiplied by $(2\pi)^{1/2}$ and $F(\omega)$ is multiplied by $(2\pi)^{-1/2}$ to give Fourier pairs that have the same pre-integral factor of $(2\pi)^{-1/2}$.

The Fourier transform of a function that is zero for negative arguments is referred to as one sided. The Laplace and inverse Laplace transforms [eqs. (1.259) and (1.264)] can then be expressed as

$$G(i\omega)=\int_{0}^{+\infty}g(t)\exp(-i\omega t)\,dt \tag{1.282}$$

and

$$g(t) = \frac{1}{2\pi}\int_0^{+\infty} G(i\omega)\exp(+i\omega t)\,d\omega \qquad (t \ge 0)$$
$$= 0 \qquad (t < 0). \tag{1.283}$$

As with Laplace transforms the product of two Fourier transforms is not the Fourier transform of the product but rather the Fourier transform of the convolution integral. For $H(\omega) = F(\omega)G(\omega)$:

$$h(t) = \int_0^t f(\tau)g(t-\tau)\,d\tau\,. \tag{1.284}$$

Many of the formulae for Fourier transforms are closely analogous to those for pure imaginary Laplace transforms. For example (cf. Appendix A):

$$g\left(\frac{t}{n}\right) \Leftrightarrow nG(n\omega), \tag{1.285}$$

$$\exp(i\omega_0 t)\,g(t) \Leftrightarrow G(\omega - \omega_0), \tag{1.286}$$

$$g(t - t_0) \Leftrightarrow \exp(-i\omega_0 t)G(\omega), \tag{1.287}$$

$$(-it)^n\,g(t) \Leftrightarrow \frac{d^n G(\omega)}{d\omega^n}, \tag{1.288}$$

and

$$\frac{d^n g(t)}{dt^n} \Leftrightarrow (-i\omega)^n\,G(\omega)\,. \tag{1.289}$$

A special result is that the *FT* of a Gaussian is another Gaussian:

$$\int_{-\infty}^{+\infty} \exp(i\omega t)\exp(-a^2t^2)\,dt = \int_{-\infty}^{+\infty} \left[\cos(\omega t) + i\sin(\omega t)\right]\exp(-a^2t^2)\,dt$$
$$= \int_{-\infty}^{+\infty} \cos(\omega t)\exp(-a^2t^2)\,dt = \frac{\pi^{1/2}}{a}\exp\left(\frac{-\omega^2}{4a^2}\right), \tag{1.290}$$

where the antisymmetric property of the sine function has been used. Placing $a^2 = 1/\sigma_t^2$, where σ_t^2 is the variance of *t*, yields $\left(\pi^{1/2}/a\right)\exp\left(-\sigma_t^2\omega^2/4\right)$ for the *FT*.

1.8.3.3 Z

For discretized functions *f*(*n*) the *Z Transform* is

$$F\left(z\right)=\sum_{n=0}^{\infty}f\left(n\right)z^{n-1}, \qquad (1.291)$$

and the integral form of the inverse is

$$f\left(n\right)=\frac{1}{2\pi i}\oint_{C}F\left(z\right)z^{n-1}dz, \qquad (1.292)$$

where C is a closed contour within the region of convergence of $F(z)$ and encircling the origin. If C is a circle of unit radius then the inverse transform simplifies to

$$f\left(n\right)=\frac{1}{2\pi}\int_{-\pi}^{+\pi}x\left[\exp\left(i\omega\right)\right].\exp\left(i\omega n\right)d\omega \qquad (1.293)$$

The Z–transform is used in digital processing applications.

1.8.3.4 Mellin

The continuous *Mellin Transform* is

$$M\left(s\right)=\int_{0}^{+\infty}m\left(t\right)t^{s-1}dt, \qquad (1.294)$$

and its inverse is

$$m\left(t\right)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}M\left(s\right)t^{-s}ds. \qquad (1.295)$$

1.8.4 Other Functions

1.8.4.1 Heaviside and Dirac Delta Functions

The Heaviside function $h(t–t_0)$ is a unit step that increases from 0 to 1 at $t = t_0$:

$$h\left(t-t_0\right)\equiv\begin{cases}0 & t<t_0\\ 1 & t\geq t_0\end{cases}. \qquad (1.296)$$

The differential of $h(t–t_0)$ is

$$dh\left(t-t_0\right)\equiv\delta\left(t-t_0\right)=\begin{cases}1 & t=t_0\\ 0 & t\neq t_0\end{cases}, \qquad (1.297)$$

where $\delta(t–t_0)$ is the *Dirac delta function* that is the limit of any peaked function whose width goes to zero and height goes to infinity in such a way as to make the area under it equal to unity (a rectangle of height h and width $1/h$ for example). The area constraint is needed to ensure consistency with the integral of $\delta(t–t_0)$ being the Heaviside function. The Dirac delta function has the useful property of singling out the value of an integrand at $(t–t_0)$. For example the Laplace transform of $\delta(t–t_0)$ is

$$\int_0^{+\infty} \delta(t-t_0)\exp(-st)\,dt = \exp(-st_0), \tag{1.298}$$

that we write as $\delta(t-t_0) \Leftrightarrow \exp(-st_0)$. The Laplace transform of $h(t-t_0) = \int \delta(t-t_0)\,dt$ is, from eq. (1.270),

$$\frac{\exp(-st_0)}{s} \Leftrightarrow h(t-t_0). \tag{1.299}$$

The Laplace transform of the ramp function

$$\begin{aligned}\mathrm{Ramp}(t-t_0) &= \int_{t_0}^{t} h(t'-t_0)\,dt' \\ &= \begin{cases} 0 & t < t_0 \\ (t-t_0) & t \ge t_0 \end{cases}\end{aligned} \tag{1.300}$$

is therefore $\exp(-s_0 t)/s^2$.

1.8.4.2 Green Functions

Consider a material that produces an output $y(t)$ when an input excitation $x(t)$ is applied to it. The relationship between $y(t)$ and $x(t)$ is determined by the circuit's transfer or response function $g(t)$. For example if x is an electrical voltage and y is an electrical current then g is the material's conductivity. The corresponding Laplace transforms are $X(s)$, $Y(s)$ and $G(s)$. When the input $x(t)$ to a system is a delta function $\delta(t–t_0)$ the response function $g(t)$ is named the system's impulse response function and is also known as the system's *Green Function*. It completely determines the output $y(t)$ for all possible inputs $x(t)$ because the latter can always be expressed in terms of $\delta(t–t_0)$:

$$x(t) = \int_0^{\infty} x(t')\delta(t-t')\,dt'. \tag{1.301}$$

Thus for any arbitrary input function $x(t)$ the response $y(t)$ of a system with Green function $g(t)$ is

$$y(t) = \int_0^{\infty} x(t')g(t-t')\,dt'. \tag{1.302}$$

This is identical to the convolution integral for an inverse Laplace transform, eq. (1.266), so that

$$Y^*(i\omega) = X^*(i\omega)G^*(i\omega). \tag{1.303}$$

1.8.4.3 Schwartz Inequality, Parseval Relation, and Bandwidth-Duration Principle

The integral

$$\int_\alpha^\beta \left|P(z)+xQ(z)\right|^2 dz = \left|P(z)\right|^2 + 2x\left|P(z)\right|\left|Q(z)\right| + x^2\left|Q(z)\right|^2 = a_0 + a_1 x + a_2 x^2 \tag{1.304}$$

cannot be negative if *x* and *z* are independent of one another. This is equivalent to the quadratic integrand having no real roots that is expressed by the discriminant condition $a_1^2 - 4a_0a_2 \le 0$ or $a_1^2 \le 4a_0a_2$ (§1.2.1). Thus, for real *P* and *Q*,

$$\left[\int_\alpha^\beta \left|P(z)Q(z)\right| dz\right]^2 \le \left[\int_\alpha^\beta \left|P^2(z)\right| dz\right]\left[\int_\alpha^\beta \left|Q^2(z)\right| dz\right], \tag{1.305}$$

a relation known as the *Schwartz inequality*. Generally speaking $\alpha = 0$ or $-\infty$ and $\beta = +\infty$ for many (most?) relaxation applications. A noteworthy consequence of the Schwartz inequality is that the reciprocal of an average, say $1/\langle F\rangle$, is not generally equal to the average of the reciprocal, $\langle 1/F\rangle$: putting $|P|^2 = F$ and $|Q|^2 = 1/F$ into eq. (1.305) gives

$$\langle F\rangle\langle 1/F\rangle \ge 1. \tag{1.306}$$

The Schwartz inequality is a special case ($n = m = 2$) of *Hölder's inequality*:

$$\int_\alpha^\beta \left|P(x)Q(x)\right| dx \le \left[\int_\alpha^\beta \left|P^n(x)\right| dx\right]^{1/n}\left[\int_\alpha^\beta \left|Q^m(x)\right| dx\right]^{1/m}, \left(\frac{1}{n}+\frac{1}{m}=1;\ n>1;\ m>1\right). \tag{1.307}$$

The equality holds if and only if $\left|P(x)\right| = c\left|Q(x)\right|^{m-1}$, where $c > 0$ is a real constant. *Minkowski's inequality* is [4]

$$\left[\int_\alpha^\beta \left|P(x)+Q(x)\right|^n dz\right]^{1/n} \le \left[\int_\alpha^\beta \left|P(x)\right|^n dx\right]^{1/n} + \left[\int_\alpha^\beta \left|Q(x)\right|^n dx\right]^{1/n}, \tag{1.308}$$

for which the equality obtains only if $P(x) = cQ(x)$ and again $c > 0$ is a real constant.

An important identity associated with Fourier transforms is the Parseval relation. Consider the integral

$$I = \int_{-\infty}^{+\infty} g_1(t)\, g_2^{\dagger}(t)\, dt\,, \tag{1.309}$$

and let the Fourier transforms of $g_1(t)$ and $g_2(t)$ be $G_1(\omega)$ and $G_2(\omega)$ respectively. Replacing $g_1(t)$ by its inverse Fourier transform [eq. (1.280)] yields

$$\begin{aligned} I &= \frac{1}{2\pi}\int_{0}^{+\infty}\left[\int_{-\infty}^{+\infty}\exp(i\omega t)\, G_1(\omega)\, d\omega\right] g_2^{\dagger}(t)\, dt \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} G_1(\omega)\left[\int_{0}^{+\infty} g_2^{\dagger}(t)\exp(i\omega t)\, dt\right] d\omega \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} G_1(\omega)\, G_2^{\dagger}(\omega)\, d\omega. \end{aligned} \tag{1.310}$$

Placing $g_1(t) = g_2(t) = \mathrm{g(t)}$ so that $G_1(\omega) = G_2(\omega) = G(\omega)$ and equating eq. (1.309) to (1.310) gives the *Parseval relation*

$$\int_{-\infty}^{+\infty} |g(t)|^2\, dt = \frac{1}{2\pi}\int_{-\infty}^{+\infty} |G(\omega)|^2\, d\omega. \tag{1.311}$$

The occurrence of the squares in the Parseval relation guarantees that both integrands in eq. (1.311) are real and positive, that are essential properties for relaxation functions such as probability and relaxation time distributions. For example, if $|g(t)|^2$ is interpreted as the probability that a signal occurs between times t and $t+dt$, the requirement that probabilities must integrate to unity is expressed as

$$\int_{-\infty}^{+\infty} |g(t)|^2\, dt = 1.0\,, \tag{1.312}$$

and the Parseval relation then implies

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} |G(\omega)|^2\, d\omega = 1.0\,, \tag{1.313}$$

where $|G(\omega)|^2\, d\omega$ is the probability that the signal contains frequencies between ω and $\omega+d\omega$.

A similar application of the Parseval relation to the time and frequency variances of a signal, when combined with the Schwartz inequality, yields the *Bandwidth-Duration relation*. The derivation of this relation is instructive. For convenience and without loss of generality the origin of time is set so that the average time is zero:

$$\langle t\rangle = \int_{-\infty}^{+\infty} t\,|g(t)|^2\, dt = 0\,, \tag{1.314}$$

so that the variance of the times of signal occurrence is

$$\sigma_t^2 = \left\langle \left(t - \langle t \rangle \right)^2 \right\rangle = \left\langle t^2 \right\rangle = \int_{-\infty}^{+\infty} t^2 \left| g(t) \right|^2 dt \,. \tag{1.315}$$

The average frequency is then

$$\langle \omega \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \omega \left| G(\omega) \right|^2 d\omega \,, \tag{1.316}$$

and the variance of the angular frequency distribution of the signal is

$$\sigma_\omega^2 = \left\langle \left(\omega - \langle \omega \rangle \right)^2 \right\rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left(\omega - \langle \omega \rangle \right)^2 \left| G(\omega) \right|^2 d\omega \,. \tag{1.317}$$

The time variance can be expressed in the frequency domain using the relation for the first derivative of the Fourier transform of $G(\omega)$ [n = 1 in eq. (1.288)]:

$$\frac{dG(\omega)}{d\omega} \Leftrightarrow -itg(t)\, dt \,, \tag{1.318}$$

application of the Parseval relation to which yields [AMPLIFY]

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \left| \frac{dG(\omega)}{d\omega} \right|^2 d\omega = \int_{-\infty}^{+\infty} t^2 \left| g(t) \right|^2 dt = \sigma_t^2 \,. \tag{1.319}$$

Applying the Schwartz inequality to $P(\omega) = dG(\omega)/d\omega$ and $Q(\omega) = \left(\omega - \langle \omega \rangle \right) G(\omega)$ then yields

$$\left\{ \int_{-\infty}^{+\infty} \left| \frac{dG(\omega)}{d\omega} \right|^2 d\omega \right\} \left\{ \int_{-\infty}^{+\infty} \left[\left(\omega - \langle \omega \rangle \right) G(\omega) \right]^2 \right\} d\omega \geq \left[\int_{-\infty}^{+\infty} \left| \frac{dG(\omega)}{d\omega} \right| \left[\left(\omega - \langle \omega \rangle \right) G(\omega) \right] d\omega \right]^2 . \tag{1.320}$$

From eqs (1.317) and (1.319) the left hand side of eq. (1.320) is $4\pi^2 \sigma_t^2 \sigma_\omega^2$, and the right hand side is

$$\left[\int_{-\infty}^{+\infty} \left| \frac{dG(\omega)}{d\omega} \right| \left[\left(\omega - \langle \omega \rangle \right) G(\omega) \right] d\omega \right]^2 = \left\{ \frac{1}{2} \int_{-\infty}^{+\infty} \left[\left(\omega - \langle \omega \rangle \right) d \left| G(\omega) \right|^2 \right] \right\}^2 , \tag{1.321}$$

where the elementary relation

$$\frac{1}{2}d\left|G(\omega)\right|^2 = \frac{dG(\omega)}{d\omega}G(\omega)d\omega \tag{1.322}$$

has been invoked. The inequality (1.305) then becomes

$$4\pi^2\sigma_t^2\sigma_\omega^2 \geq \left[\frac{1}{2}\int_{-\infty}^{+\infty}\left(\omega - \langle\omega\rangle\right)d\left|G(\omega)\right|^2\right]^2. \tag{1.323}$$

The functions $\left|G(\omega)\right|^2$ and $\omega\left|G(\omega)\right|^2$ (eq. (1.316)) are integrable so that their limits at $\omega \to \pm\infty$ are zero:

$$\langle\omega\rangle\int_{-\infty}^{+\infty}d\left|G(\omega)\right|^2 = 0, \tag{1.324}$$

and eq. (1.323) becomes

$$4\pi^2\sigma_t^2\sigma_\omega^2 \geq \left|\tfrac{1}{2}\int_{-\infty}^{+\infty}\omega\, d\left|G(\omega)\right|^2\right|^2. \tag{1.325}$$

Thus

$$\left[\int_{-\infty}^{+\infty}d\left|\omega G(\omega)\right|^2\right]^2 = \omega\left|G(\omega)\right|^2\Big|_{-\infty}^{+\infty} = 0 = \int_{-\infty}^{+\infty}\omega d\left|G(\omega)\right|^2 + \int_{-\infty}^{+\infty}\left|G(\omega)\right|^2 d\omega, \tag{1.326}$$

from which

$$\int_{-\infty}^{+\infty}\omega d\left|G(\omega)\right|^2 = -\int_{-\infty}^{+\infty}\left|G(\omega)\right|^2 d\omega \tag{1.327}$$

$$= -2\pi\int_{-\infty}^{+\infty}\left|g(t)\right|^2 dt \qquad \text{(Parseval relation)} \tag{1.328}$$

$$= -2\pi. \qquad \text{[from eq. (1.312)]} \tag{1.329}$$

Equation (1.325) then becomes

$$4\pi^2\sigma_t^2\sigma_\omega^2 \geq \pi^2 \tag{1.330}$$

or

$$2\sigma_t\sigma_\omega \geq 1.0. \tag{1.331}$$

Equation (1.331) expresses the *Bandwidth-Duration principle*, that has important implications for both relaxation science and physics in general. For example it implies that an instantaneous pulse signal described by the Dirac delta function $\delta(t\text{–}t_0)$ has an infinitely broad frequency content, so that detection of short duration signals requires instrumentation of wide bandwidth. Conversely, limited bandwidth instruments (or transmission cables etc.) will smear a signal out in time: using a narrow bandwidth filter (to remove noise for example) slows down the response to a signal and results in longer times for transients to decay. Although quantum mechanics lies outside the scope of this book, it is of interest to note that the quantum mechanical consequence of the Bandwidth–Duration relation is none other than the famous Heisenberg uncertainty principle. Applying the Einstein relation between energy and frequency, $E = \hbar\omega = h\nu$, to eq. (1.331) yields $2\hbar\sigma_t\sigma\omega = 2\Delta E\Delta t \geq \hbar$, so that $\Delta E\Delta t \geq \hbar/2$ (often stated as $\Delta E\Delta t \geq \hbar$ but as has been noted elsewhere [17] this inequality is "less precise" than the relation given here, although the factor of 2 is eliminated if the uncertainties are taken to be root mean square values). Similarly the deBroglie relation $p = h/\lambda$, where p is momentum and λ is wavelength, results in the uncertainty principle for position x and momentum, $\Delta p\Delta x \geq \hbar/2$.

