APPENDIX

1. Series Expansions

Many common functions (such as sin x, cos x, e^x, ln(1+x) ...) can be represented by power series, i.e., a sum of terms with increasing powers of the relevant argument x. Such series are useful in allowing the function itself to be replaced by an algebraically simple approximation appropriate in some limit (e.g., $x \rightarrow 0$, $x \rightarrow 1$, $x \rightarrow \infty$). These series approximations can be looked up in many handbooks, but they can also often be derived from the *McLaurin series*. A function f(x) is said to be *analytic* if all derivatives (first, second, third...) exist over the relevant range of x. The McLaurin series representation of an analytic function f(x) is given by

$$f(x) = \sum_{i=1}^{\infty} \frac{1}{i!} \left(\frac{d^i f}{dx^i} \right)_{i=0} x^i \qquad \text{(A.1.1)}$$

where the ith derivative of f(x) is to be evaluated at i = 0, and where i factorial is i! = i x (i–1) x (i–2)... x 1. By definition, 0! = 1.

As an example, consider e^x, and recall that $d(e^x)/dx = e^x$. Therefore from eq A.1.1

$$\begin{aligned} e^x &= \frac{1}{0!}e^{(0)}x^0 + \frac{1}{1!}e^{(0)}x^1 + \frac{1}{2!}e^{(0)}x^2 + \ldots \\ &= 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \ldots \end{aligned} \qquad \text{(A.1.2)}$$

Series expansions for trigonometric functions can also be readily obtained, recalling that d(sin x)/dx = cos x, d(cos x)/dx = – sin x, sin 0 = 0, and cos 0 = 1:

$$\sin x = \frac{1}{0!}\sin(0)x^0 + \frac{1}{1!}\cos(0)x^1 - \frac{1}{2!}\sin(0)x^2 + \dots$$

$$= x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 + \dots \tag{A.1.3}$$

$$\cos x = \frac{1}{0!}\cos(0)x^0 - \frac{1}{1!}\sin(0)x^1 - \frac{1}{2!}\cos(0)x^2 + \dots$$

$$= 1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 + \dots \tag{A.1.4}$$

The natural logarithm of (1+x) where $|x| < 1$ also arises often. Recall that $d(\ln x)/dx = 1/x$, and that $d(x^{-i})/dx = -ix^{-(i+1)}$:

$$\ln(1+x) = \frac{1}{0!}\ln(1+0)x^0 + \frac{1}{1!}\frac{1}{(1+0)}x^1 - \frac{1}{2!}\frac{1}{(1+0)^2}x^2 + \dots$$

$$= x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots \tag{A.1.5}$$

Finally, when $f(x) = (1+x)^n$ we have

$$(1+x)^n = \frac{1}{0!}(1+0)^n x^0 + \frac{1}{1!}n(1+0)^{n-1}x^1 + \frac{1}{2!}n(n-1)(1+0)^{n-2}x^2 + \dots$$

$$= 1 + nx + \frac{1}{2!}n(n-1)x^2 + \frac{1}{3!}n(n-1)(n-2)x^3 + \dots \tag{A.1.6}$$

These results can be readily extended to related functions, for example by replacing x with –x, ax, or a complex number z.

2. Summation Formulae

These arise in several contexts, especially molecular weight distributions. For example, let x_i be the mole fraction of i-mer in a polycondensation that follows the most probable distribution (eq 2.4.1),

$$x_i = (1-p)\,p^{i-1} \tag{A.2.1}$$

where p is the probability that a monomer has reacted. Are we sure that this distribution is normalized, that is

$$\sum_{i=1}^{\infty} x_i = 1 = (1-p)\sum_{i=1}^{\infty} p^{i-1} \ ?$$

Comparison with the distribution expression therefore requires that

$$\sum_{i=0}^{\infty} p^i = \frac{1}{1-p} \tag{A.2.2}$$

(Note an important but subtle point: the mole fraction of i-mer only makes sense for $i \geq 1$, but the summation above runs from $i = 0$. This is because the sum of p^{i-1} starting from i=1 is the same as the sum of p^i starting from i=0, and the solution is easier to obtain in the latter case). To show that this is, in fact, correct, consider a slightly different, *finite* sum:

$$S_1 = \sum_{i=0}^{n} p^i = 1 + p + p^2 + p^3 + \ldots + p^n \tag{A.2.3}$$

If we multiply S_1 by p and subtract it from S_1, we have a term-by-term cancellation:

$$S_1 - pS_1 = (1 + p + p^2 + ... + p^n) - (p + p^2 + p^3 + ... + p^{n+1})$$

$$= 1 - p^{n+1} \qquad \text{(A.2.4)}$$

and therefore

$$S_1 = \frac{1 - p^{n+1}}{1 - p}$$

$$= \frac{1}{1 - p} \quad \text{as} \quad n \to \infty \quad \text{(and assuming } p < 1\text{)} \qquad \text{(A.2.5)}$$

Of course, for the polymerization case p will always be < 1.

To obtain the number average degree of polymerization, we required the related summation (eq 2.4.4)

$$S_2 = \sum_{i=1}^{\infty} i\, p^{i-1} \qquad \text{(A.2.6)}$$

The trick here is to recognize ip^{i-1} as the derivative of p^i with respect to p, and that the derivative with respect to p can be taken outside the summation:

$$S_2 = \sum_{i=1}^{\infty} \frac{dp^i}{dp} = \frac{d}{dp}\left(\sum_{i=1}^{\infty} p^i\right) = \frac{d}{dp}\left(\left(\sum_{i=0}^{\infty} p^i\right) - 1\right)$$

$$= \frac{d}{dp}(S_1 - 1) = \frac{d}{dp}\left(\frac{1}{1 - p}\right) = \frac{1}{(1 - p)^2} \qquad \text{(A.2.7)}$$

Similarly, on the way to obtaining the weight average degree of polymerization we encountered the following sum:

$$S_3 = \sum_{i=1}^{\infty} i^2 \, p^{i-1} \qquad \text{(A.2.8)}$$

and this can be evaluated using the same "derivative trick":

$$\sum_{i=1}^{\infty} i^2 \, p^{i-1} = \frac{d}{dp}\left(\sum_{i=1}^{\infty} i \, p^i\right) = \frac{d}{dp}\left(p\sum_{i=1}^{\infty} i \, p^{i-1}\right)$$

$$= \frac{d}{dp}\left(pS_2\right) = \frac{d}{dp}\left(\frac{p}{(1-p)^2}\right) = \frac{(1-p)^2 + 2(1-p)p}{(1-p)^4} \qquad \text{(A.2.9)}$$

$$= \frac{1+p}{(1-p)^3}$$

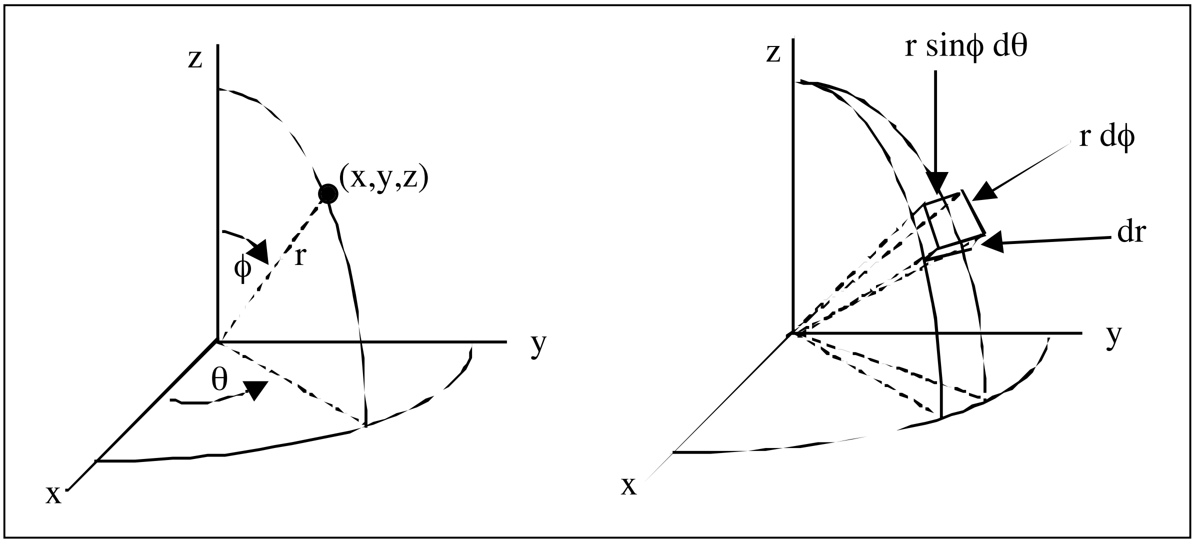
3. Transformation to Spherical Coordinates

In situations where we need to integrate something over all space, and there is no preferred direction, a transformation to spherical coordinates can be extremely useful. A prime example occurred in Chapter 6, where we convert the Gaussian distribution function for the end-to-end vector into the distribution function for the end-to-end distance. Another instance arose in Chapter 8, in considering the form factor for an arbitrary particle.