1.8.4.4 Decay Functions and Distributions

In the time domain the response function $R(t)$ is usually expressed in terms of the normalized decay function following a step (Heaviside) function in the perturbing variable P at an earlier time t', $R(t - t')$. The normalized decay function $\phi(t - t')$ is unity at $t = t'$, zero in the limit of long time, and is always positive for relaxation processes. Such a decay function can always be expanded as an infinite sum of exponential functions

$$\phi(t) = \sum_{n=1}^{\infty} g_n \exp(-t/\tau_n) \qquad \left(\sum g_n = 1\right), \tag{1.332}$$

in which τ_n are relaxation or retardation times (the distinction is discussed later in this section), and all g_n are positive. In practice eq. (1.332) is usually truncated to a Prony series

$$\phi(t) = \sum_{n=1}^{N} g_n \exp(-t/\tau_n). \tag{1.333}$$

The best value for N is not usually apparent because larger values of N can (counterintuitively) sometimes lead to poorer fits to any data set $\{\phi(t_i)\}$. In the absence of any rigorous method a common empirical technique is to fit data with a range of N and find the value of N that produces the best fit (using a reiterative algorithm for example). Software algorithms are also available that constrain the best fit g_n values to be positive that must be for relaxation applications.

The integral form of eq. (1.332) is

$$\phi(t) = \int_0^{+\infty} g(\tau) \exp\left(\frac{-t}{\tau}\right) d\tau, \tag{1.334}$$

in which the *distribution function* $g(\tau)$ is normalized to unity:

$$\int_{0}^{+\infty} g(\tau)\,d\tau = 1. \tag{1.335}$$

Depending on context the distribution function is sometimes referred to as a density of states, especially in the physics literature. For many relaxation phenomena $g(\tau)$ is so broad that it is better to express it in terms of $\ln(\tau)$:

$$\phi(t) = \int_{-\infty}^{+\infty} g(\ln\tau)\exp\left(\frac{-t}{\tau}\right) d\ln\tau\,, \tag{1.336}$$

with

$$\int_{-\infty}^{+\infty} g(\ln\tau)\,d\ln\tau = 1. \tag{1.337}$$

Clearly

$$g(\ln\tau) = \tau g(\tau). \tag{1.338}$$

The factor τ relating $g(\ln\tau)$ and $g(\tau)$ is a common source of confusion. In this book $g(\ln\tau)$ is almost always used.

Equations (1.334) and (1.336) indicate that a nonexponential decay function and a distribution of relaxation/retardation times are mathematically equivalent. Physically, however, they may signify different relaxation mechanisms. If physical significance is attached to $g(\tau)$ a distribution of physically distinct processes is implied. The number of such processes may be quite small, because the superposition of a small number of sufficiently close Debye peaks in the frequency domain is difficult to distinguish from functions derived from a continuous distribution (see §1.12.1 for example). On the other hand, if physical significance is attached to the nonexponentiality of the decay function $\phi(t)$ then there is an implication that the relaxation mechanism is cooperative in some way, i.e. that relaxation of a particular nonequilibrium state requires the movement of more than one molecular grouping. An example of such a mechanism is the Glarum model described in §1.11.6. Additional experimental information is needed to determine if $g(\tau)$, $\phi(t)$ or both have physical significance (from nmr for example).

In many applications it is convenient to approximate $\phi(t)$ as the finite (Prony) series analog of eq. (1.332):

$$\phi(t) = \sum_{n=1}^{N} g_n \exp(-t/\tau_n) \qquad \left(\sum g_n = 1\right). \tag{1.339}$$

This must be done with care because the coefficients g_n for a particular τ_n change as the number of terms and/or their separation is changed, i.e. the finite series is not unique. For example increasing the number of terms N can (counter-intuitively) sometimes yield poorer best fits to any functional form for $\phi(t)$ (e.g. WW). The coefficients g_n and the function $g(\tau)$ must be positive in relaxation applications and indeed positive values for all g_n can be regarded as a definition of a relaxation process, as opposed to a process with resonance character that can be described (for example) by an exponentially under-damped sinusoidal function for $\phi(t)$ (see §1.8.5.4)

$$\phi(t) = \exp\left(\frac{-t}{\tau}\right)\cos(\omega_0 t). \tag{1.340}$$

The cosine factor produces negative values of $\phi(t)$ provided a certain condition relating τ and ω_0 is met (§1.8.5.4), so that g_n and $g(\tau)$ can also attain negative values. Because of the importance of eq. (1.339) to relaxation processes algorithms for least squares fitting nonexponential decay functions $\phi(t)$ have been published that are constrained to generate only positive values of g_n [18], and are usually (always?) available in software packages. As noted earlier, the required positivity of g_n and $g(\tau)$ for relaxation applications is assured when the square of the complex modulus is used, hence the general applicability of the Schmidt inequality and the Parseval relation to relaxation phenomena discussed above.

The distribution function $g(\ln\tau)$ is characterized by its moments $\langle \tau^n \rangle$ defined by

$$\langle \tau^n \rangle = \int_{-\infty}^{+\infty} \tau^n g(\ln\tau)\, d\ln\tau \tag{1.341}$$

or equivalently

$$\langle \tau^n \rangle = \frac{1}{\Gamma(n)} \int_0^{+\infty} t^{n-1}\phi(t)\, dt, \tag{1.342}$$

where Γ is the gamma function (§1.3.1). Equation (1.342) is easily derived by inserting eq. (1.336) for $\phi(t)$ into the integrand of eq. (1.336):

$$\begin{aligned} \int_{-\infty}^{+\infty} t^{n-1}\phi(t)\, dt &= \int_0^{+\infty} t^{n-1}\left[\int_{-\infty}^{+\infty} g(\ln\tau)\exp\left(\frac{-t}{\tau}\right) d\ln\tau\right] dt = \int_{-\infty}^{+\infty} g(\ln\tau)\left[\int_0^{+\infty} t^{n-1}\exp\left(\frac{-t}{\tau}\right) dt\right] d\ln\tau \\ &= \int_{-\infty}^{+\infty} g(\ln\tau)\left[\frac{\Gamma(n)}{(1/\tau)^n}\right] d\ln\tau = \Gamma(n)\langle \tau^n \rangle. \end{aligned} \tag{1.343}$$

Multiple differentiations of eq. (1.336) yield

$$\langle \tau^{-n} \rangle = \left.\frac{d^n\phi(t)}{dt^n}\right|_{t=0}. \qquad (n \text{ a positive integer}) \tag{1.344}$$

The generalized forms of $Q^*(i\omega)$ and its components are

$$Q^*(i\omega) = \int_{-\infty}^{+\infty} \frac{g(\ln\tau)}{1+i\omega\tau}\, d\ln\tau\,, \qquad \text{(retardation)} \tag{1.345}$$

$$= \int_{-\infty}^{+\infty} g(\ln\tau)\left(\frac{i\omega\tau}{1+i\omega\tau}\right) d\ln\tau\,, \qquad \text{(relaxation)} \tag{1.346}$$

$$Q''(\omega) = \int_{-\infty}^{+\infty} g(\ln\tau)\left[\frac{\omega\tau}{1+\omega^2\tau^2}\right] d\ln(\tau)\,, \tag{1.347}$$

$$Q'(\omega) = \int_{-\infty}^{+\infty} g(\ln\tau)\left(\frac{1}{1+\omega^2\tau^2}\right) d\ln\tau \qquad \text{(retardation)} \tag{1.348}$$

$$= \int_{-\infty}^{+\infty} g(\ln\tau)\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) d\ln\tau \qquad \text{(relaxation).} \tag{1.349}$$

The special case $n = 1$ in eq. (1.344) yields

$$-\frac{d\phi}{dt} = \int_{-\infty}^{+\infty} \left(\frac{1}{\tau}\right) g(\ln\tau)\, \exp\left(\frac{-t}{\tau}\right) d\ln\tau\,, \tag{1.350}$$

Laplace transformation of which gives

$$\begin{aligned} LT\left(-\frac{d\phi}{dt}\right) &= \int_{0}^{+\infty} \left[\int_{-\infty}^{+\infty} \left(\frac{1}{\tau}\right) g(\ln\tau) \exp\left(\frac{-t}{\tau}\right) d\ln\tau\right] \exp(-i\omega t)\, dt \\ &= \int_{0}^{+\infty} g(\ln\tau)\left[\int_{-\infty}^{+\infty} \left(\frac{1}{\tau}\right) \exp\left(\frac{-t}{\tau}\right) \exp(-i\omega t)\, dt\right] d\ln\tau \\ &= \int_{0}^{+\infty} g(\ln\tau)\left[\frac{1}{1+i\omega\tau}\right] d\ln\tau = Q(i\omega) \end{aligned} \tag{1.351}$$

so that

$$Q^*(i\omega) = \int_{0}^{+\infty} \left(\frac{-d\phi}{dt}\right) \exp(-i\omega t)\, dt\,. \tag{1.352}$$

1.8.4.5 Underdamping and Overdamping

Decay functions can also be defined for under-damped resonances. Consider the differential equation for a one dimensional, damped, unforced, classical harmonic oscillator:

$$\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}+\omega_0^2 x=0, \tag{1.353}$$

where ω_0 is the natural frequency of the undamped oscillator and $\gamma(> 0)$ is a damping coefficient (to be identified below with a relaxation time τ_0). For $\gamma = 0$ this is the equation for a harmonic oscillator and for $\omega_0 = 0$ it is the equation for an exponential decay in x with time. Laplace transformation of eq. (1.353) gives

$$\left[s^2X(s)-\left(\frac{dx}{dt}\right)\bigg|_{t=0}-sx(0)\right]+\left[s\gamma X(s)-\gamma x(0)\right]+\omega_0^2X(s)=0, \tag{1.354}$$

where the formulae for the Laplace transforms of first and second derivatives have been invoked [eq. (1.270)]. Rearranging eq. (1.354), and expressing the boundary conditions that the oscillator is released from rest at $x = x_{\max}$ at $t = 0$ by placing $x(0) = x_{\max}$ and $dx/dt|_{t=0}=0$, yields

$$X(s)=\frac{(s+\gamma)x_{\max}}{s^2+\gamma s+\omega_0^2}, \tag{1.355}$$

the denominator of which has roots [eq. (1.2)]

$$\begin{aligned} s_+ &= -\frac{\gamma}{2}+\left[\left(\frac{\gamma}{2}\right)^2-\omega_0^2\right]^{1/2}, \\ s_- &= -\frac{\gamma}{2}-\left[\left(\frac{\gamma}{2}\right)^2-\omega_0^2\right]^{1/2}, \end{aligned} \tag{1.356}$$

so that

$$s_+-s_-=2\left[\left(\frac{\gamma}{2}\right)^2-\omega_0^2\right]^{1/2}=\left[\gamma^2-4\omega_0^2\right]^{1/2}. \tag{1.357}$$

Expanding eq. (1.355) as partial fractions (§1.2.7) yields

$$X(s)=\left(\frac{x_{\max}}{s_+-s_-}\right)\left(\frac{s_++\gamma}{s-s_+}-\frac{s_-+\gamma}{s-s_-}\right), \tag{1.358}$$

and noting that the inverse *LT* of $(z-a)^{-1}$ is $\exp(at)$ [eq. A4] gives

$$X(t) \equiv \frac{x(t)}{x_{\max}} = \left(\gamma^2 - 4\omega_0^2\right)^{-1/2}\left[\left(s_+ + \gamma\right)\exp\left(s_+ t\right) - \left(s_- + \gamma\right)\exp\left(s_- t\right)\right]. \tag{1.359}$$

The functions $\exp\left(s_\pm t\right)$ decay monotonically or oscillate depending on whether s_+ and s_- are real or not, i.e. on whether or not $\gamma^2 - 4\omega^2\tau_0^2 > 0$.

Overdamping

For $\gamma^2 - 4\omega_0^2 \equiv D^2 > 0$, insertion of the expressions for s_+ and s_- into eq. (1.359) and rearranging terms yields two exponential decays with time constants $2/(\gamma \pm D)$:

$$X(t) = \left(\frac{\gamma + D}{2D}\right)\exp\left\{-\left[\frac{(\gamma - D)t}{2}\right]\right\} - \left(\frac{\gamma - D}{2D}\right)\exp\left\{-\left[\frac{(\gamma + D)t}{2}\right]\right\}. \tag{1.360}$$

Thus $\gamma - D$ is always positive because $D = \left(\gamma^2 - 4\omega_0^2\right)^{1/2} < \gamma$ and eq. (1.360) therefore cannot admit unphysical exponential increases in *X* with time *t*. Equation (1.360) can be written as

$$\begin{aligned} X(t) &= \exp\left(\frac{-\gamma t}{2}\right)\left\{\left(\frac{\gamma}{2D} + \frac{1}{2}\right)\exp\left(\frac{Dt}{2}\right) - \left(\frac{\gamma}{2D} - \frac{1}{2}\right)\exp\left(\frac{-Dt}{2}\right)\right\} \\ &= \frac{1}{2}\exp\left(\frac{-\gamma t}{2}\right)\left\{\left(\frac{\gamma}{D} + 1\right)\exp\left(\frac{Dt}{2}\right) - \left(\frac{\gamma}{D} - 1\right)\exp\left(\frac{-Dt}{2}\right)\right\} \\ &= \frac{1}{2}\exp\left(\frac{-\gamma t}{2}\right)\left\{\exp\left(\frac{Dt}{2}\right) + \exp\left(\frac{-Dt}{2}\right)\right\} + \frac{1}{2}\left(\frac{\gamma}{D}\right)\left\{\exp\left(\frac{Dt}{2}\right) - \exp\left(\frac{-Dt}{2}\right)\right\}. \end{aligned} \tag{1.361}$$

Underdamping

For $D^2 < 0$ and $D \to i|D|$ eq. (1.361) yields

$$X(t)=\frac{1}{2}\exp\left(\frac{-\gamma t}{2}\right)\left\{\exp\left(\frac{i|D|t}{2}\right)+\exp\left(\frac{-i|D|t}{2}\right)\right\}+\frac{1}{2}\left(\frac{\gamma}{i|D|}\right)\left\{\exp\left(\frac{i|D|t}{2}\right)-\exp\left(\frac{-i|D|t}{2}\right)\right\}$$
$$=\exp\left(\frac{-\gamma t}{2}\right)\left\{\cos\left(\frac{|D|t}{2}\right)+\left(\frac{\gamma}{|D|}\right)\sin\left(\frac{|D|t}{2}\right)\right\}$$
$$=\exp\left(\frac{-\gamma t}{2}\right)\left\{\cos\left(\frac{|D|t}{2}\right)+\tan\delta\sin\left(\frac{|D|t}{2}\right)\right\} \tag{1.362}$$
$$=\exp\left(\frac{-\gamma t}{2}\right)\left(\frac{1}{\cos\delta}\right)\left\{\cos\left(\frac{|D|t}{2}\right)\cos\delta+\sin\delta\left(\frac{|D|t}{2}\right)\right\}$$
$$=\exp\left(\frac{-\gamma t}{2}\right)\left(1+\frac{\gamma^2}{D^2}\right)^{1/2}\left\{\cos\left(\frac{|D|t}{2}-\delta\right)\right\}=\exp\left(\frac{-\gamma t}{2}\right)\left(\frac{2\omega_0}{|D|}\right)\cos\left(\frac{|D|t}{2}-\delta\right),$$

that is a sinusoidal oscillation with frequency

$$\omega_{osc}=\left(\omega_0^2-\gamma^2/4\right)^{1/2}<\omega_0 \tag{1.363}$$

and an amplitude that decreases exponentially with time constant $\tau_0=2/\gamma$.

Critical Damping

When $D = 0$ the repeated roots in eq. (1.355) invalidate the expansion into the partial fractions given above. Instead,

$$X(s)=\frac{x_{\max}(s+\gamma)}{(s+\gamma/2)^2}=\frac{x_{\max}}{(s+\gamma/2)}+\frac{x_{\max}(\gamma/2)}{(s+\gamma/2)^2}, \tag{1.364}$$

so that

$$X(t)=x_{\max}\left[\exp(-\gamma t/2)+(\gamma/2)t\exp(-\gamma t/2)\right], \tag{1.365}$$

where the Laplace transform $(s-a)^{-n}\Leftrightarrow\frac{1}{\Gamma(n)}t^{n-1}\exp(-at)$ has been applied and the time constant for exponential decay is now 2/γ. Equation (1.365) is therefore the decay function for a critically damped harmonic oscillator. The critical damping condition $D=0$ corresponds to $\omega_0=\gamma/2=1/\tau_0$ or $\omega_0\tau_0=1$.

For a *forced oscillator* (driven by a sinusoidal voltage for example), the right hand side of eq. (1.353) is a time dependent force:

$$\frac{d^2x}{dt^2}+\gamma\frac{dx}{dt}+\omega_0^2x=f(t), \tag{1.366}$$

and the transform is

$$\left(s^2+\gamma s+\omega_0^2\right)X\left(s\right)=F\left(s\right). \tag{1.367}$$

The *admittance* $A(s)$ of the system is

$$A(s)\equiv\frac{X\left(s\right)}{F\left(s\right)}=\frac{1}{s^2+\gamma s+\omega_0^2}, \tag{1.368}$$

whose zeros are associated with *resonance*. Putting $s = i\omega$ into eq. (1.368) yields

$$A^*(i\omega)\equiv\frac{X^*(i\omega)}{F^*(i\omega)}=\frac{1}{\omega_0^2-\omega^2+i\omega\gamma}=\frac{\omega_0^2-\omega^2+i\omega\gamma}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\gamma^2}. \tag{1.369}$$

Examples of A^* are the complex relative permittivity $\varepsilon^*(i\omega)$ and complex refractive index $n^*(i\omega)$, where $\varepsilon^*=n^{*2}$ (see Chapter Two). Note that the resonance at $\omega=\omega_0$ indicated by eq. (1.369) differs from the frequency of an unforced oscillator $\omega_{osc}=\left(\omega_0^2-\gamma^2/4\right)^{1/2}<\omega_0$ [eq. (1.363)].

1.9 Response Functions for Time Derivative Excitations

It commonly happens that relaxation and retardation functions describe the responses to some form of perturbation and the time derivative of that perturbation, for example the relative permittivity ε (see Chapter 2 for exact definition) and the specific electrical conductance σ [ratio of current density (= time derivative of charge density) to electric field]. The relationship is simple because the Laplace transform of a first time derivative is just [eqs. (1.270)-(1.271)] $LT\left(df/dt\right)=sF\left(s\right)-F\left(\infty\right)=i\omega F\left(i\omega\right)-F_\infty$. Thus electrical permittivity $e_0\varepsilon^*(i\omega)\Leftrightarrow q(t)/V_0$ and conductivity $\sigma^*(i\omega)\Leftrightarrow\left[dq(t)/dt\right]/V_0$ are related as $e_0\varepsilon^*(i\omega)=\sigma^*(i\omega)/i\omega$ (see Chapter Two for details).

1.10 Computing $g(\tau)$ from Frequency Domain Relaxation Functions

Distribution functions $g(\ln\tau)$ can be found from the corresponding functional forms of $Q''(\omega)$ and $Q'(\omega)$. The derivations of the relations are instructive because they use many of the results discussed above. The method of Fuoss and Kirkwood [19] using $Q''(\omega)$ is described first and then extended to include $Q'(\omega)$, although in order to maintain consistency with the rest of this chapter the Fuoss-Kirkwood method is slightly modified here. The derived formulae are then applied to several empirical frequency domain relaxation functions in §1.11.

Recall that [eq. (1.347)]

$$Q''(\omega)=\int_{-\infty}^{+\infty}g\left(\ln\tau\right)\left[\frac{\omega\tau}{1+\omega^2\tau^2}\right]d\ln\left(\tau\right). \tag{1.370}$$

Let τ_0 be a characteristic time for the relaxation/retardation process and define the variables:

$$T = \ln\left(\tau / \tau_0\right), \tag{1.371}$$

$$W = -\ln\left(\omega \tau_0\right), \tag{1.372}$$

$$G\left(T\right) = g\left(\ln \tau\right), \tag{1.373}$$

so that $\omega\tau = \exp(T - W)$ and eq. (1.370) becomes

$$Q''\left(\omega\right) = \int_{-\infty}^{+\infty} \frac{G\left(T\right)\exp\left(T - W\right)}{1 + \exp\left[2\left(T - W\right)\right]} dT \ . \tag{1.374}$$

Now define the *kernel* $K\left(Z\right)$

$$K\left(Z\right) = \frac{\exp\left(Z\right)}{1 + \exp\left(2Z\right)} = \frac{\operatorname{sech}\left(Z\right)}{2} \qquad \left(Z = T - W\right) \tag{1.375}$$

so that

$$Q''\left(W\right) = \int_{-\infty}^{+\infty} G\left(T\right) K\left(T - W\right) dT \ . \tag{1.376}$$

Equation (1.376) is the convolution integral for a Fourier transform, eq. (1.284), so that

$$q''\left(s\right) = g\left(s\right) k\left(s\right) \ , \tag{1.377}$$

where

$$q''\left(s\right) = \int_{-\infty}^{+\infty} Q''\left(W\right)\exp\left(isW\right) dW \ , \tag{1.378}$$

$$g\left(s\right) = \int_{-\infty}^{+\infty} G\left(T\right)\exp\left(isT\right) dT \ , \tag{1.379}$$

$$k\left(s\right) = \int_{-\infty}^{+\infty} K\left(X\right)\exp\left(isX\right) dX = \int_{-\infty}^{+\infty} \left[\frac{\operatorname{sech}\left(X\right)}{2}\right]\exp\left(isX\right) dX \ . \tag{1.380}$$

Rearrangement of eq. (1.377) and taking the inverse Fourier transform yields

$$G(T)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{q''(\omega)}{k(\omega)}\exp(-i\omega T)\,ds\,, \tag{1.381}$$

so that $G(T)$ can be computed from $q''(s) = q''(i\omega)$ or $Q''(W)$ once $k(\omega)$ is known.

To obtain $k(\omega)$ consider eq. (1.380) as part of the contour integral

$$\tfrac{1}{2}\oint \operatorname{sech}(Z)\exp(isZ)\,dZ \quad (Z = X + iY) \tag{1.382}$$

and evaluate it using the residue theorem. The contour used by Fuoss and Kirkwood was an infinite rectangle bounded by the real axis, two vertical paths at $X = \pm\infty$, and a path parallel to the real axis at $Y = \infty$. An alternative contour is used here that comprises the real axis between $\pm\infty$ (the desired integral), and a connecting semicircle in the positive imaginary part of the complex plane $Y > 0$. For the latter the complex exponential $\exp(isZ) = \exp(isX)\exp(-sY)$ is oscillatory with infinite frequency as $X\rightarrow\pm\infty$. A theorem due to Titchmarsh [13] states that the integral of a function with infinite frequency is zero if the integral is finite as the argument goes to infinity, as is the case here for the function $\operatorname{sech}(X)\exp(-Y) = \operatorname{sech}(X)$ along the real axis:

$$\int_{-\infty}^{+\infty}\operatorname{sech}(X)\,dX = \arctan\left[\sinh(X)\right]\Big|_{-\infty}^{+\infty} = \arctan(+\infty) - \arctan[-\infty] = \frac{\pi}{2} - \frac{-\pi}{2} = \pi\,. \tag{1.383}$$

Thus the semicircular part of the contour integral is indeed zero and the only surviving part of the contour integral is the desired segment along the real axis (which is not zero because $\exp(iY) = 1$ for $Y = 0$ and is not oscillatory).

The contour integral is evaluated using the residue theorem. The poles enclosed by the contour are located on the imaginary Y axis when $\operatorname{sech}(iY) = \sec(Y)$ is infinite, i.e. when $\cos(Y) = 1/\sec(Y) = 0$ that occurs when $Y = (n+½)i\pi$. The residues $c_{-1}(n)$ for the poles of the function $K(Z) = \exp(isX)\operatorname{sech}(Z)/2 = \exp(isX)/\left[2\cosh(Z)\right]$ are obtained from eq. (1.231) with $a = (n+½)i\pi$, $g = \exp(isY)$ and $h = \cosh(Y) \Rightarrow dh/dY = \sinh(Y)$. Thus for each value of n,

$$\begin{aligned} c_{-1}(n) &= \frac{\exp\left[is(n+½)i\pi\right]}{\sinh\left[(n+½)i\pi\right]} = \frac{\exp\left[is(n+½)i\pi\right]}{-i\sin\left[-(n+½)i\pi\right]} = \frac{\exp\left[-s(n+½)\pi\right]}{i\sin\left[(n+½)\pi\right]} \\ &= \frac{\exp\left[-s(n+½)\pi\right]}{i(-1)^n} = -i(-1)^n\exp\left[-s(n+½)\pi\right]. \end{aligned} \tag{1.384}$$

The sum of residues is therefore a geometric series (eq. (1.12)):

$$S=\sum_{n=0}^{\infty}c_{-1}(n)=-i\sum_{n=0}^{\infty}(-1)^n\exp\left[-s\left(n+\tfrac{1}{2}\right)\pi\right]=-i\exp\left(-\frac{s\pi}{2}\right)\sum_{n=0}^{\infty}\left[-\exp(s\pi)\right]^n=$$
$$=\frac{-i\exp\left(-\dfrac{s\pi}{2}\right)}{1+\exp[-s\pi]}=\frac{-i}{\exp[+s\pi/2]+\exp[-s\pi/2]}=-\left(\frac{i}{2}\right)\operatorname{sech}\left(\frac{s\pi}{2}\right), \tag{1.385}$$

so that

$$k(s)=(2\pi i)S/2=\frac{\pi}{\exp(+s\pi/2)+\exp(-s\pi/2)}. \tag{1.386}$$

Insertion of eq (1.386) into eq. (1.381) yields

$$G(T)=\left(\frac{1}{2}\right)\int_{-\infty}^{+\infty}\left\{q''(s)\exp\left[-is\left(T+\frac{i\pi}{2}\right)\right]+q''(s)\exp\left[-is\left(T-\frac{i\pi}{2}\right)\right]\right\}ds, \tag{1.387}$$

that is the sum of Fourier transforms of $q''(s)$ with complementary variables $(T+i\pi/2)$ and $(T-i\pi/2)$ and multiplied by π^{-1}. The expression for $g[\ln(\tau/\tau_0)]$ (necessarily real and positive) is then obtained by replacing $\ln(\omega\tau_0)$ in $Q''[\ln(\omega\tau_0)]$ with $\ln(\tau/\tau_0)\pm i\pi/2$:

$$g(\ln\tau)=\left(\frac{1}{2}\right)\mathrm{Re}\left\{Q''\left[\ln\left(\frac{\tau}{\tau_0}\right)+\frac{i\pi}{2}\right]+Q''\left[\ln\left(\frac{\tau}{\tau_0}\right)-\frac{i\pi}{2}\right]\right\}. \tag{1.388}$$

For $Q''(\omega\tau_0)=Q''\{\exp[\ln(\omega\tau_0)]\}$ eq. (1.388) becomes

$$g(\ln\tau)=\left(\frac{1}{\pi}\right)\mathrm{Re}\left\{Q''\left[\left(\frac{\tau}{\tau_0}\right)\exp\left(+\frac{i\pi}{2}\right)\right]+Q''\left[\left(\frac{\tau}{\tau_0}\right)\exp\left(-\frac{i\pi}{2}\right)\right]\right\}. \tag{1.389}$$

The phase factors $\exp(\pm i\pi/2)$ correspond to a difference in the sign of the imaginary part of the argument of $Q''(z=x+iy)$. The effect of this on the sign of $\mathrm{Re}[Q''(z)]$ is obtained by expanding the factor $\omega\tau/(1+\omega^2\tau^2)$ of eq. (1.370), since $g(\ln\tau)$ is real and positive:

$$\mathrm{Re}\left(\frac{z}{1+z^2}\right)=\mathrm{Re}\left\{\frac{(x+iy)\left[\left(1+x^2-y^2\right)-2ixy\right]}{\left(1+x^2-y^2\right)^2+4x^2y^2}\right\}=\frac{x\left[\left(1+x^2-y^2\right)+2y^2\right]}{\left(1+x^2-y^2\right)^2+4x^2y^2}. \tag{1.390}$$

Equation (1.390) contains only the squares of y and is therefore independent of the sign of y. Thus eq. (1.389) simplifies to

$$g(\ln\tau) = \mathrm{Re}\left\{Q''\left[\left(\frac{\tau}{\tau_0}\right)\exp\left(+\frac{i\pi}{2}\right)\right]\right\}. \tag{1.391}$$

The term exp($i\pi/2$) is shorthand for $\lim_{\varepsilon\to 0}(i+\varepsilon)$ and in most cases can be equated to i. An exception occurs when $g(\ln\tau)$ comprises discrete lines (the simplest case of which is the Dirac delta function for a single relaxation time), see Appendix D for example.

The derivation of $g(\ln\tau)$ from $Q'(\omega)$ is similar except that a different definition of the kernel $K(Z)$ is needed. Recall that [eq. (1.345)]

$$Q'(\omega) = \int_{-\infty}^{+\infty} \frac{g(\ln\tau)}{1+\omega^2\tau^2}\, d\ln\tau \qquad (a) \qquad \text{(retardation)}$$
$$Q'(\omega) = \int_{-\infty}^{+\infty} g(\ln\tau)\left[\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right] d\ln\tau \qquad (b) \qquad \text{(relaxation)} \tag{1.392}$$

and redefine the retardation kernel as (the relaxation case is considered later)

$$K(Z) = \frac{1}{1+\exp(2Z)} = \frac{\exp(-Z)}{\exp(-Z)+\exp(Z)} = \frac{1}{2}\exp(-Z)\,\mathrm{sech}(Z), \tag{1.393}$$

so that

$$k(s) = \int_{-\infty}^{+\infty} \frac{\exp(isZ)\exp(-Z)}{\exp(Z)+\exp(-Z)}\, dZ = \frac{1}{2}\int_{-\infty}^{+\infty} \exp(isZ)\exp(-Z)\,\mathrm{sech}(Z)\, dZ. \tag{1.394}$$

Equation (1.394) can be made a part of a semicircular closed contour as before and evaluated in the same way, because the semicircular contour integral in the positive imaginary half plane is again zero. The poles lie at the same positions on the iY axis as those of the kernel of the Q'' analysis but the residues are different because of the additional exp($-Z$) term [cf. eq. (1.384)] that for $Z = (n + 1/2)i\pi$ gives residues equal to $i(-1)^n$. Thus the geometric series corresponding to eq. (1.385) is

$$S = \frac{-i\exp\left(-\dfrac{s\pi}{2}\right)\displaystyle\sum_{n=0}^{\infty}\left[i(-1)^n\exp(s\pi)\right]^n}{i(-1)^n} = \exp\left(-\frac{s\pi}{2}\right)\frac{1}{1-\exp(s\pi)}. \tag{1.395}$$

Thus

$$k(s) = 2\pi i\frac{S}{2} = \frac{i\pi\exp(-s\pi/2)}{1-\exp(-s\pi)} = \frac{i\pi\exp(-s\pi/2)}{1-\exp(-s\pi)} = \frac{i\pi}{\exp(+s\pi/2)-\exp(-s\pi/2)}, \tag{1.396}$$

and from eq. (1.381)

$$G(T)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{q''(s)}{k(s)}\exp(-isT)\,ds \tag{1.397}$$

so that

$$G(T)=\left(\frac{1}{2\pi}\right)(i\pi)\int_{-\infty}^{+\infty}\left\{q'(s)\exp\left[-is(T+i\pi/2)\right]-q'(s)\exp\left[-is(T-i\pi/2)\right]\right\}ds \tag{1.398}$$

$$=\left(\frac{1}{2}\right)\mathrm{Im}\left\{Q'\left[\ln\left(\tau/\tau_0+i\pi/2\right)\right]-Q'\left[\ln\left(\tau/\tau_0-i\pi/2\right)\right]\right\}. \tag{1.400}$$

In this case the sign of $Q'(z)$ changes when the imaginary component y of its argument changes sign:

$$\mathrm{Im}\left(\frac{1}{1+z^2}\right)=\mathrm{Im}\left[\frac{\left(1+x^2-y^2\right)-2ixy}{\left(1+x^2-y^2\right)+4x^2y^2}\right]=\frac{-2xy}{\left(1+x^2-y^2\right)+4x^2y^2}, \tag{1.401}$$

so that

$$g(\ln\tau)=\mathrm{Im}\left\{Q'\left[(\tau/\tau_0)\exp(i\pi/2)\right]\right\}. \tag{1.402}$$

The same result is obtained for the relaxation form of $Q'(\omega)$. Reversing the signs of T and W so that $T=-\ln(\tau/\tau_0)=\ln(\tau_0/\tau)$ and $W=+\ln(\omega\tau_0)$ gives $(\omega\tau)^{-1}=\exp(T-W)$ and the calculation of the kernel proceeds as before. Substituting $\ln(\tau_0/\tau)$ in $g(\ln\tau)$ for $(\omega\tau_0)^{-1}$ in $Q'(\omega)$ at the end is the same as replacing $(\omega\tau_0)$ with $\ln(\tau/\tau_0)$ for the retardation case, except for a change in the sign of $\mathrm{Im}\left[Q'(\omega\tau_0)\right]$ that compensates for $\exp(\pm i\pi/2)\rightarrow\exp(\mp i\pi/2)$ from the changes in signs of T and W, and the change in sign of the imaginary component of $Q'(\omega)$:

$$\mathrm{Im}\left(\frac{z^2}{1+z^2}\right)=\mathrm{Im}\left\{\frac{\left(x^2-y^2+2ixy\right)\left[1+x^2-y^2-2ixy\right]}{\left(1+x^2-y^2\right)^2+4x^2y^2}\right\}=\frac{2xy}{\left(1+x^2-y^2\right)^2+4x^2y^2}. \tag{1.403}$$

An expression for $g(\ln\tau)$ in terms of $Q^*(i\omega)$ can be derived using the Titchmarsh result [12] that the solution to

$$f(x)=\int_{0}^{+\infty}\frac{g(u)}{x+u}\,du \tag{1.404}$$

is

$$g(u) = \frac{i}{2\pi}\left\{ f\left[u\exp(i\pi)\right] - f\left[u\exp(-i\pi)\right]\right\}. \tag{1.405}$$

Equation (1.404) is brought into the desired form using the variables

$$\begin{aligned}
&x = i\omega\tau_0, \\
&u = \tau_0 / \tau, \\
&du = \left(-\tau_0 / \tau^2\right) d\tau = \left(-\tau_0 / \tau\right) d\ln\tau, \\
&i\omega\tau = x / u, \\
&f = Q^* = \begin{cases} \dfrac{1}{1+i\omega\tau_0} & \text{(retardation)} \\ \dfrac{i\omega\tau_0}{1+i\omega\tau_0} & \text{(relaxation)} \end{cases}
\end{aligned} \tag{1.406}$$

so that for retardation processes

$$Q^*(i\omega\tau_0) = \int_{-\infty}^{+\infty} \frac{g(\tau_0/\tau)\left[\tau_0/\tau\right]}{\tau_0/\tau + i\omega\tau_0} d\ln\tau = \int_{-\infty}^{+\infty} \frac{g(\tau_0/\tau)}{\tau 1 + i\omega\tau} d\ln\tau \tag{1.407}$$

and

$$g(\ln\tau) = \left(\frac{-1}{2\pi}\right)\mathrm{Im}\left\{Q^*\left[\left(\tau_0/\tau\right)\exp\{+i\pi\}\right] - Q^*\left[\left(\tau_0/\tau\right)\exp\{-i\pi\}\right]\right\}. \tag{1.408}$$

The symmetry properties of eq. (1.408) are found by noting that $-\mathrm{Im}\left[Q^*\left(i\omega\tau_0\right)\right] = \mathrm{Re}\left[Q''\left(\omega\tau_0\right)\right]$ and examining eq. (1.390). In this case the different phase factors make it necessary to find the effects of changing the sign of the real component of the argument, and eq. (1.390) informs us that $\mathrm{Re}\left[Q''(x,iy)\right] = -\mathrm{Re}\left[Q''(-x,iy)\right]$. Thus the final result is

$$g(\ln\tau) = \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{Q^*\left[\left(\tau_0/\tau\right)\exp(+i\pi)\right]\right\}. \tag{1.409}$$

In this case also exp($i\pi$) is shorthand for $\lim\limits_{\varepsilon\to 0}(-1+i\varepsilon)$ and in situations where the imaginary component of $Q^*\left[\left(\tau_0/\tau\right)\exp(i\pi)\right]$ appears to be zero this limiting formula should be used. This again occurs for a single relaxation time, for example.