Suppose we wish to find the integral over all space of some function of f(x,y,z):

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x,y,z)\, dx\, dy\, dz$$

There are two steps required to transform this integral into spherical coordinates: transform f(x,y,z) itself, and transform the volume element dx dy dz. These steps are facilitated by the coordinate axes below.



An arbitrary point (x,y,z) is represented by a distance from the origin, r, an angle away from the x axis in the x-y plane, θ, and an angle away from the z axis, φ: (r,θ,φ). From the figure it can be seen that

$$x = r \sin\phi \cos\theta, \quad y = r \sin\phi \sin\theta, \quad z = r \cos\phi \qquad \text{(A.3.1)}$$

These expressions can be substituted directly into f(x,y,z) to obtain f(r,θ,φ). Note also that

$$\begin{aligned} x^2 + y^2 + z^2 &= r^2 \left(\sin^2\phi[\cos^2\theta + \sin^2\theta] + \cos^2\phi\right) \\ &= r^2 \left(\sin^2\phi + \cos^2\phi\right) = r^2 \end{aligned} \qquad \text{(A.3.2)}$$

Thus, in the case where f(x,y,z) can be written as $f(x^2+y^2+z^2)$, as is the case for the Gaussian distribution, then f(r,θ,φ) becomes simply f(r).

The volume element dx dy dx is now replaced by a volume element with sides dr, r dϕ, and r sinϕ dθ, as shown in the figure. For a function such as the Gaussian which is only a function of r, the integral over all space can be reduced to a single integral:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x,y,z)\,dx\,dy\,dz \;=\; \int_{0}^{\infty}\int_{0}^{2\pi}\int_{0}^{\pi} f(r)\,r^2 \sin\phi\,dr\,d\theta\,d\phi$$

$$= \int_{0}^{\infty} f(r)\,r^2 dr \int_{0}^{2\pi}\int_{0}^{\pi} \sin\phi\,d\theta\,d\phi \;=\; \int_{0}^{\infty} f(r)\,r^2 dr \left(2\pi(-\cos\phi)\Big|_0^{\pi}\right) \qquad \text{(A.3.3)}$$

$$= 4\pi\int_{0}^{\infty} f(r)\,r^2 dr$$

4. Some Integrals of Gaussian Functions

A common class of integrals that arose for example in Chapter 6 are these:

$$I_n = \int_{0}^{\infty} x^n \exp(-ax^2)\,dx \qquad \text{(A.4.1)}$$

where n is an integer and a is a positive number. The results are quite simple, and can of course be looked up in any table of integrals, but it is actually instructive to work out the answers. In so doing, we will utilize the transformation to spherical coordinates just described, as well as use the two most common methods for simplifying integrals: change of variable and integration by parts.

The hardest one to do is actually the first, namely I_0. All of the higher powers can be reduced back to this one, as we shall see. We begin by taking I_0^3, and recognizing it can be written as the product of the same integrals along x, y, and z:

$$I_0^3 = \left(\int_0^\infty \exp(-ax^2)\,dx\right)^3 = \left(\int_0^\infty \exp(-ax^2)\,dx\right)\left(\int_0^\infty \exp(-ay^2)\,dy\right)\left(\int_0^\infty \exp(-az^2)\,dz\right)$$

$$= \int_0^\infty\int_0^\infty\int_0^\infty \exp(-a[x^2+y^2+z^2])\,dxdydz$$

$$= \frac{1}{8}\int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty \exp(-a[x^2+y^2+z^2])\,dxdydz$$

(A.4.2)

The last step was allowed because the argument of I_0 (and I_n for all even values of n) is an *even function*, that is one for which f(x) = f(–x). The integral of even function from 0 to ∞ is just half the integral from –∞ to ∞. Now the integrals extend over all of space, and we make the transformation to spherical coordinates r, θ, φ. This is particularly simple in this case, because the argument of the integral only depends on $r^2 = x^2+y^2+z^2$:

$$\frac{1}{8}\int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty \exp(-a[x^2+y^2+z^2])\,dxdydz = \frac{1}{8}4\pi\int_0^\infty r^2\exp(-ar^2)dr$$