****

1.11 Distribution Functions

1.11.1 Single Relaxation Time

For an exponential decay function the frequency domain functions are:

$$\frac{Q^*[i\omega]-Q_\infty}{Q_0-Q_\infty}=\frac{1}{1+i\omega\tau}, \qquad \text{(retardation)}, \qquad (1.410)$$

$$\frac{Q^*[i\omega]-Q_0}{Q_\infty-Q_0}=\frac{i\omega\tau}{1+i\omega\tau}, \qquad \text{(relaxation)}, \qquad (1.411)$$

$$\frac{Q''[\omega]}{\pm\left(Q_0-Q_\infty\right)}=\frac{\omega\tau}{1+\omega^2\tau^2}, \qquad \left(+\text{for retardation}, -\text{for relaxation}\right) \qquad (1.412)$$

$$\frac{Q'[\omega]-Q_\infty}{Q_0-Q_\infty}=\frac{1}{1+\omega^2\tau^2}, \qquad \text{(retardation)} \qquad (1.413)$$

$$\frac{Q'[\omega]-Q_0}{Q_\infty-Q_0}=\frac{\omega^2\tau^2}{1+\omega^2\tau^2}, \qquad \text{(relaxation)} \qquad (1.414)$$

where the subscripts 0 and ∞ denote limiting low and high frequency values respectively. A discussion of the physical and mathematical distinctions between relaxation and retardation functions is deferred to §1.13.

For convenience the function $Q''(\omega)$ is referred to here as a "Debye peak": it has a maximum of 0.5 at $\omega\tau = 1$ and a full-width at half height (FWHH) that is computed from $Q''(\omega) = 0.25$:

$$\frac{\omega\tau}{1+\omega^2\tau^2}=0.25 \Rightarrow \left(\omega\tau\right)^2-4\omega\tau+1=0 \Rightarrow \omega\tau=2\pm\left(3\right)^{1/2}=0.268 \,\text{and}\, 3.732, \qquad (1.415)$$

so that the FWHH of the Debye peak (symmetric when when plotted on a $\log_{10}(\omega)$ scale) is $\log_{10}\left(3.732/0.268\right)\approx 1.144$ decades. This is very broad compared with resonance peaks and the resolution of adjacent peaks is correspondingly much poorer. For example the sum of two Debye peaks of equal height will exhibit a single combined peak for peak separations of up to $\left(3+2^{3/2}\right)\approx 5.83 \approx 0.766$ decades; the mathematical details of computing this separation are given in Appendix B1. For two peaks of different amplitudes the mathematics is intractable. A numerical analysis for two peaks with amplitudes A and $2A$ shows that a peak separation of greater than about 1.2 decades is required for incipient resolution, defined here as an inflection point between the peaks with zero slope. Details for other amplitude ratios are given in Appendix B2, where two empirical and approximate equations are given that relate these amplitude ratios to the component peak separations for resolution. For three peaks of equal amplitude the separation from one another for resolution (once again defined as the occurrence of minima between the maxima) also involves intractable mathematics. Distributions of relaxation or retardation times that comprise a number of delta functions separated by a decade or less will therefore produce smoothly varying loss peaks without any indication of an underlying discontinuous distribution function. Thus it is not surprising that as noted in §1.9.5.4 different distribution functions will sometimes produce experimentally indistinguishable frequency domain functions. This possibility goes unrecognized by too many researchers.

Complex plane plots of Q' vs. Q'' are often useful for data analysis. In the dielectric literature such plots are known as Cole-Cole plots. For the retardation eqs. (1.412) - (1.413) the plots are semi-circles of radius $\left(Q_0 - Q_\infty\right)/2$ centered at $\left\{\left(Q_0 + Q_\infty\right)/2, 0\right\}$:

$$Q''^2 + \left[\tfrac{1}{2}\left(Q_0 + Q_\infty\right) - Q'\right]^2 = \tfrac{1}{4}\left(Q_0 - Q_\infty\right)^2, \tag{1.416}$$

where Q' is along the x-axis and Q'' is along the y-axis. Equation (1.416) is derived in Appendix C as a special case of the Cole-Cole distribution function (§1.12.4).

The distribution function for a single relaxation/retardation time τ_0 is a Dirac delta function located at $\tau = \tau_0$. It is instructive to demonstrate this from the formulae given above. From $Q''\left(\omega\tau_0\right) = \omega\tau_0 / \left(1 + \omega^2\tau_0^2\right)$ one obtains from eq (1.391) the unphysical result that $g\left(\ln\tau\right) = \mathrm{Re}\left[\left(i\tau/\tau_0\right)/\left(1 - \tau^2/\tau_0^2\right)\right] = 0$. Applying $\exp\left(i\pi/2\right) \to \lim_{\varepsilon\to 0}\left(i + \varepsilon\right)$ provides the correct result (for convenience τ/τ_0 is replaced here by θ):

$$\begin{aligned} \frac{\omega\tau_0}{1+\omega^2\tau_0^2} &\to \mathrm{Re}\left\{\lim_{\varepsilon\to 0}\left[\frac{\theta\left(i+\varepsilon\right)}{1+\left(i+\varepsilon\right)^2\theta^2}\right]\right\} = \mathrm{Re}\left\{\lim_{\varepsilon\to 0}\left[\frac{\theta\left(i+\varepsilon\right)\left[1-\theta^2-2i\varepsilon\theta^2\right]}{1-\theta^2}\right]\right\} \\ &= \lim_{\varepsilon\to 0}\left[\frac{\varepsilon\theta\left(1-\theta^2\right)+2\varepsilon\theta^3}{\left(1-\theta^2\right)^2}\right] = \lim_{\varepsilon\to 0}\left[\frac{\varepsilon\theta\left(1+\theta^2\right)}{\left(1-\theta^2\right)^2}\right] = \delta\left(\theta-1\right). \end{aligned} \tag{1.417}$$

The proof of the last equality in eq. (1.417) is given in Appendix D.

For $Q'\left(\omega\tau_0\right) = 1/\left(1+\omega^2\tau_0^2\right)$,

$$\begin{aligned} \frac{1}{1+\omega^2\tau_0^2} &\to -\mathrm{Im}\left\{\lim_{\varepsilon\to 0}\left[\frac{2}{1+\left(i+\varepsilon\right)^2\theta^2}\right]\right\} = \mathrm{Im}\left\{\lim_{\varepsilon\to 0}\left[\frac{2\left(1-\theta^2\right)-4i\varepsilon\theta^2}{\left(1-\theta^2\right)}\right]\right\} \\ &= \lim_{\varepsilon\to 0}\left[\frac{2\varepsilon\theta^2}{\left(1-\theta^2\right)}\right] = \delta\left(\theta-1\right). \end{aligned} \tag{1.418}$$

The proof of the last equality in eq. (1.418) is similar to that given in Appendix D.

For $Q^*\left(i\omega\tau_0\right) = 1/\left(1+i\omega\tau_0\right)$,

$$\begin{aligned} \frac{1}{1+i\omega\tau_0} &= \mathrm{Im}\left\{\lim_{\varepsilon\to 0}\left[\frac{1}{1+\left(-1+i\varepsilon\right)\theta}\right]\right\} = \mathrm{Im}\left\{\lim_{\varepsilon\to 0}\left[\frac{1-\theta+i\varepsilon\theta}{\left(1-\theta\right)^2}\right]\right\} \\ &= \lim_{\varepsilon\to 0}\left[\frac{\varepsilon\theta}{\left(1-\theta\right)^2}\right] = \delta\left(\theta-1\right). \end{aligned} \tag{1.419}$$

All three of these limiting functions are infinite at θ=1 and it is readily confirmed numerically that they are indeed Dirac delta functions. It is also easy (albeit tedious) to demonstrate this algebraically and this is done for eq. (1.417) in Appendix D, where it is shown that the area under the peak is indeed unity when $\varepsilon \to 0$.

1.11.2 Logarithmic Gaussian

This function is used in lieu of the linear Gaussian distribution because the latter is too narrow to describe most experimental relaxation data. The log Gaussian function is [cf. eq. (1.79)]

$$g(\ln\tau) = \left[\frac{1}{(2\pi)^{1/2}\sigma_\tau}\right]\exp\left\{\frac{-\left[\ln\left(\tau/\tau_0\right)\right]^2}{2\sigma_\tau^2}\right\}, \tag{1.420}$$

that has average relaxation times $\langle\tau^n\rangle$ of

$$\langle\tau^n\rangle = \tau_0^n\exp\left(\frac{n^2\sigma^2}{2}\right) \tag{1.421}$$

for all n (positive or negative, integer or noninteger). Note that $\langle\tau\rangle\langle 1/\tau\rangle = \exp\left(\sigma^2\right) > 1$, consistent with eq. (1.306).

The log gaussian function can arise in a physically reasonable way from a Gaussian distribution of Arrhenius activation energies (see §1.4.1.1):

$$g(E_a) = \left[\frac{1}{(2\pi)^{1/2}\sigma_E}\right]\exp\left\{\frac{-\left(E_a - \langle E_a\rangle\right)^2}{2\sigma_E^2}\right\}. \tag{1.422}$$

Note that $g(E_a) \to \delta\left(\langle E_a\rangle - E_a\right)$ as $\sigma_E \to 0$, as required. From the Arrhenius relation $\ln\left(\tau/\tau_0\right) = E_a/RT$ the standard deviations in $g(\tau)$ and $g(E_a)$ are related as

$$\sigma_\tau = \frac{\sigma_E}{RT}, \tag{1.423}$$

so that a constant σ_E will produce a temperature dependent σ_τ that increases with decreasing temperature.

1.11.3 Fuoss-Kirkwood

In the same paper in which the expression for $g(\ln\tau)$ in terms of $Q''(\omega)$ was derived, Fuoss and Kirkwood [19] introduced an empirical function for $Q''(\omega)$. They noted that the single relaxation time expression for $Q''(\omega)$ could be expressed as a hyperbolic secant function:

$$Q''(\omega)=\frac{\omega\tau_0}{1+\omega^2\tau_0^2}=\frac{\exp\left[\ln\left(\omega\tau_0\right)\right]}{1+\left\{\exp\left[\ln\left(\omega\tau_0\right)\right]\right\}^2}=\frac{1}{\left\{\exp\left[\ln\left(\omega\tau_0\right)\right]\right\}^{+1}+\left\{\exp\left[\ln\left(\omega\tau_0\right)\right]\right\}^{-1}}$$
$$=\frac{1}{2}\operatorname{sech}\left[\ln\left(\omega\tau_0\right)\right]. \qquad (1.424)$$

Since loss functions are almost always broader than the single relaxation time (Debye) form they proposed that the $\omega\tau_0$ axis simply be stretched,

$$Q''(\omega)=\left(\frac{1}{2}\right)\operatorname{sech}\left[\kappa\ln\left(\omega\tau_0\right)\right], \qquad 0<\kappa\le 1 \qquad (1.425)$$

that has a maximum of $\kappa/2$ at $\omega\tau_0=1$ (since the y-axis is uniformly stretched by a factor $1/\kappa$ the maximum must also decrease by a factor κ for the area to be the same). The full width at half height (FWHH) Δ_{FK} of $Q''(\log\omega)$ is approximately given (in decades) by

$$\Delta_{FK}\approx\frac{1.14}{\kappa}, \qquad (1.426)$$

that is accurate to within about ±0.1 decades for Δ_{FK}. The distribution function from eq. (1.398) is then

$$g(\ln\tau)=\left(\frac{2}{\pi}\right)\operatorname{Re}\left[Q''\left(\kappa T+i\kappa\pi/2\right)\right]=\left(\frac{2}{\pi}\right)\operatorname{Re}\left[\operatorname{sech}\left(\kappa T+i\kappa\pi/2\right)\right] \qquad (1.427)$$

where $T=\ln\left(\tau/\tau_0\right)$ as before. Invoking the relation

$$\operatorname{sech}(x+iy)=\frac{1}{\cosh(x+iy)}=\frac{1}{\cosh(x)\cos(y)+i\sinh(x)\sin(y)} \qquad (1.428)$$

yields

$$g(\ln\tau)=\left(\frac{2}{\pi}\right)\operatorname{Re}\left\{\frac{\cosh(\kappa T)\cos(\kappa\pi/2)-i\sinh(\kappa T)\sin(\kappa\pi/2)}{\cosh^2(\kappa T)\cos^2(\kappa\pi/2)+\sinh^2(\kappa T)\sin 2(\kappa\pi/2)}\right\}. \qquad (1.429)$$

Equation (1.429) can be expressed in other forms using the identities $\cos^2(\theta)+\sin^2(\theta)=1$ and $\cosh^2(\theta)-\sinh^2(\theta)=1$. One of these was cited by Fuoss and Kirkwood themselves:

$$g_{FK}(\ln\tau)=\frac{2\cosh\left[\kappa\ln\left(\tau/\tau_0\right)\right]\cos\left(\kappa\pi/2\right)}{\cos^2\left(\kappa\pi/2\right)+\sinh^2\left[\kappa\ln\left(\tau/\tau_0\right)\right]}. \qquad (1.430)$$

There are no closed expressions for $Q^*(i\omega)$, $Q'(\omega)$ or $\phi(t)$ for the Fuoss-Kirkwood distribution.

1.11.4 Cole-Cole

The Cole-Cole function is specified in the frequency domain as [20]

$$Q^*(i\omega) = \frac{1}{1+(i\omega\tau_0)^{\alpha'}} \qquad (0 < \alpha' \le 1)\ , \tag{1.431}$$

where α' has been used rather than the original $(1-\alpha)$ so that, as with the parameters of the other functions considered here, Debye behavior is recovered as $\alpha'\to 1$ rather than $\alpha\to 0$. *This difference should be remembered when comparing the formulae here with those in the literature.* Expanding eq. (1.431) gives

$$\begin{aligned} Q^*(i\omega) &= \frac{1}{1+(\omega\tau_0)^{\alpha'}\left[\cos(\alpha'\pi/2)+i\sin(\alpha'\pi/2)\right]} \\ &= \frac{1+(\omega\tau_0)^{\alpha'}\left[\cos(\alpha'\pi/2)-i\sin(\alpha'\pi/2)\right]}{\left[1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)\right]^2+(\omega\tau_0)^{2\alpha'}\sin^2(\alpha'\pi/2)}, \end{aligned} \tag{1.432}$$

and separating the imaginary and real components yields

$$\begin{aligned} Q''(\omega) &= \frac{(\omega\tau_0)^{\alpha'}\sin(\alpha'\pi/2)}{1+2(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)+(\omega\tau_0)^{2\alpha'}} = \frac{\sin(\alpha'\pi/2)}{(\omega\tau_0)^{-\alpha'}+2\cos(\alpha'\pi/2)+(\omega\tau_0)^{\alpha'}} \\ &= \frac{\sin(\alpha'\pi/2)}{2\left\{\cosh\left[\alpha\ln(\omega\tau_0)\right]+\cos(\alpha'\pi/2)\right\}} \end{aligned} \tag{1.433}$$

and

$$Q'(\omega) = \frac{1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)}{1+2(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)+(\omega\tau_0)^{2\alpha'}}\ . \tag{1.434}$$

The function $g_{CC}(\ln\tau)$ is obtained from eq. (1.388) and placing $(-1)^{\alpha'} = \cos(\alpha'\pi)+i\sin(\alpha'\pi)$:

$$g_{CC}(\ln\tau) = \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{1+\left(\frac{\tau}{\tau_0}\right)^{\alpha'}\left[\cos(\alpha'\pi)+i\sin(\alpha'\pi)\right]\right\}^{-1}$$

$$= \left(\frac{1}{\pi}\right)\left[\frac{\left(\frac{\tau}{\tau_0}\right)^{\alpha'}\sin(\alpha'\pi)}{1+2\left(\frac{\tau}{\tau_0}\right)^{\alpha'}\cos(\alpha'\pi)+\left(\frac{\tau}{\tau_0}\right)^{2\alpha'}}\right] \quad (1.435)$$

$$= \left(\frac{1}{2\pi}\right)\left[\frac{\sin(\alpha'\pi)}{\cosh\left[\alpha'\ln(\tau/\tau_0)\right]+\cos(\alpha'\pi)}\right].$$

The distribution $g_{CC}(\ln\tau)$ is symmetric about $\ln(\tau_0)$ since $\cosh\left[\alpha'\ln(\tau/\tau_0)\right]=\cosh\left[-\alpha'\ln(\tau/\tau_0)\right]$. The function $Q''(\ln\omega)$ is symmetric for the same reason; its maximum value at $\tau = \tau_0$ is

$$Q''_{\max} = \frac{1}{2}\tan(\alpha'\pi/4). \quad (1.436)$$

The FWHH of $Q''(\log\omega)$ is approximately given (in decades) by

$$\Delta_{CC} \approx -0.32+\frac{1.58}{\alpha'}, \quad (1.437)$$

that is accurate to within about ±0.1 decades in Δ_{CC}. Elimination of $(\omega\tau_0)^{\alpha'}$ between eqs. (1.433) and (1.434) yields (Appendix C)

$$\left(Q'-\tfrac{1}{2}\right)^2+\left[Q''+\tfrac{1}{2}\mathrm{cotan}(\alpha'\pi/2)\right]^2=\left[\tfrac{1}{2}\mathrm{cosec}(\alpha'\pi/2)\right]^2, \quad (1.438)$$

that is the equation of a circle in the $Q'-iQ''$ plane centered at $\left[\tfrac{1}{2},-\tfrac{1}{2}\mathrm{cotan}(\alpha'\pi/2)\right]$ with radius $\tfrac{1}{2}\mathrm{cosec}(\alpha'\pi/2)$. The upper half of this circle ($Q'' > 0$ as physically required) is known as a *Cole-Cole plot*. Since $\mathrm{cotan}(\alpha'\pi/2)=\tan\left[(1-\alpha')\pi/2\right]$ the center is seen to lie on a line emanating from the origin and making an angle $-(1-\alpha')\pi/2$ with the real axis. There is no closed expression for the Cole-Cole form for $\phi(t)$.

The Cole-Cole and Fuoss Kirkwood functions for $Q''(\omega)$ are similar and various approximate expressions relating κ and α' have been proposed. For example equating the two expressions for $Q''_{\max}$ gives $\kappa=\tan(\alpha'\pi/4)$ and equating the limiting low and high frequency power law for each function gives $\kappa = \alpha'$.

1.11.5 Davidson-Cole

Among all the functions discussed here the Davidson-Cole (DC) function is unique in having closed forms for the distribution function $g(\ln\tau)$, the decay function $\phi(t)$, and the complex response function $Q^*(i\omega)$. The DC function for $Q^*(i\omega)$ is [21]

$$Q_{DC}^*(i\omega) = \frac{1}{\left(1+i\omega\tau_0\right)^{\gamma}} \qquad 0 < \gamma \le 1. \tag{1.439}$$

The real and imaginary components of $Q_{DC}^*(i\omega)$ are obtained by putting $\left(1+i\omega\tau_0\right) = r\exp(i\phi)$ so that $r = \left(1+\omega^2\tau_0^2\right)^{1/2}$ and ϕ=arctan($\omega\tau_0$). Then

$$\begin{aligned}\left(1+i\omega\tau_0\right)^{-\gamma} &= r^{-\gamma}\left[\exp(-i\gamma\phi)\right] = r^{-\gamma}\left[\cos(\gamma\phi) - i\sin(\gamma\phi)\right] \\ &= \left[\cos(\phi)\right]^{\gamma}\left[\cos(\gamma\phi) - i\sin(\gamma\phi)\right],\end{aligned} \tag{1.440}$$

so that

$$Q'\left(\omega\tau_0\right) = \left[\cos(\phi)\right]^{\gamma}\cos(\gamma\phi), \tag{1.441}$$

and

$$Q''\left(\omega\tau_0\right) = \left[\cos(\phi)\right]^{\gamma}\sin(\gamma\phi). \tag{1.442}$$

The maximum in $Q''(\omega)$ occurs at $\omega_{\max}\tau_0 = \tan\left\{\pi/\left[2\left(1+\gamma\right)\right]\right\}$, and the limiting low and high frequency slopes $d\ln Q''/d\ln\omega$ are +1 and $-\gamma$, respectively. The Cole-Cole plot of Q'' vs. Q' is asymmetric, having the shape of a semicircle at low frequencies and a limiting slope of $dQ''/dQ' = -\gamma\pi/2$ at high frequencies. An approximate value of γ is obtained from the FWHH (in decades) of $Q''[\log_{10}(\omega)]$, Δ_{DC}, by the empirical relation

$$\gamma^{-1} \approx -1.2067 + 1.6715\Delta_{DC} + 0.222569\Delta_{DC}^2 \;\left(0.15 \le \gamma \le 1.0; 1.14 \le \Delta \le 3.3\right). \tag{1.443}$$

The decay function $\phi(t)$ is derived from eq. (1.352) and replacing the variable $i\omega$ with s:

$$Q^*(i\omega) = Q^*(s) = \frac{1}{\left(1+s\tau_0\right)^{\gamma}} = \left[\frac{1}{\tau_0^{\gamma}\left(s+\tau_0^{-1}\right)^{\gamma}}\right] = LT\left(\frac{-d\phi}{dt}\right). \tag{1.444}$$

The inverse Laplace transform $(LT)^{-1}$ of the central term in eq. (1.444) is obtained from the generic expression

$$LT^{-1}\left[\frac{\Gamma(k)}{(s+a)^k}\right]=LT^{-1}\left[\frac{\Gamma(k)}{a^k(1+s/a)^k}\right]=t^{k-1}\exp(-at) \tag{1.445}$$

that, with variables $a = 1/\tau_0$ and $k = \gamma$ in eq. (1.445), yields

$$\left(\frac{-d\phi}{dt}\right)=LT^{-1}\left[\frac{1}{\tau_0^\gamma\left(s+\tau_0^{-1}\right)^\gamma}\right]=\frac{t^{\gamma-1}}{\tau_0^\gamma\Gamma(\gamma)}\exp(-t/\tau_0). \tag{1.446}$$

Integration of eq. (1.446) from 0 to t yields

$$-\phi(t)+\phi(0)=1-\phi(t)=\frac{1}{\tau_0^\gamma\Gamma(\gamma)}\int_0^t t'^{\gamma-1}\exp(-t'/\tau_0)\,dt', \tag{1.447}$$

and substituting $x = t'/\tau_0$ so that $dt'=\tau_0\,dx$ and $t'^{(\gamma-1)}=x^{(\gamma-1)}\tau_0^{(\gamma-1)}$ yields

$$1-\phi(t)=\frac{1}{\Gamma(\gamma)}\int_0^{t/\tau_0} x^{\gamma-1}\exp(-x)\,dx=G(\gamma,t/\tau_0), \tag{1.448}$$

where $G(\gamma,t/\tau_0)$ is the incomplete gamma function [eq. (1.34)] that varies between zero and unity. The Cole-Davidson decay function is therefore

$$\phi(t/\tau_0)=1-G(\gamma,t/\tau_0). \tag{1.449}$$

The Davidson-Cole distribution function $g_{DC}(\ln\tau)$ is obtained from $Q^*(i\omega)$ using eq. (1.398):

$$g_{DC}(\ln\tau)=\frac{1}{\pi}\mathrm{Im}\left[(1-\tau_0/\tau)^{-\gamma}\right]. \tag{1.450}$$

The quantity $\left[(1-\tau_0/\tau)^\gamma\right]$ is real for $\tau_0/\tau<1$ so that $g_{DC}\left[\ln(\tau)>\tau_0\right]=0$. For $\tau_0/\tau\geq 1$

$$\begin{aligned}g_{DC}(\ln\tau)&=\frac{1}{\pi}\mathrm{Im}\left[(1-\tau_0/\tau)^{-\gamma}\right]=\frac{1}{\pi}\mathrm{Im}\left[\left(\frac{\tau}{\tau-\tau_0}\right)^\gamma\right]=\frac{1}{\pi}\mathrm{Im}\left[\left(\frac{-\tau}{\tau_0-\tau}\right)^\gamma\right]\\&=\frac{1}{\pi}\mathrm{Im}\left[(-1)^\lambda\left(\frac{\tau}{\tau_0-\tau}\right)^\gamma\right]=\frac{1}{\pi}\mathrm{Im}\left\{\left[\left(\cos(\gamma\pi)+i\sin(\gamma\pi)\right)\left(\frac{\tau}{\tau_0-\tau}\right)^\gamma\right]\right\},\end{aligned} \tag{1.451}$$

so that

$$g_{DC}\left(\ln\tau\right)=\begin{cases}\dfrac{\sin\left(\gamma\pi\right)}{\pi}\left[\dfrac{\tau}{\tau_0-\tau}\right]^{\gamma} & \tau\le\tau_0\\ 0 & \tau>\tau_0.\end{cases} \tag{1.452}$$

The average relaxation times $\left\langle\tau^n\right\rangle$ are:

$$\left\langle\tau^n\right\rangle=\left(\frac{\tau_0^n}{n}\right)\frac{\Gamma\left(n+\gamma\right)}{\Gamma\left(n\right)\Gamma\left(\gamma\right)}=\frac{\tau_0^n}{nB\left(\gamma,n\right)}\ , \tag{1.453}$$

where $B(\gamma,n)$ is the beta function (eq. (1.32)). Two examples of $\left\langle\tau^n\right\rangle$ are

$$\begin{aligned}\left\langle\tau\right\rangle&=\gamma\tau_0,\\ \left\langle\tau^2\right\rangle&=\left(\frac{\tau_0^2}{2}\right)\gamma\left(1+\gamma\right).\end{aligned} \tag{1.454}$$

1.11.6 Glarum Model

This is a defect diffusion model [22] that yields a nonexponential decay function and is the only one discussed here that is not empirical. Rather it is derived from specific assumptions, some of which were introduced for mathematical convenience. The model comprises a one dimensional array of dipoles each of which can relax either by reorientation to give an exponential decay function or by the arrival of a diffusing defect of some sort that instantly relaxes the dipole. The decay function is given by

$$\phi\left(t\right)=\exp\left(-t/\tau_0\right)\left[1-P\left(t\right)\right] \tag{1.455}$$

so that

$$\frac{-\phi\left(t\right)}{dt}=\frac{1}{\tau_0}\phi\left(t\right)+\exp\left(-t/\tau_0\right)\frac{dP\left(t\right)}{dt}, \tag{1.456}$$

where τ_0 is the single relaxation time for dipole orientation and $P(t)$ is the probability of a defect arriving at time t. If the nearest defect at t = 0 lies a distance ℓ from the dipole an expression for $P(t)$ is obtained from the solution to a one dimensional diffusion problem with a boundary condition of complete absorption [23]:

$$\frac{dP\left(t,\ell\right)}{dt}=\left[\frac{\ell}{\left(4\pi D\right)^{1/2}}\right]t^{-3/2}\exp\left[\frac{-\ell^2}{4Dt}\right], \tag{1.457}$$

where D is the diffusion coefficient of the defect. The probability $P(\ell)d\ell$ that the nearest defect is at a distance between ℓ and $\ell+d\ell$ is obtained by assuming a spatial distribution of defects given by

$$P(\ell)d\ell = \left(\frac{1}{\ell_0}\right)\exp\left[-\left(\frac{\ell}{\ell_0}\right)\right]d\ell, \tag{1.458}$$

where ℓ_0 is the average value of ℓ and $1/(2\ell_0)$ is the average number of defects per unit length. Averaging $dP(t,\ell)/dt$ over values of ℓ that are distributed according to eq. (1.458) yields

$$\frac{dP(t)}{dt} = \left(\frac{D}{\ell_0^2}\right)^{1/2}\left\{\frac{1}{(\pi t)^{1/2}} - \left(\frac{D}{\ell_0^2}\right)^{1/2}\exp\left(\frac{Dt}{\ell_0^2}\right)\mathrm{erfc}\left(\frac{Dt}{\ell_0^2}\right)^{1/2}\right\}, \tag{1.459}$$

and substitution of this expression into eq. (1.456) gives

$$\frac{d\phi(t)}{dt} = \frac{1}{\tau_0}\phi(t) + \left(\frac{D}{\ell_0^2}\right)^{1/2}\exp\left[-\left(\frac{\tau}{\tau_0}\right)\right]\left\{\frac{1}{(\pi t)^{1/2}} - \left(\frac{D}{\ell_0^2}\right)^{1/2}\exp\left(\frac{Dt}{\ell_0^2}\right)\mathrm{erfc}\left(\frac{Dt}{\ell_0^2}\right)^{1/2}\right\}. \tag{1.460}$$

The Laplace transform of $-d\phi/dt$ is $Q^*(i\omega)$ and that of $\phi(t)$ is obtained from re-arrangement of the expression for the Laplace transform of a time derivative [eq. (1.270)]:

$$LT\left[\phi(t)\right] = \frac{1}{s}\left[LT\left(\frac{d\phi(t)}{dt}\right)\right] + 1 = \frac{1}{i\omega}\left[1 - Q^*(i\omega)\right]. \tag{1.461}$$

Laplace transformation of eq. (1.460) yields ($s = i\omega$)

$$Q^*(i\omega) = \frac{1}{i\omega\tau_0}\left[1 - Q^*(i\omega)\right] + \left(\frac{D}{\ell_0^2}\right)^{1/2} LT\left(\exp\left[-\left(\frac{\tau}{\tau_0}\right)\right]\left\{\frac{1}{(\pi t)^{1/2}} - \left(\frac{D}{\ell_0^2}\right)^{1/2}\exp\left(\frac{Dt}{\ell_0^2}\right)\mathrm{erfc}\left(\frac{Dt}{\ell_0^2}\right)^{1/2}\right\}\right). \tag{1.462}$$

Inserting the Laplace transform of eq. (1.462) [eq. (A25)] yields after minor re-arrangement

$$Q^*(i\omega)\left[\frac{1}{i\omega\tau_0} + 1\right] - i\omega\tau_0 = \left(\frac{D}{\ell_0^2}\right)^{1/2}\left\{\frac{1}{\left[(1/\tau_0) + i\omega\right]^{1/2} + \left(D/\ell_0^2\right)^{1/2}}\right\}, \tag{1.463}$$

so that

$$Q^*(i\omega)\left[\frac{1 + i\omega\tau_0}{i\omega\tau_0}\right] = \frac{1}{i\omega\tau_0} + \left(\frac{D\tau_0}{\ell_0^2}\right)^{1/2}\left\{\frac{1}{\left[1 + i\omega\tau_0\right]^{1/2} + \left(D\tau_0/\ell_0^2\right)^{1/2}}\right\}. \tag{1.464}$$

Equation (1.464) is simplified by introducing the dimensionless parameters

$$a = \frac{\ell_0^2}{D\tau},\ a_0 = \frac{\ell_0^2}{D\tau_0} \tag{1.465}$$

to give, after multiplying through by $i\omega\tau_0 / \left(1+i\omega\tau_0\right)$,

$$Q^*\left(i\omega\right) = \frac{1}{1+i\omega\tau_0} + \frac{i\omega\tau_0}{1+i\omega\tau_0}\left\{\frac{a_0^{1/2}}{\left[1+i\omega\tau_0\right]^{1/2} + a_0^{1/2}}\right\}. \tag{1.466}$$

The distribution function is obtained by applying eq. (1.409) to eq. (1.466) and noting that $\left(1/\tau\right)\exp\left|+i\pi\right| = -1/\tau$. Substituting i for $(-1)^{1/2}$ then yields:

$$g_G\left(\ln\tau\right) = \frac{1}{\pi}\operatorname{Im}\left\{\frac{1}{1-\tau_0/\tau} - \left(\frac{\tau_0/\tau}{1-\tau_0/\tau}\right)\frac{1}{\left[1+a_0^{1/2}\left(1-\tau_0/\tau\right)^{1/2}\right]}\right\}. \tag{1.467}$$

Replacing τ_0/τ by a/a_0 and rearranging yields

$$g_G\left(\ln\tau\right) = \frac{1}{\pi}\operatorname{Im}\left\{\frac{a_0}{a_0-a} - \frac{a}{\left(a_0-a\right)\left[1+\left(a_0-a\right)^{1/2}\right]}\right\} = \frac{1}{\pi}\operatorname{Im}\left\{\frac{a_0\left[1+\left(a_0-a\right)^{1/2}\right]-a}{\left(a_0-a\right)\left[1+\left(a_0-a\right)^{1/2}\right]}\right\}. \tag{1.468}$$

The expression enclosed in the {} braces is real for $a < a_0$ whence $g_G(\ln\tau) = 0$. For $a > a_0$ insertion of $-i$ for $\left(-1\right)^{1/2}$ when it occurs (to ensure $g_G(\ln\tau)$ is positive) yields

$$\begin{aligned} g_G\left(\ln\tau\right) &= \frac{1}{\pi}\operatorname{Im}\left\{\frac{a_0\left[1-i\left(a_0-a\right)^{1/2}\right]-a}{-\left(a-a_0\right)\left[1-i\left(a-a_0\right)^{1/2}\right]}\right\} \\ &= \frac{1}{\pi}\operatorname{Im}\left\{\frac{\left\{\left(a-a_0\right)+ia_0\left(a-a_0\right)^{1/2}\right\}}{\left(a_0-a\right)\left[1-i\left(a-a_0\right)^{1/2}\right]}\right\} \\ &= \frac{1}{\pi}\operatorname{Im}\left\{\frac{\left(a-a_0\right)^{1/2}\left[\left(a-a_0\right)^{1/2}+ia_0\right]\left[1+i\left(a-a_0\right)^{1/2}\right]}{\left(a-a_0\right)\left[1+a-a_0\right]}\right\} \\ &= \frac{a}{\pi\left(a-a_0\right)^{1/2}\left[1+a-a_0\right]} \end{aligned}, \tag{1.469}$$

so that the final result is

$$g_G(\ln\tau)=\begin{cases}\dfrac{1}{\pi(a-a_0)^{1/2}}\left(\dfrac{a}{(a-a_0+1)}\right) & a\ge a_0\\ 0 & a<a_0\,.\end{cases} \tag{1.470}$$

The shape of the distribution is seen to be determined by a_0 that is the ratio of a diffusional relaxation time ℓ_0^2/D and the dipole orientation relaxation time τ_0. Glarum noted that the three special cases of $a_0 >> 1$, $a_0 = 1$ and $a_0 = 0$ correspond to a single relaxation time, a Davidson-Cole distribution with $\gamma = 0.5$ and a Cole-Cole distribution with $\alpha = \alpha' = 0.5$, respectively. For $a_0 = 1$ the Glarum and Davidson-Cole distributions are indeed similar but with the Glarum function for $Q''(\omega)$ having a small high frequency excess over the Davidson-Cole function. An approximate relation between a_0 and the Davidson-Cole parameter γ is obtained by expanding the two expressions for $Q^*(i\omega)$. The linear approximation to eq. (1.466) for the Glarum function is:

$$Q^*(i\omega)\approx(1-i\omega\tau_0)+\frac{i\omega\tau_0(1-i\omega\tau_0)}{1+a_0^{1/2}}\approx1-\frac{i\omega\tau_0}{1+a_0^{1/2}}=\frac{a_0^{1/2}}{1+a_0^{1/2}}, \tag{1.471}$$

comparison of which with the linear approximation to the Davidson-Cole function yields

$$Q^*(i\omega)\approx1-\gamma(i\omega\tau_0) \tag{1.472}$$

so that

$$\gamma\approx\frac{a_0^{1/2}}{1+a_0^{1/2}}. \tag{1.473}$$

As noted above this relation is exact for $a_0=1$ $(\gamma=0.5)$ and $a_0\gg1$ $(\gamma=1)$. If the dipole and defect relaxation times have different activation energies the distribution g_G will be temperature dependent.