(A.4.3)

$$= \frac{\pi}{2}I_2$$

So far, this is not looking promising; we only have a simple relation between I_0^3 and I_2. However, let's attack I_0 directly by integration by parts:

$$\int_a^b u\,dv = uv\Big|_a^b - \int_a^b v\,du \qquad \text{(A.4.4)}$$

where we make the substitutions $u = \exp(-ax^2)$, v = x, so $du = -2ax\exp(-ax^2)dx$ and dv = dx:

$$I_0 = \int_0^\infty \exp(-ax^2)dx = \exp(-ax^2)x\Big|_0^\infty - \int_0^\infty (-2a)x^2\exp(-ax^2)dx$$

$$= 0 + 2a\,I_2 \tag{A.4.5}$$

Thus there is another simple relation between I_0 and I_2. Combining these, we see

$$I_0^3 = \frac{\pi}{2} I_2 = \frac{\pi}{4a} I_0 \tag{A.4.6}$$

or

$$I_0 = \frac{\sqrt{\pi}}{2\sqrt{a}}; \quad I_2 = \frac{\sqrt{\pi}}{4a\sqrt{a}} \tag{A.4.7}$$

Continuing along the sample line, we apply integration by parts to I_2,with $u = \exp(-ax^2)$ again but now $v = x^3/3$ (so $dv = x^2dx$):

$$I_2 = \int_0^\infty x^2\exp(-ax^2)dx = \exp(-ax^2)\frac{x^3}{3}\Big|_0^\infty - \int_0^\infty (-\frac{2a}{3})x^4\exp(-ax^2)dx$$

$$= 0 + \frac{2a}{3} I_4 \tag{A.4.8}$$

In this way, one can arrive at the general formula for even n:

$$I_n = \frac{(n-1)(n-3)...(1)}{2\,(2a)^{n/2}}\sqrt{\frac{\pi}{a}}, \quad \text{even n} \tag{A.4.9}$$

The situation for odd n can be approached by a change of variable, e.g. $u = x^2$, $du = 2xdx$:

$$I_1 = \int_0^\infty x \exp(-ax^2)\, dx = \frac{1}{2}\int_0^\infty \exp(-au)\, du$$

$$= \frac{1}{2}\left(\frac{-1}{a}\right) \exp(-au)\Big|_0^\infty = \frac{1}{2a} \qquad \text{(A.4.10)}$$

and so forth. The general result for odd n becomes:

$$I_n = \frac{1}{2}((n-1)/2)!\,\frac{1}{a^{(n+1)/2}}, \quad \text{odd } n \qquad \text{(A.4.11)}$$

5. Complex Numbers

A complex number z can always be written as the sum of two parts, referred to as the "real part", a, and the "imaginary part", i b:

$$z = a + i\,b \qquad \text{(A.5.1)}$$

where a and b are real numbers and $i = \sqrt{-1}$. The rules for addition and subtraction of two complex numbers are straightforward:

$$z_1 \pm z_2 = (a_1 + i\,b_1) \pm (a_2 + i\,b_2) = (a_1 \pm a_2) + i\,(b_1 \pm b_2) \qquad \text{(A.5.2)}$$

Multiplication also follows directly, recalling that $i^2 = -1$.

$$z_1\, z_2 = (a_1 + i\,b_1)\,(a_2 + i\,b_2) = (a_1\, a_2) + i\,(b_1\, a_2) + i\,(a_1\, b_2) - (b_1 b_2)$$

$$= (a_1\, a_2 - b_1\, b_2) + i\,(a_1\, b_2 + b_1\, a_2). \qquad \text{(A.5.3)}$$

Division is a little more complicated, and is helped by introduction of the *complex conjugate* of a complex number, z*, which is obtained by replacing i with – i.

$$z \;=\; a_1 + i\, b_1, \quad z^* \;=\; a_1 - i\, b_1 \tag{A.5.4}$$

The product of a complex number and its complex conjugate is always purely real:

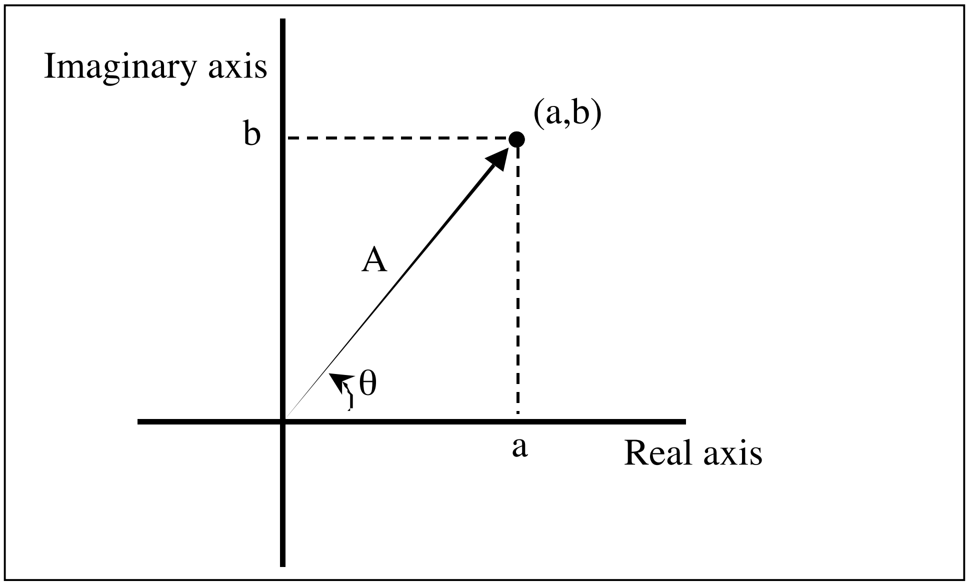
$$z\, z^* = a_1\, a_1 + b_1\, b_1 \tag{A.5.5}$$

To divide by a complex number, it is helpful to multiply numerator and denominator by the complex conjugate of the denominator, thereby restricting complex numbers to the numerator alone:

$$\begin{aligned} \frac{z_1}{z_2} &= \frac{a_1 + ib_1}{a_2 + ib_2} = \frac{a_1 + ib_1}{a_2 + ib_2}\,\frac{a_2 - ib_2}{a_2 - ib_2} \\ &= \frac{a_1a_2 + b_1b_2 + i(b_1a_2 - a_1b_2)}{a_2{}^2 + b_2{}^2} = \frac{a_1a_2 + b_1b_2}{a_2{}^2 + b_2{}^2} + i\,\frac{b_1a_2 - a_1b_2}{a_2{}^2 + b_2{}^2} \end{aligned} \tag{A.5.6}$$

As a complex number is represented by a pair of numbers (a,b) it can also be mapped uniquely onto a point on a Cartesian coordinate system, with horizontal axis reflecting the real part and the vertical axis representing the imaginary part. Similarly, as the following figure illustrates, a complex number can be viewed as a vector from the origin, with a length given by A and a direction specified by the angle θ:

$$\begin{aligned} A &= \sqrt{a^2 + b^2} \\ \tan\theta &= \frac{b}{a} \end{aligned} \tag{A.5.7}$$



The standard trigonometric relations apply, such that

$$\begin{aligned} a &= A\cos\theta \\ b &= A\sin\theta \end{aligned} \qquad (A.5.8)$$

and therefore any complex number can be written as

$$z = A \cos \theta + i\, A \sin \theta. \qquad (A.5.9)$$

Recall the series expansions of e^x, cos x, and sin x given above, and consider the complex number e^{ix}:

$$\begin{aligned} e^{ix} &= 1 + ix + \frac{1}{2!}(ix)^2 + \frac{1}{3!}(ix)^3 \ldots \\ &= 1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 \ldots \quad + \quad i\left(x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 \ldots\right) \\ &= \cos x \quad + \quad i \sin x \end{aligned} \qquad (A.5.10)$$

Thus any complex number can also be written $z = A\,e^{i\theta}$. This particular form is extremely useful in various mathematical operations, for example taking powers and roots:

$$z^n = \left(A\,e^{i\theta}\right)^n = A^n\,e^{in\theta} \qquad \text{(A.5.11)}$$

The product of z and its complex conjugate z* is easily seen to be A^2

$$z\,z^* = \left(A\,e^{i\theta}\right)\left(A\,e^{-i\theta}\right) = A^2\,e^{(i\theta - i\theta)} = A^2 \qquad \text{(A.5.12)}$$

In this way the product of a complex number and its conjugate is analogous to taking the dot product of a vector with itself; the result is a real number (scalar), equal to the length squared.