1.11.7 Havriliak-Negami

Simple combination of the Cole-Cole and Davidson-Cole equations yields the two parameter Havriliak-Negami equation [24]

$$Q^*(i\omega\tau_0)=\frac{1}{\left[1+(i\omega\tau_0)^{\alpha'}\right]^{\gamma}}\quad(0<\alpha'\le1,0<\gamma\le1). \tag{1.474}$$

Inserting the relation $i^{\alpha'}=\cos(\alpha'\pi/2)+i\sin(\alpha'\pi/2)$ into eq. (1.474) yields [24]

$$
\begin{aligned}
Q^*(i\omega\tau_0) &= \left\{1+\left[\cos(\alpha'\pi/2)+i\sin(\alpha'\pi/2)\right](\omega\tau_0)^{\alpha'}\right\}^{-\gamma} \\
&= \left\{1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)+i(\omega\tau_0)^{\alpha'}\sin(\alpha'\pi/2)\right\}^{-\gamma} \\
&= \frac{\left\{1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)-i(\omega\tau_0)^{\alpha'}\sin(\alpha'\pi/2)\right\}^{\gamma}}{\left\{\left[(\omega\tau_0)^{\alpha'}\sin(\alpha'\pi/2)\right]^2+\left[1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)\right]^2\right\}^{\gamma}\equiv R^2},
\end{aligned}
\tag{1.475}
$$

so that

$$Q'(\omega\tau_0) = R^{-\gamma}\cos(\gamma\theta), \tag{1.476}$$

$$Q''(\omega\tau_0) = R^{-\gamma}\sin(\gamma\theta)\ , \tag{1.477}$$

where

$$\theta = \arctan\left[\frac{(\omega\tau_0)^{\alpha'}\sin(\alpha'\pi/2)}{1+(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)}\right]\ . \tag{1.478}$$

The distribution function is then

$$
\begin{aligned}
g_{HN}(\ln\tau) &= \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{\left[1+\left(\frac{-\tau_0}{\tau}\right)^{\alpha'}\right]^{-\gamma}\right\} = \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{\left[1+T^{\alpha'}\left[\cos(\alpha'\pi)+i\sin(\alpha'\pi)\right]\right]^{-\gamma}\right\} \\
&= \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{\frac{1+T^{\alpha'}\cos(\alpha'\pi)-iT^{\alpha'}\sin(\alpha'\pi)}{1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}}\right\} \\
&= \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{\frac{\left[\cos\theta-i\sin\theta\right]^{\gamma}}{\left[1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}\right]^{\gamma/2}}\right\} \\
&= \left(\frac{1}{\pi}\right)\mathrm{Im}\left\{\frac{\left[\cos(\gamma\theta)-i\sin(\gamma\theta)\right]}{\left[1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}\right]^{\gamma/2}}\right\},
\end{aligned}
\tag{1.479}
$$

so that

$$g_{HN}(\ln\tau) = \left(\frac{1}{\pi}\right)\left\{\frac{\sin(\gamma\theta)}{\left[1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}\right]^{1/2}}\right\} \tag{1.480}$$

with

$$\theta = \arcsin\left\{\frac{T^{\alpha'}\sin(\alpha'\pi)}{\left[1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}\right]^{1/2}}\right\}, \tag{1.481}$$

$$\theta = \arccos\left\{\frac{1+T^{\alpha'}\cos(\alpha'\pi)}{\left[1+2T^{\alpha'}\cos(\alpha'\pi)+T^{2\alpha'}\right]^{1/2}}\right\}, \tag{1.482}$$

and

$$\theta = \arctan\left\{\frac{T^{\alpha'}\sin(\alpha'\pi)}{\left[1+T^{\alpha'}\cos(\alpha'\pi)\right]}\right\}, \tag{1.483}$$

where as before $T = \tau_0/\tau$ and the denominator of eq. (1.480) is real and positive. For $\alpha' = 1$ eq. (1.481) reveals that θ is either 0 or π [since $\sin(\alpha'\pi) = \sin(\theta) = 0$] but provides no information on how the ambiguity is to be resolved. On the other hand, eq. (1.482) yields

$$\cos\theta = \frac{1-T}{\left(1-2T+T^2\right)^{1/2}} = \frac{1-T}{\pm(1-T)}, \tag{1.484}$$

so that whether θ is 0 or π depends on which sign of the square root is chosen. The positive square root corresponds to $\theta = 0$ ($\cos\theta = +1$) and the negative root yields $\theta = \pi$ ($\cos\theta = -1$). Equation (1.480) reveals that $g_{HN}(\ln\tau) = 0$ for $\theta = 0$, for which $(1-T) > 0$ (since the argument of the denominator must be real) so that $\tau > \tau_0$. Also $\tau < \tau_0$ for $\theta = \pi$ $(1-T) < 0$. These conditions correspond to the Davidson-Cole distribution eq. (1.452), as required. For $\gamma = 1$ eq. (1.480) yields the Cole-Cole distribution by simple inspection.

Consider now $\alpha' = \gamma = 0.5$ for which

$$\theta = \arcsin\left(\frac{T^{1/2}}{1+T^{1/2}}\right) = \arccos\left(\frac{1}{1+T^{1/2}}\right). \tag{1.485}$$

Equation (1.480) then yields

$$\begin{aligned} g_{HN}(\ln\tau) &= \frac{\sin(\theta/2)}{\pi(1+T)^{1/4}} = \frac{\left[(1-\cos\theta)/2\right]^{1/2}}{\pi(1+T)^{1/4}} = \frac{\left[1-1/(1+T)^{1/2}\right]^{1/2}}{2^{1/2}\pi(1+T)^{1/4}} \\ &= \left(\frac{1}{2^{1/2}\pi}\right)\left[\frac{1}{(1+T)^{1/2}} - \frac{1}{(1+T)}\right]^{1/2} = \left(\frac{1}{2^{1/2}\pi}\right)\left[\frac{(1+T)^{1/2}-1}{(1+T)}\right]. \end{aligned} \tag{1.486}$$

Note that the argument of the square root is always positive for $T > 0$ and the root itself is therefore real, as required. Equating the differential of eq. (1.486) to zero yields a maximum in $g_{HN}(\ln\tau)$ of magnitude $\left(2^{2/3}\pi\right)^{-1}$ at $T = 3$. Integration of eq. (1.486) yields unity, as also required (easily demonstrated after a change of variable from $(1 + T)$ to x^2).

The HN function is often found to provide the best fit to experimental data but this might just be a statistical effect because it has two adjustable parameters $(\alpha'$ and $\gamma)$ compared with just one for the other most often used asymmetric distributions [Davidson-Cole (§1.12.5) and Williams-Watt (§1.12.8 below)].

1.11.8 Williams-Watt

This function is also known as Kohlrausch-Williams-Watt (KWW) after Kohlrausch's initial introduction of it [25,26] for other phenomena. Williams and Watt [27] found it independently and were the first to apply it to dielectric relaxation and since then it has been used to analyze or characterize many other relaxation phenomena – thus it is referred to as WW here. It is defined by

$$\phi_{WW}(t) = \exp\left[-(t/\tau_0)^{\beta}\right] \qquad 0 < \beta \le 1. \tag{1.487}$$

None of the functions $g_{WW}(\ln\tau)$, $Q^*(i\omega)$, $Q''(i\omega)$, or $Q'(i\omega)$ can be written in closed form except when $\beta = 0.5$:

$$Q^*(i\omega) = \left[\frac{\pi^{1/2}(1-i)}{(8\omega\tau_0)^{1/2}}\right]\exp(-z^2)\operatorname{erfc}(iz) \qquad z \equiv \frac{1+i}{(8\omega\tau_0)^{1/2}}, \tag{1.488}$$

$$g_{WW}(\ln\tau) = \left(\frac{\tau}{4\pi\tau_0}\right)^{1/2}\exp\left[-\left(\frac{\tau}{4\tau_0}\right)\right]. \tag{1.489}$$

Tables of $w = \exp(-z^2)\operatorname{erfc}(iz)$ are available [4] and the function is contained in some software packages. The average relaxation times obtained from eq. (1.342) are:

$$\langle\tau^n\rangle = \frac{\tau_0^n}{\Gamma(n)\beta}\Gamma\left(\frac{n}{\beta}\right) = \frac{\tau_0^n}{\Gamma(n+1)}\Gamma\left(1+\frac{n}{\beta}\right), \tag{1.490}$$

specific examples of which are

$$\begin{aligned}\langle\tau\rangle &= \frac{\tau_0}{\beta}\Gamma\left(\frac{1}{\beta}\right) = \tau_0\Gamma\left(1+\frac{1}{\beta}\right),\\ \langle\tau^2\rangle &= \frac{\tau_0^2}{\beta}\Gamma\left(\frac{2}{\beta}\right) = \tau_0^2\Gamma\left(1+\frac{2}{\beta}\right).\end{aligned} \tag{1.491}$$

The full width at half height (Δ_{WW} in decades) of $g_{WW}(\log_{10}\tau)$ is roughly

$$\Delta_{WW} \approx \frac{1.27}{\beta} - 0.8, \tag{1.492}$$

that is accurate to about ±0.1 decades in Δ_{WW} for $0.15 \le \beta \le 0.6$ but gives $\Delta_{WW} \approx 0.5$ rather than 1.44 for $\beta = 1$. A more accurate relation between β and the FWHH (in decades) of $Q''(\log_{10}\omega)$ is

$$\beta^{-1} \approx -0.08984 + 0.96479\Delta_{WW} - 0.004604\Delta_{WW}^{2}, \ (0.3 \le \beta \le 1.0), \ (1.14 \le \Delta \le 3.6). \tag{1.493}$$

1.12 Boltzmann Superposition

Consider a physical system subjected to a series of Heaviside steps $dX(t')$ that define a time dependent input excitation $X(t)$. For each such step the change in a retarded response $dY(t - t')$ at a later time t is given by

$$dY(t-t') = R_\infty X(t) + (R_0 - R_\infty)\left[1-\phi(t-t')\right] dX(t'), \tag{1.494}$$

in which $R(t) = R_\infty + (R_0 - R_\infty)\left[1-\phi(t)\right]$ is a time dependent material property defined by $R = Y/X$ with a limiting infinitely short time (high frequency) value of R_∞ and a limiting long time (low frequency) value of R_0. The function $\left[1-\phi(t-t')\right]$ can be regarded as a dimensionless form of $R(t)$ normalized by $(R_0 - R_\infty)$ with a short time limit of zero and a long time limit of unity. The total response $Y(t)$ to a time dependent excitation $dX(t)$ is obtained by integrating eq. (1.494) from the infinite past $(t' = -\infty)$ to the present $(t' = t)$:

$$\begin{aligned} Y(t) &= R_\infty X(t) + (R_0 - R_\infty)\int_{X(-\infty)}^{X(t)} \left[1-\phi(t-t')\right] dX(t') \\ &= R_\infty X(t) + (R_0 - R_\infty)\int_{-\infty}^{t} \left[1-\phi(t-t')\right]\left[\frac{dX(t')}{dt'}\right] dt'. \end{aligned} \tag{1.495}$$

Integrating eq. (1.495) by parts [eq (1.21)] yields

$$\int_{-\infty}^{t} \left[1-\phi(t-t')\right]\left[\frac{dX(t')}{dt'}\right] dt' = \left\{\left[1-\phi(t-t')\right] X(t')\right\}\Big|_{-\infty}^{t}\Big| - \int_{-\infty}^{t} X(t')\left[\frac{d\left[1-\phi(t-t')\right]}{dt'}\right] dt'. \tag{1.496}$$

The first term on the right hand side is zero because $\left[1-\phi(t-t')\right] \to 0$ as $(t-t') \to 0$, $\left[1-\phi(t-t')\right] \to 1$ as $(t-t') \to \infty$, and $X(t' \to -\infty) = 0$. Applying the transformation $t'' = t - t'$ to eqs. (1.495) and (1.496) yields:

$$Y(t) = R_\infty X(t) + (R_0 - R_\infty)\int_{0}^{+\infty} X(t-t'')\left[\frac{-d\phi(t'')}{dt''}\right] dt''. \tag{1.497}$$

Equation (1.497) has the same form as the deconvolution integral for the product of the Laplace transforms of $X^*(i\omega)$ and $Q^*(i\omega)$, eq. (1.266). Thus Laplace transforming the functions $X(t)$, $Y(t)$ and $R(t) = Q(t)$ to $X^*(i\omega)$, $Y^*(i\omega)$ and $R^*(i\omega)$ yields $(s=i\omega)$

$$\begin{aligned} Y^*(i\omega) &= R_\infty X^*(i\omega) + R^*(i\omega)X^*(i\omega) \\ &= \left[R_\infty + R^*(i\omega)\right]X^*(i\omega). \end{aligned} \tag{1.498}$$

Now consider the common case that $X(t) = X_0\exp(-i\omega t)$. Insertion of this relation into eq. (1.497) for a retardation process gives

$$Y(t) = R_\infty X_0 \exp(-i\omega t) + (R_0 - R_\infty) X_0 \exp(-i\omega t)\int_0^\infty \exp(+i\omega t'')\left[\frac{-d\phi(t'')}{dt''}\right]dt'' \tag{1.499}$$

so that

$$R^*(i\omega) = \frac{Y(t)\exp(-i\omega t)}{X_0} = R_\infty + (R_0 - R_\infty)\int_0^\infty \exp(+i\omega t'')\left[\frac{-d\phi(t'')}{dt''}\right]dt'' \tag{1.500}$$

or

$$\frac{R^*(i\omega) - R_\infty}{(R_0 - R_\infty)} = \int_0^\infty \exp(+i\omega t'')\left[\frac{-d\phi(t'')}{dt''}\right]dt''. \tag{1.501}$$

Proceeding through the same steps for a relaxation response gives

$$\frac{P^*(i\omega) - P_0}{(P_\infty - P_0)} = \left[1 + \int_0^\infty \exp(+i\omega t'')\left[\frac{-d\phi(t'')}{dt''}\right]dt''\right]. \tag{1.502}$$

The quantities $(R_0 - R_\infty)$ (retardation) and $(P_\infty - P_0)$ (relaxation) are referred to in the literature as the *dispersions* in $R'(\omega)$ and $P'(\omega)$. This use of the term "dispersion" differs from that used in the optical and quantum mechanical literature, for example the term "dispersion relations" also denotes the Kronig-Kramer and similar relations between real and imaginary components of a complex function.

1.13 Relaxation and Retardation Processes

The distinction between these two has been mentioned several times already, and is now described in detail. It will be shown that the average relaxation and retardation times are different for nonexponential decay functions, and that the frequency dependencies of the real component of complex relaxation and retardation functions also differ (reflecting the difference in the corresponding time dependent functions). For these purposes, it is convenient to discuss relaxation and retardation processes in terms of the functions $P(t)$ and $Q(t)$ introduced in §1.10.

To demonstrate that relaxation and retardation times are different for nonexponential response functions consider

$$R(\omega) = S(\omega) P^*(i\omega) \tag{1.503}$$

and

$$S(\omega) = R(\omega) Q^*(i\omega) \tag{1.504}$$

so that

$$P^*(i\omega) = 1/Q^*(i\omega). \tag{1.505}$$

For $P^*(i\omega) = P'(\omega) + iP''(\omega)$ and $Q^*(i\omega) = Q'(\omega) - iQ''(\omega)$ eq. (1.505) implies [cf. eqs (1.170)]

$$P'' = \frac{Q''}{Q'^2 + Q''^2} \tag{1.506}$$

and

$$Q'' = \frac{P''}{P'^2 + P''^2}. \tag{1.507}$$

Now consider the specific functional forms for $P^*(i\omega)$ and $Q^*(i\omega)$ when $\phi(t)$ is the exponential function $\exp(-t/\tau)$. For a retardation function

$$\begin{aligned} \frac{Q^*(i\omega) - Q_\infty}{Q_0 - Q_\infty} &= LT\left(\frac{-d\phi}{dt}\right) = LT\left\{\left(\frac{1}{\tau_Q}\right)\exp\left[-\left(\frac{t}{\tau_Q}\right)\right]\right\} \\ &= \frac{1}{1 + i\omega\tau_Q} = \frac{1}{1+\omega^2\tau_Q^2} + \frac{i\omega\tau_Q}{1+\omega^2\tau_Q^2}, \end{aligned} \tag{1.508}$$

where τ_Q denotes the retardation time. For a relaxation function

$$\begin{aligned} \frac{P^*(i\omega) - P_0}{P_\infty - P_0} &= LT\left(\frac{-d\phi}{dt}\right) = LT\left\{\left(\frac{1}{\tau_P}\right)\exp\left[-\left(\frac{t}{\tau_P}\right)\right]\right\} \\ &= \frac{i\omega\tau_P}{1 + i\omega\tau_P} = \frac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2} - \frac{i\omega\tau_P}{1+\omega^2\tau_P^2}. \end{aligned} \tag{1.509}$$

The relation between the retardation time τ_Q and relaxation time τ_P is derived by inserting the expressions for P'', Q' and Q'' into eq. (1.506):

$$P''(\omega)=(P_\infty-P_0)\left[\frac{\omega\tau_P}{1+\omega\tau_P^2}\right]=\frac{Q''}{Q'^2+Q''^2}$$
$$=\frac{(Q_0-Q_\infty)\left[\dfrac{\omega\tau_Q}{1+\omega\tau_Q^2}\right]}{\left\{(Q_0-Q_\infty)\left[\dfrac{1}{1+\omega\tau_Q^2}+Q_\infty\right]\right\}^2+\left\{(Q_0-Q_\infty)\left[\dfrac{\omega\tau_Q}{1+\omega\tau_Q^2}\right]\right\}^2}. \tag{1.510}$$

The denominator D of eq. (1.510) is

$$D=\frac{(Q_0-Q_\infty)\omega^2\tau_Q^2+\left[Q_\infty\left(1+\omega^2\tau_Q^2\right)+(Q_0-Q_\infty)\right]^2}{\left(1+\omega^2\tau_Q^2\right)}$$
$$=\frac{\left(1+\omega^2\tau_Q^2\right)\left[(Q_0-Q_\infty)^2+2Q_\infty(Q_0-Q_\infty)+Q_\infty^2\left(1+\omega^2\tau_Q^2\right)^2\right]}{\left(1+\omega^2\tau_Q^2\right)^2} \tag{1.511}$$
$$=\frac{\left(1+\omega^2\tau_Q^2\right)\left[\left(Q_0^2-Q_\infty^2\right)+Q_\infty^2\left(1+\omega^2\tau_Q^2\right)\right]}{\left(1+\omega^2\tau_Q^2\right)^2}=\frac{\left(Q_0^2-Q_\infty^2\right)+Q_\infty^2\left(1+\omega^2\tau_Q^2\right)}{\left(1+\omega^2\tau_Q^2\right)},$$

so that

$$(P_\infty-P_0)\left(\frac{\omega\tau_P}{1+\omega^2\tau_P^2}\right)=\frac{(Q_0-Q_\infty)\omega\tau_Q}{\left(Q_0^2-Q_\infty^2\right)+Q_\infty^2\left(1+\omega^2\tau_Q^2\right)}=\frac{(Q_0-Q_\infty)\omega\tau_Q}{Q_0^2+Q_\infty^2\omega^2\tau_Q^2}$$
$$=\frac{\left\{(Q_0-Q_\infty)\left(\dfrac{Q_0}{Q_\infty}\right)\right\}\omega\tau_Q\left(\dfrac{Q_\infty}{Q_0}\right)}{Q_0^2\left[1+\omega^2\tau_Q^2\left(\dfrac{Q_\infty}{Q_0}\right)^2\right]}=\frac{\left[\dfrac{1}{Q_\infty}-\dfrac{1}{Q_0}\right]\omega\tau_Q\left(\dfrac{Q_\infty}{Q_0}\right)}{1+\omega^2\tau_Q^2\left(\dfrac{Q_\infty}{Q_0}\right)^2}. \tag{1.512}$$

Equations (1.512) and (1.510) reveal that

$$\tau_P=\left(\frac{Q_\infty}{Q_0}\right)\tau_Q \tag{1.513}$$

and

$$P_\infty-P_0=\frac{1}{Q_\infty}-\frac{1}{Q_0}. \tag{1.514}$$

Equation (1.514) results from Q_∞, Q_0, $P_\infty=1/Q_\infty$ and $P_0=1/Q_0$ all being real, and eq. (1.513) expresses the important fact that τ_P and τ_Q differ by an amount that depends on the dispersion in Q'. This dispersion can be substantial, amounting to several orders of magnitude for polymers for example. Since Q_∞/Q_0 is less than unity for retardation processes eq. (1.513) indicates that relaxation times are smaller than retardation times. Similar analyses of P' as a function of Q' and Q'', and of Q'' and Q' as functions of P' and P'', yield the same results. These different derivations must be equivalent for mathematical consistency, of course, but it is not immediately obvious that this is so because the frequency dependencies of P' and Q' are apparently different [compare eq. (1.509) with eq. (1.508)]. Comparison of the full expressions for P' and Q' indicates that all is well, however, since their frequency dependencies are indeed equivalent:

$$P_0+\left(P_\infty-P_0\right)\left(\frac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2}\right)=Q_\infty+\left(Q_0-Q_\infty\right)\left(\frac{1}{1+\omega^2\tau_Q^2}\right) \tag{1.515}$$

$$\Rightarrow\frac{\left(P_\infty-P_0\right)\omega^2\tau_P^2+P_0\left(1+\omega^2\tau_P^2\right)}{1+\omega^2\tau_P^2}=\frac{Q_0+Q_\infty\omega^2\tau_Q^2}{1+\omega^2\tau_Q^2} \tag{1.516}$$

$$\Rightarrow\frac{P_0+P_\infty\omega^2\tau_P^2}{1+\omega^2\tau_P^2}=\frac{Q_0+Q_\infty\omega^2\tau_Q^2}{1+\omega^2\tau_Q^2}. \tag{1.517}$$

The *loss tangent*, $\tan\delta = P''/P' = Q''/Q'$ has yet a different time constant:

$$\tau_{\tan\delta}=\tau_Q\left(\frac{Q_0}{Q_\infty}\right)^{1/2}=\tau_P\left(\frac{P_\infty}{P_0}\right)^{1/2}, \tag{1.518}$$

so that $\tau_{\tan\delta}$ lies between τ_P and τ_Q.

Equations (1.508) for retardation and (1.509) for relaxation are readily generalized to the nonexponential case by combining them with eq. (1.345). The results are

$$\frac{Q^*(i\omega)-Q_\infty}{Q_0-Q_\infty}=\int_{-\infty}^{+\infty}g\left(\ln\tau_Q\right)\left[\frac{1}{1+i\omega\tau_Q}\right]d\ln\tau_Q=\left\langle\frac{1}{1+i\omega\tau_Q}\right\rangle \tag{1.519}$$

and

$$\frac{P^*(i\omega)-P_0}{P_\infty-P_0}=\int_{-\infty}^{+\infty}g\left(\ln\tau_P\right)\left[\frac{i\omega\tau_P}{1+i\omega\tau_P}\right]d\ln\tau_P=\left\langle\frac{i\omega\tau_P}{1+i\omega\tau_P}\right\rangle, \tag{1.520}$$

where $\langle\ldots\rangle$ denotes g weighted averages. A similar analysis to that just given, when applied to non-exponential functions of $\phi(t)$, reveals important relations between the limiting low and high frequency limits of $Q^*(i\omega)$:

$$Q'(\omega) = \left\langle \frac{P'}{P'^2 + P''^2} \right\rangle = \left(\frac{(P_\infty - P_0)\left\langle \dfrac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2} \right\rangle + P_0}{\left[(P_\infty - P_0)\left\langle \dfrac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2} \right\rangle + P_0 \right]^2 + \left| (P_\infty - P_0)\left\langle \dfrac{\omega\tau_P}{1+\omega^2\tau_P^2} \right\rangle \right|^2} \right). \tag{1.521}$$

In the limit $\omega\tau_P \to 0$ this expression gives $Q_0 = 1/P_0$, as expected. However, if P_0 is zero then Q_0 is not infinite but rather approaches a limiting value that is a function of how broad $g(\ln\tau_P)$ is. Rewriting eq. (1.521) with $P_0 = 0$ yields

$$Q'(\omega) = \left(\frac{P_\infty \left\langle \dfrac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2} \right\rangle}{\left[P_\infty \left\langle \dfrac{\omega^2\tau_P^2}{1+\omega^2\tau_P^2} \right\rangle \right]^2 + \left| P_\infty \left\langle \dfrac{\omega\tau_P}{1+\omega^2\tau_P^2} \right\rangle \right|^2} \right), \tag{1.522}$$

and the value of Q_0 is then

$$Q_0 = \frac{\left\langle \omega^2\tau_P^2 \right\rangle}{P_\infty \left\langle \omega\tau_P \right\rangle^2} = \frac{Q_\infty \left\langle \tau_P^2 \right\rangle}{\left\langle \tau_P \right\rangle^2} \tag{1.523}$$

so that

$$\frac{Q_0}{Q_\infty} = \frac{P_\infty}{P_0} = \frac{\left\langle \tau_P^2 \right\rangle}{\left\langle \tau_P \right\rangle^2}. \tag{1.524}$$

If $\phi(t)$ is exponential then $g(\ln\tau_P)$ is a delta function and the average of the square equals the square of the average and no dispersion in Q' occurs. Thus broader $g(\ln\tau_P)$ functions generate greater differences between the two averages and increase the dispersion in Q'. As noted above this dispersion in Q' can be substantial because $g(\ln\tau_P)$ is often several decades wide.

The distribution functions for relaxation and retardation processions, written here as $g(\ln\tau_P)$ and $h(\ln\tau_Q)$ respectively, are not equal but are clearly related. Their nonequivalence is evident from the relations

$$g(\ln\tau) = \operatorname{Im}\left\{ P\left[\tau^{-1}\exp(\pm i\pi)\right]\right\} = \operatorname{Im}\left\{ \frac{1}{Q\left[\tau^{-1}\exp(\pm i\pi)\right]} \right\} \neq \operatorname{Im}\left\{ Q\left[\tau^{-1}\exp(\pm i\pi)\right]\right\}, \tag{1.525}$$

and

$$h(\ln\tau) = \mathrm{Im}\left\{Q\left[\tau^{-1}\exp(\pm i\pi)\right]\right\} = \mathrm{Im}\left\{\frac{1}{P\left[\tau^{-1}\exp(\pm i\pi)\right]}\right\} \neq \mathrm{Im}\left\{P\left[\tau^{-1}\exp(\pm i\pi)\right]\right\}. \tag{1.526}$$

Specific relations between $g(\ln\tau)$ and $h(\ln\tau)$ have been given by Gross [28,29] and have been restated in modern terminology by Ferry [14] for the viscoeleasticity of polymers (see Chapter 3). Simplified versions of the Ferry expression, in which contributions from nonzero limiting low frequency dissipative properties such as viscosity or electrical conductivity are neglected, are

$$g(\tau) = \frac{h(\tau)}{\left[K_h(\tau)\right]^2 + \left[\pi h(\tau)\right]^2} \tag{1.527}$$

and

$$h(\tau) = \frac{g(\tau)}{\left[K_g(\tau)\right]^2 + \left[\pi g(\tau)\right]^2}, \tag{1.528}$$

where

$$K_g(\tau) \equiv \int_0^\infty \left[\frac{g(u)}{(\tau/u-1)}\right] d\ln u, \tag{1.529}$$

$$K_h(\tau) \equiv \int_0^\infty \left[\frac{h(u)}{(1-u/\tau)}\right] d\ln u. \tag{1.530}$$

The considerable difference between the two distribution functions is illustrated by the fact that if $g(\tau)$ is bimodal then $h(\tau)$ can exhibit a single peak lying between those in $g(\tau)$ [28].

1.14 Relaxation in the Temperature Domain

Isothermal frequency dependencies correspond to constant τ and variable ω. Constant ω and variable τ is readily achieved by changing the temperature. However many things change with temperature, including relaxation parameters such as the distribution function $g(\ln\tau)$ and the dispersions [$\Delta R = (R_\infty - R_0)$ and $\Delta S = (S_0 - S_\infty)$]. The forms of $\tau(T)$ are often well described by the Arrhenius or Fulcher/WLF equations:

$$\tau(T) = \tau_\infty \exp\left(\frac{E_a}{RT}\right) \qquad \text{(Arrhenius)}, \tag{1.531}$$

$$\tau(T) = \tau_\infty \exp\left(\frac{B}{T-T_0}\right) \qquad \text{(Fulcher)}, \tag{1.532}$$

$$\tau(T) = \tau(T_r)\exp\left[\frac{\ln(10)C_1C_2}{T - T_r + C_2}\right] \qquad (\text{WLF}), \tag{1.533}$$

where R is the ideal gas constant, τ_∞ is the limiting high temperature value of τ, $\{E_a, B, T_0, C_1, C_2\}$ are experimentally determined parameters, and T_r is a reference temperature (usually within the glass transition temperature range). The T_r dependent WLF parameters and T_r invariant Fulcher parameters are related as

$$C_1 = \frac{B}{\ln(10)(T_r - T_0)}, \qquad C_2 = T_r - T_0. \tag{1.534}$$

The effective activation energy for the Fulcher equation is

$$\frac{E_a}{R} \approx \frac{B}{(1 - T_0/T)^2}. \tag{1.535}$$

Thus E_a/RT and $B/(T\text{–}T_0)$ are approximately equivalent to $\ln(\omega)$. The biggest advantage of temperature as a variable is the easy access to the wide range in τ it provides – much larger than the usual isothermal frequency ranges. For an activation energy of $E_a/R = 10\,\text{kK}$ a temperature excursion from the nitrogen boiling point (77K) to room temperature (300K) corresponds to about 21 decades in τ. For E_a/R = 100kK (not at all unreasonable) the range is 210 decades (!). However, different relaxation processes have different effective activation energies so a temperature scan may contain overlapping different scales. Nonetheless, $1/T$ or $1/(T\text{–}T_0)$ are both preferable to T as an independent variable.

For an Arrhenius temperature dependence the dispersion ΔP in a material property $P(\omega\tau)$ is proportional to the area of the loss peak as a function of $1/T$,

$$\Delta P \approx \left(\frac{2}{\pi R}\right)\left\langle\frac{1}{E_a}\right\rangle^{-1}\int_0^{+\infty} P''(T)\,d(1/T), \tag{1.536}$$

the derivation of which [15] however depends on approximating ΔP as independent of temperature (for mathematical tractability). It is also usual (because of a lack of needed information) to equate $\langle 1/E_a\rangle^{-1}$ to E_a even though eq. (1.306) indicates that $\langle E_a\rangle\langle 1/E_a\rangle > 1$.

The equivalence of $\ln(\omega)$ and E_a/RT breaks down even as an approximation when ω and τ are not invariably multiplied. A representative example of this occurs for the imaginary component of the complex electrical resistivity $\rho''(\omega,\tau)$:

$$\begin{aligned}
\rho'' &= \left(\frac{1}{\mathrm{e}_0\varepsilon'(\omega\tau)}\right)\left(\frac{\omega\tau^2}{1+\omega^2\tau^2}\right) \approx \left(\frac{1}{\mathrm{e}_0\varepsilon_\infty}\right)\left(\frac{\omega\tau^2}{1+\omega^2\tau^2}\right) \\
&\approx \left(\frac{\tau}{\mathrm{e}_0\varepsilon_\infty}\right)\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) && \text{(peak in } \omega \text{ domain)} \qquad (1.537) \\
&\approx \left(\frac{\tau}{\mathrm{e}_0\varepsilon_\infty\omega}\right)\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) && \text{(no peak in } \omega \text{ domain)}
\end{aligned}$$

Appendix A Laplace Transforms

$$f(t) \equiv \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} F(s)\exp(st)\,ds \qquad\qquad F(s) \equiv \int_0^{\infty} f(t)\exp(-st)\,dt$$

(A1)	$\dfrac{d^n f(t)}{dt^n}$	$s^n F(s) - \sum_{k=0}^{n-1}\left(\dfrac{df^k}{dt^k}\right)_{t=0} s^{n-k-1}$
(A1a)	$\dfrac{df}{dt}$	$sF(s) - f(+0)$
(A1b)	$\dfrac{d^2 f}{dt^2}$	$s^2F(s) - sf(+0) - \left(\dfrac{df}{dt}\right)_{t=0}$
(A2)	$\int_0^t f(\tau)$	$\dfrac{1}{s}F(s)$
(A3)	$t^n f(t)$	$(-1)^n \dfrac{d^n F(s)}{ds^n}$
(A4)	$\exp(at) f(t)$	$F(s-a)$
(A5)	$f(t+a) = f(t)$ (periodic)	$\dfrac{1}{1-\exp(-as)}\int_0^{+\infty}\exp(-st) f(t)\,dt$
(A6)	$f\left(\dfrac{t}{n}\right)$	$nF(ns)$
(A7)	$\left.\begin{matrix} f(t-t_0) & (t \ge t_0 > 0) \\ 0 & t < t_0 \end{matrix}\right\} \equiv h(t-t_0)$	$\exp(-st_0)F(s)$
(A8)	$t^{k-1}\exp(-at)$	$\Gamma(k)(s+a)^{-k}$
(A9)	t^{k-1}	$\Gamma(k)s^{-k}$
(A10)	$\sin(bt)$	$\dfrac{b}{s^2+b^2}$
(A11)	$\cos(bt)$	$\dfrac{s}{s^2+b^2}$
(A12)	$\exp(-at)\sin(bt)$	$\dfrac{b}{(s+a)^2+b^2}$
(A13)	$\exp(-at)\cos(bt)$	$\dfrac{s+a}{(s+a)^2+b^2}$
(A14)	$\sinh(bt)$	$\dfrac{b}{s^2-b^2}$
(A15)	$\cosh(bt)$	$\dfrac{s}{s^2-b^2}$
(A16)	$\dfrac{1}{(\pi t)^{1/2}}\exp\left(\dfrac{-k^2}{4t}\right)$	$s^{-1/2}\exp\left(-ks^{1/2}\right)$

(A17)	$\operatorname{erf}\left(t/2k\right)$	$s^{-1}\exp\left(k^2s^2\right)\operatorname{erfc}\left(ks\right)$
(A18)	$\exp\left(a^2t\right)\operatorname{erf}\left(at^{1/2}\right)$	$\dfrac{a}{s^{1/2}\left(s-a^2\right)}$
(A19)	$\operatorname{erfc}\left(\dfrac{k}{2t^{1/2}}\right)$	$s^{-1}\exp\left(-ks^{1/2}\right)$
(A20)	$\exp\left(a^2t\right)\operatorname{erf}c\left(at^{1/2}\right)$	$\dfrac{1}{s^{1/2}\left(s^{1/2}+a\right)}$
(A21)	$\dfrac{1}{\left(\pi t\right)^{1/2}}-a\exp\left(a^2t\right)\operatorname{erfc}\left(at^{1/2}\right)$	$\dfrac{1}{s^{1/2}+a}$
(A22)	$\dfrac{1}{\left(\pi t\right)^{1/2}}+a\exp\left(a^2t\right)\operatorname{erfc}\left(at^{1/2}\right)$	$\dfrac{s^{1/2}}{s-a^2}$
(A23)	$h\left(t-k\right)$	$s^{-1}\exp\left(-ks\right)$
(A24)	$\sum_{n=0}^{\infty}h\left(t-nk\right)$	$\dfrac{1}{s\left[1-\exp\left(-ks\right)\right]}$
(A25)	$\dfrac{1}{\left(\pi t\right)^{1/2}}-a\exp\left(a^2t\right)\operatorname{erfc}\left(\mathrm{a}t^{1/2}\right)$	$\dfrac{1}{s^{1/2}+a}$

Appendix B1 Resolution of Two Debye Peaks of Equal Amplitude

Consider two Debye peaks of equal amplitude with relaxation times τ/R and τR so that their ratio is R^2. This ensures that the average relaxation time of their sum is $\langle\tau\rangle = 1$ and that when plotted against $\log_{10}(\omega\tau)$ the two peaks, if resolved, appear an equal number of decades on each side of $\ln\langle\tau\rangle = 0$. This symmetry and the equality of amplitudes greatly simplify the mathematics. For convenience place $\omega\tau = x$ so that the sum of the two Debye peaks is

$$y = \frac{x/R}{1+x^2/R^2} + \frac{Rx}{1+R^2x^2}. \qquad \text{(B1)}$$

The extrema in y are then obtained from

$$\frac{dy}{dx} = 0 = \frac{1/R}{1+x^2/R^2} - \frac{x/R\left(2x/R^2\right)}{\left(1+x^2/R^2\right)^2} + \frac{R}{1+R^2x^2} - \frac{Rx\left(2R^2x\right)}{\left(1+R^2x^2\right)^2} \qquad \text{(B2a)}$$

$$= \frac{1/R\left(1-x^2/R^2\right)}{\left(1+x^2/R^2\right)^2} + \frac{R\left(1-R^2x^2\right)}{\left(1+R^2x^2\right)^2}$$

(B2b)

$$= \frac{1/R\left(1-x^2/R^2\right)\left(1+R^2x^2\right)^2 + R\left(1-R^2x^2\right)\left(1+x^2/R^2\right)^2}{\left(1+x^2/R^2\right)^2\left(1+R^2x^2\right)^2} \qquad \text{(B2c)}$$

$$= \frac{1/R\left[\left(1-x^2/R^2\right)\left(1+R^2x^2\right)^2 + R^2\left(1-R^2x^2\right)\left(1+x^2/R^2\right)^2\right]}{\left(1+x^2/R^2\right)^2\left(1+R^2x^2\right)^2} \qquad \text{(B2d)}$$

Defining $r \equiv R^2$ and $z \equiv x^2$ and placing the numerator of eq. (B2d) equal to zero yields

$$\left(1-z/r\right)\left(1+2rz+r^2z^2\right) + r\left(1-rz\right)\left(1+2z/r+z^2/r^2\right) = 0 \qquad \text{(B3)}$$

Rearranging eq. (B3) yields

$$-\left(r+1\right)z^3 + \left[\frac{1}{r}\left(r+1\right)\left(r^2-3r+1\right)\right]z^2 - \left[\frac{1}{r}\left(r+1\right)\left(r^2-3r+1\right)\right]z + \left(r+1\right) \qquad \text{(B4a)}$$

$$= a_3z^3 + a_2z^2 + a_1z + a_0 = 0. \qquad \text{(B4b)}$$

Equation (B4) is appropriately a cubic equation in z whose solutions for resolved peaks correspond to the two maxima and the intervening minimum. The condition for no resolution is that eq. (B4) has one real root and two complex conjugate roots. The condition for borderline resolution is that there are three identical solutions, i.e that eq. (B4) is a perfect cube $\left(z-1\right)^3 = 0$ [note that $\left(r=1; z=1\right)$ is a solution of eq. (B4a)]. For eq. (B4b) to have three equal roots it is required that $3a_3 = -a_2 = a = -3a_0$ so that for $3a_3 = -a_2$

$$a_2 = \frac{1}{r}(r+1)\left(r^2 - 3r + 1\right) = -3a_3 = 3(r+1) \quad \text{(B5a)}$$

$$\Rightarrow \left(r^2 - 3r + 1\right) = 3r \quad \text{(B5b}$$

$$\Rightarrow r^2 - 6r + 1 = 0\,. \quad \text{(B5c)}$$

From eq. (1.2) the solutions to eq. (B5c) are

$$r = \frac{6 \pm (36-4)^{1/2}}{2} = \frac{6 \pm (32)^{1/2}}{2} = 3 \pm 2^{3/2}\,, \quad \text{(B6)}$$

so that $R = \left(3 \pm 2^{3/2}\right)^{1/2} = \pm\left(1 \pm 2^{1/2}\right)$. Note that $\left(1 + 2^{1/2}\right) = -1/\left(1 - 2^{1/2}\right)$, consistent with the equivalence of R and $1/R$ in eq (B1). On a logarithmic scale the ratio of the relaxations times $r = R^2$ is therefore $\log_{10}\left(3 + 2^{3/2}\right) = 0.7656$ decades.

Appendix B2 Resolution of Two Debye Peaks of Unequal Amplitude

There is no general solution for two Debye peaks of unequal amplitude because the mathematics is intractable (the solution to an 18th order polynomial appears to be necessary!). Consider two Debye peaks of amplitudes unity and A with relaxation times τ/R and τT so that their ratio is again R^2. The analysis given above for equal amplitudes is not appropriate in this case because the criterion for the edge of resolution is now an inflection point with zero slope. An approximate solution can however be obtained numerically:

$$R^2 \approx 8A \qquad (1.5 \le A \le 5)\,, \quad \text{(B7)}$$

$$R^2 \approx \left[2.40 + 2.367\ln(A)\right]^2 \qquad \left(1.0 \le A \le 5\right), \quad \text{(B8)}$$

where as before R^2 is the ratio of the component peak frequencies. Equations (B7) and (B8) agree remarkably well for $1.5 \le A \le 5$: the percentage differences are about $+6\%$ for $A = 1.5$, -4% for $A = 3$, and $+4\%$ $A = 5$.

Appendix C Cole-Cole Complex Plane Plot

We derive the equation for Q' versus Q'' for the Cole-Cole distribution function and show that it is a semicircle with center below the real axis. The derivation follows that given in [30] although intermediate steps are spelled out here. For convenience eqs (1.433) and (1.434) are rewritten in an expanded form in which Q^* is treated as a retardation function with dispersion $\Delta Q \equiv Q_0 - Q_\infty$, where Q_0 and Q_∞ are the limiting low and high frequency limits of Q':

$$\frac{Q''}{\Delta Q} = \frac{\sin(\alpha'\pi/2)}{2\left\{\cosh\left[\alpha'\ln(\omega\tau_0)\right] + \cos(\alpha'\pi/2)\right\}}, \tag{C1}$$

$$\frac{Q' - Q_\infty}{\Delta Q} = \frac{1 + (\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2)}{1 + 2(\omega\tau_0)^{\alpha'}\cos(\alpha'\pi/2) + (\omega\tau_0)^{2\alpha'}}. \tag{C2}$$

The strategy is to eliminate the terms $\sinh\theta$ and $\cosh\theta$ arising from the definitions

$$(\omega\tau_0)^{\alpha'} = \exp(\theta) \tag{C3}$$

and

$$\theta = \alpha'\ln(\omega\tau_0), \tag{C4}$$

using $\cosh^2\theta - \sinh^2\theta = 1$. The relation $\exp(-\theta) = \cosh\theta - \sinh\theta$ is also used and for convenience the variables $s = \sin(\alpha'\pi/2)$ and $c = \cos(\alpha'\pi/2)$ are introduced. Equations (D1) and (D2) then become

$$\frac{Q''}{\Delta Q} = \frac{s}{2\{\cosh\theta + c\}} \tag{C5}$$

and

$$\begin{aligned} \frac{Q' - Q_\infty}{\Delta Q} &= \frac{1 + c\exp\theta}{1 + 2c\exp\theta + \exp(2\theta)} = \frac{\exp(-\theta) + c}{\exp(-\theta) + 2c + \exp\theta} && (a) \\ &= \frac{\cosh\theta - \sinh\theta + c}{2(\cosh\theta + c)} && (b) \\ &= \frac{1}{2}\left[1 - \frac{\sinh\theta}{\cosh\theta + c}\right] && (c) \end{aligned} \tag{C6}$$

The next step is to solve for $\cosh\theta$ and $\sinh\theta$ from eqs. (D5) and (D6d). From eq. (D5):

$$\cosh\theta = \frac{s\Delta Q}{2Q''} - c = \frac{s\Delta Q - 2cQ''}{2Q''} \tag{C7}$$

Insertion of eq. (D7) into eq. (D6c) yields

$$\begin{aligned}
&\frac{Q'-Q_\infty}{\Delta Q}=\frac{1}{2}\left[1-\frac{2Q''\sinh\theta}{s\Delta Q}\right] && (a)\\
&\Rightarrow \frac{Q''\sinh\theta}{s\Delta Q}=\frac{1}{2}-\frac{2\left(Q'-Q_\infty\right)}{\Delta Q}=\frac{\left(Q_0+Q_\infty-2Q'\right)}{2\Delta Q} && (b)
\end{aligned}, \qquad \text{(C8)}$$

from which

$$\sinh\theta=\frac{\left(Q_0+Q_\infty-2Q'\right)s}{2Q''}. \qquad \text{(C9)}$$

Now apply $\cosh^2\theta-\sinh^2\theta=1$ to eqs. (D7) and (D9):

$$\begin{aligned}
&\left[\frac{s\Delta Q-2cQ''}{2Q''}\right]^2-\left[\frac{\left(Q_0+Q_\infty-2Q'\right)s}{2Q''}\right]^2=1 && (a)\\
&\Rightarrow \left[s\Delta Q-2cQ''\right]^2-4Q''^2-\left[\left(Q_0+Q_\infty-2Q'\right)s\right]^2=0. && (b)
\end{aligned} \qquad \text{(C10)}$$

The objective is now to express eq. (Cl0b) as the sum of two terms, one of which is a function of Q' only and the other of Q'' only, and placing the sum equal to a constant. Expanding the first term in eq. (C10b) gives

$$s^2\Delta Q^2-4cs\Delta QQ''+4c^2Q''^2-4Q''^2-\left[\left(Q_0+Q_\infty-2Q'\right)s\right]^2=0 \qquad \text{(C11)}$$

and using $1-c^2=s^2$ then yields

$$\begin{aligned}
&s^2\Delta Q^2-4cs\Delta QQ''-4s^2Q''^2-\left[\left(Q_0+Q_\infty-2Q'\right)s\right]^2=0\\
&\Rightarrow c\Delta QQ''/s+Q''^2+\left[\left(Q_0+Q_\infty-2Q'\right)/2\right]^2=\left(\Delta Q/2\right)^2
\end{aligned}. \qquad \text{(C12)}$$

Completing the square of the Q'' terms then gives

$$\begin{aligned}
\left[c\Delta Q/2s+Q''\right]^2+\left[\left(Q_0+Q_\infty-2Q'\right)/2\right]^2&=\Delta Q^2/4+c^2\Delta Q^2/4s^2\\
&=\left(\Delta Q/2\right)^2\left[1+\frac{c^2}{s^2}\right]=\left(\Delta Q/2s\right)^2
\end{aligned} \qquad \text{(C13)}$$

The final expression is obtained from eq. (C13) by restoring the original variables and constants:

$$\left[Q''+\tfrac{1}{2}\left(Q_0-Q_\infty\right)\cot\left(\alpha'\pi/2\right)\right]^2+\left[\tfrac{1}{2}\left(Q_0+Q_\infty\right)-Q'\right]^2=\tfrac{1}{4}\left(Q_0-Q_\infty\right)^2\operatorname{cosec}^2\left(\alpha'\pi/2\right) \qquad \text{(C14)}$$

This is eq. (1.438). Equation (D14) is that of circle with its center at $\left\{\tfrac{1}{2}\left(Q_0+Q_\infty\right),-\tfrac{1}{2}\left(Q_0-Q_\infty\right)\cot\left(\alpha'\pi/2\right)\right\}$ and radius $\tfrac{1}{2}\left(Q_0-Q_\infty\right)\operatorname{cosec}\left(\alpha'\pi/2\right)$. For a single relaxation time (Debye relaxation) α' = 1 so that cot(π/2) = 0 and cosec(π/2) = 1. Equation (C14) then simplifies to (eq (1.416))

$$Q''^2+\left[\tfrac{1}{2}\left(Q_0+Q_\infty\right)-Q'\right]^2=\tfrac{1}{4}\left(Q_0-Q_\infty\right)^2 \tag{C15}$$

Appendix D Dirac Delta Distribution Function for a Single Relaxation Time

We prove that $\lim_{\varepsilon\to 0}\left[\varepsilon\theta\left(1+\theta^2\right)/\left(1-\theta^2\right)^2\right]=\delta\left(\theta-1\right)$ (eq. (1.417)). The appropriate indefinite integrals obtained from tables are:

$$\begin{aligned}\int\frac{\theta d\theta}{\left(1-\theta^2\right)^2}&=\frac{1}{2\left(1-\theta^2\right)}, && \left(\theta<1\right)\\ &=\frac{-1}{2\left(\theta^2-1\right)}, && \left(\theta>1\right)\end{aligned}\tag{D1}$$

and

$$\begin{aligned}\int\frac{\theta^3 d\theta}{\left(1-\theta^2\right)^2}&=\frac{1}{2\left(1-\theta^2\right)}+\frac{\ln\left(1-\theta^2\right)}{2}\quad, && \left(\theta<1\right)\\ &=\frac{-1}{2\left(\theta^2-1\right)}+\frac{\ln\left(\theta^2-1\right)}{2}, && \left(\theta>1\right).\end{aligned}\tag{D2}$$

Because of the singularity at $\theta = 1$ these integrals need to be evaluated using the Cauchy principal value eq. (1.216). The total integral in eq. (1.417) is then

$$\begin{aligned}\int_0^\infty\frac{\left(\theta+\theta^3\right)d\theta}{\left(1-\theta^2\right)^2}&=\int_0^{1-\varepsilon}\frac{\theta d\theta}{\left(1-\theta^2\right)^2}+\int_{1+\varepsilon}^{\infty}\frac{\theta d\theta}{\left(\theta^2-1\right)^2}+\int_0^{1-\varepsilon}\frac{\theta^3 d\theta}{\left(1-\theta^2\right)^2}+\int_{1+\varepsilon}^{\infty}\frac{\theta^3 d\theta}{\left(\theta^2-1\right)^2}\\
&=\left(\frac{1}{2\left(1-\theta^2\right)}\right]_0^{1-\varepsilon} && (a)\\
&+\left(\frac{-1}{2\left(\theta^2-1\right)}\right]_{1+\varepsilon}^{\infty} && (b)\\
&+\left(\frac{1}{2\left(1-\theta^2\right)}+\frac{\ln\left(1-\theta^2\right)}{2}\right]_0^{1-\varepsilon} && (c)\\
&+\left(\frac{-1}{2\left(\theta^2-1\right)}+\frac{\ln\left(\theta^2-1\right)}{2}\right]_{1+\varepsilon}^{\infty} && (d)\end{aligned}\tag{D3}$$

The results are:

Equation (D3a):

$$\left(\frac{1}{2\left(1-\theta^2\right)}\right]_0^{1-\varepsilon} = \frac{1}{2\left(1-1+2\varepsilon\right)} - \frac{1}{2} = \left\{\frac{1}{4\varepsilon} - \frac{1}{2}\right\} \tag{D4a}$$

Equation (D3b):

$$\left(\frac{-1}{2\left(\theta^2-1\right)}\right]_{1+\varepsilon}^{\infty} = 0 + \frac{1}{2\left(1+2\varepsilon-1\right)} = \left\{\frac{1}{4\varepsilon}\right\} \tag{D4b}$$

Equation (D3c):

$$\left(\frac{1}{2\left(1-\theta^2\right)} + \frac{\ln\left(1-\theta^2\right)}{2}\right]_0^{1-\varepsilon} = \frac{1}{2\left(2\varepsilon\right)} + \frac{1}{2}\ln\left(2\varepsilon\right) - \frac{1}{2} - 0 = \left\{\frac{1}{4\varepsilon} + \frac{1}{2}\ln\left(2\varepsilon\right) - \frac{1}{2}\right\} \tag{D4c}$$

Equation (D3d):

$$\left(\frac{-1}{2\left(\theta^2-1\right)} + \frac{\ln\left(\theta^2-1\right)}{2}\right]_{1+\varepsilon}^{\infty} = 0 + \ln\left(\infty\right) + \frac{1}{4\varepsilon} - \frac{1}{2}\ln\left(2\varepsilon\right) = \left\{\ln\left(\infty\right) + \frac{1}{2\varepsilon} - \frac{1}{2}\ln\left(2\varepsilon\right)\right\} \tag{D4d}$$

The sum of eqs. (D4) is

$$\begin{aligned}&\left\{\frac{1}{4\varepsilon} - \frac{1}{2}\right\} + \left\{\frac{1}{4\varepsilon}\right\} + \left\{\frac{1}{4\varepsilon} + \frac{1}{2}\ln\left(2\varepsilon\right) - \frac{1}{2}\right\} + \left\{\ln\left(\infty\right) + \frac{1}{4\varepsilon} - \frac{1}{2}\ln\left(2\varepsilon\right)\right\}\\ &= \left\{\frac{1}{\varepsilon} - 1 + \ln\left(\infty\right)\right\}.\end{aligned} \tag{D5}$$

When multiplied by $\varepsilon \to 0$ according to eq. (1.417) the final term in eq. (D5) is $\lim_{\varepsilon\to 0}\left[1-\varepsilon+\varepsilon\ln\left(\infty\right)\right]=1$ since $\lim_{\varepsilon\to 0}\left[\varepsilon\ln\left(\infty\right)\right]=0$ because the logarithmic divergence is weaker than that produced by ε approaching ∞ linearly. Thus the integral is unity and eq. (1.417) is indeed a Dirac delta function.

****

REFERENCES

[1] A. Kyrala, "*Applied Functions of a Complex Variable*", Wiley-Interscience, 1972.
[2] A. Pais, "*Inward Bound*", Oxford, 1986.
[3] A. Pais, "*Subtle is the Lord*", Oxford, 1982.
[4] I. Stegun and M. Abramowitz, "*Handbook of Mathematical Functions*", Dover (1965) ISBN 486-61272-4
[5] G. Chantry, "*Long-Wave Optics*" (pp 31-32), Academic Press (1984) ISBN 0-12-168101-7
[6] M. Boas, "*Mathematical Methods in the Physical Sciences 3rd Edition*", Wiley (2006) ISBN 0-471-19826-9
[7] E. T. Copson, "*An Introduction to the Theory of Functions of a Complex Variable*", Oxford (1960)
[8] L. A. Pipes and L. R. Harvill, "*Applied Mathematics for Engineers and Physicists*", Dover (2014)
[9] W. Mendenhall, "*Introduction to Probability and Statistics*", Duxbury Press (1971) ISBN 0-87872-046-4
[10] C. Chatfield, "*Statistics for Technology*", Chapman and Hall (1983) ISBN 0-412-25340-2
[11] E. W. Montroll and J. T. Bendler, *J. Statistical Physics* 34 129 (1984)
[12] I.M Hodge and G. S. Huvard, *Macromolecules* 16 371 (1983)
[13] E. C. Titchmarsh, "*The Theory of Functions*", *2nd Edition*, Oxford, 1948 [downloadable for free].
[14] E. C. Titchmarsh, "*Introduction to the Theory of Fourier Integrals*", *2nd Edition*, Oxford, 1948.
[15] N. G. McCrum, B. E. Read and G. Williams, *"Anelastic and Dielectric Effects in Polymeric Solids"*, Dover 1991.
[16] J. D. Ferry, *"Viscoelastic Properties of Polymers", 3rd Edition*, Wiley, 1980
[17] M. Jammer in *"The Conceptual Development of Quantum Mechanics"*, p. 335, McGraw-Hill, 1966 (cited in [2])
[18] J. W. Evans, W. B. Gragg and R. J. LeVeque, *Math. Comp*. **34** 149, 203 (1980)
[19] R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.* **63** 385 (1941)
[20] R. H. Cole and K. S. Cole, *J. Chem. Phys.* **9** 341 (1941)
[21] D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19** 1484 (1951)
[22] S. H. Glarum, *J. Chem. Phys*. **33** 639 (1960)
[23] S. Chandresekhar, *Rev. Modern Phys*. **15** 1 (1943)
[24] S. Havriliak and S. Negami, *Polymer* **8** 161 (1967)
[25] R.Kohlrausch, *Pogg. Ann. Phys*. **91** 198 (1854)
[26] R.Kohlrausch, *Pogg. Ann. Phys*. **119** 352 (1863)
[27] G. Williams and D. C. Watt, *Trans. Faraday Soc*. **66** 80 (1970)
[28] B. Gross, "*Mathematical Structure of the Theories of Viscoelasticity"*, Hermann et Cie (Paris) 1953
[29] B. Gross, *J. Appl. Phys*. **19** 257 (1948)
[30] N. E. Hill, Chapter One of "*Dielectric Properties and Molecular Behaviour*", Van Nostrand (London) 1969.