$e = 1000$ it is $\sim 2 \times 10^{-47}$. Evaluating the energy sum above to $e = 100$ gives $<e> = 9.9971$. Evaluating to $e = 200$, Mathematica returns $<e> = 9.9999999$. It seems pretty clear that the average is converging to 10.

1.19 The first moment of the Gaussian distribution can be calculated using Equation 1.43, namely

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{+\infty} x\rho_G(x)dx \\ &= \int_{-\infty}^{+\infty} x\frac{1}{\sigma\sqrt{2\pi}}e^{-(x-\bar{x})^2/2\sigma^2}dx \\ &= \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{+\infty} xe^{-(x-\bar{x})^2/2\sigma^2}dx\end{aligned}$$

This integral can be calculated by a substitution of variables:

$$\begin{aligned}u &= \frac{(x-\bar{x})}{\sigma\sqrt{2}} \quad (\text{or } x = \sigma u\sqrt{2} + \bar{x}) \\ du &= \frac{dx}{\sigma\sqrt{2}}\end{aligned}$$

This substitution simplifies the exponent, and it transforms the distribution to a new variable on which it is centered and symmetrical. Such transformations often allow integrals to be eliminated based on simple symmetry arguments. And although the transformation makes the leading term more complicated by introducing a second term, these two terms can be integrated separately:

$$\begin{aligned}\int_{-\infty}^{+\infty} x\rho_G(x)dx &= \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{+\infty}\sigma\sqrt{2}\left(u\sigma\sqrt{2}+\bar{x}\right)e^{-u^2}du \\ &= \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{+\infty}\sigma\sqrt{2}\left(u\sigma\sqrt{2}\right)e^{-u^2}du \\ &\quad + \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{+\infty}\sigma\sqrt{2}\bar{x}e^{-u^2}du \\ &= \frac{\sigma\sqrt{2}}{\sqrt{\pi}}\int_{-\infty}^{+\infty}ue^{-u^2}du + \frac{\bar{x}}{\sqrt{\pi}}\int_{-\infty}^{+\infty}e^{-u^2}du\end{aligned}$$

$$\begin{aligned}&= \sigma\sqrt{\frac{2}{\pi}}\int_{-\infty}^{+\infty}ue^{-u^2}du + \frac{\bar{x}}{\sqrt{\pi}}\times\sqrt{\pi} \\ &= 0 + \bar{x} = \bar{x}\end{aligned}$$

With respect to the new, centered variable u, the first integral is the product of an odd symmetrical function and an even symmetrical function. This product has odd symmetry, and its integral over all space is zero. Thus, the leading integral is zero, no matter what the value of sigma.

CHAPTER 2

2.14 As the above function is well-behaved (continuous and differentiable), its differential can be calculated using the exact differential formula given above (Equation 2.22).

$$
\begin{aligned}
dz &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \\
&= \left(\frac{\partial\left\{x^2+y^2\right\}}{\partial x}\right)_y dx + \left(\frac{\partial\left\{x^2+y^2\right\}}{\partial y}\right)_x dy \\
&= 2xdx + 2ydy
\end{aligned}
$$

2.15 We can compare the differential calculated in Question 1.1 to the general differential relationship (Equation 2.38) we used to state the Euler criterion for exactness:

$$df = S(x,y)dx + T(x,y)dy = 2xdx + 2ydy$$

Because x and y are independent variables, and can each be incremented by any amount (including dx=0, dy≠0, and vice versa), the above equation implies that two separate equalities hold:

$$
\begin{aligned}
&S(x,y)dx = 2xdx, \text{ thus } S(x,y) = 2x \\
&\text{and} \\
&T(x,y)dy = 2ydy, \text{ thus } \mathrm{T}(x,y) = 2y
\end{aligned}
$$

Using these expressions in the Euler criterion (Equation 2.41) gives

$$
\begin{aligned}
&\left(\frac{\partial}{\partial y} S(x,y)\right)_x = \left(\frac{\partial}{\partial y} 2x\right)_x = 0, \text{ and} \\
&\left(\frac{\partial}{\partial x} T(x,y)\right)_y = \left(\frac{\partial}{\partial x} 2y\right)_y = 0 = \left(\frac{\partial}{\partial y} S(x,y)\right)_x
\end{aligned}
$$

The differential satisfies the Euler criterion and is thus exact.

2.16 Starting with the differential of the paraboloid $dz = 2xdx+2ydy$, the first step integrates as follows:

$$
\begin{aligned}
\Delta z_1 &= \int_{x=1,y=1}^{x=2,y=1} \left\{2xdx + 2ydy\right\} \\
&= \int_{x=1}^{x=2} 2xdx = \left.\frac{2x^2}{2}\right|_{x=1}^{x=2} = 4 - 1 = 3
\end{aligned}
$$

Similarly, the second step integrates as

$$
\begin{aligned}
\Delta z_2 &= \int_{x=2,y=1}^{x=2,y=2} \left\{2xdx + 2ydy\right\} \\
&= \int_{y=1}^{y=2} 2ydy = \left.\frac{2y^2}{2}\right|_{y=1}^{y=2} = 4 - 1 = 3
\end{aligned}
$$

Because $z = x^2+y^2$ is a well-behaved state function, we can calculate the overall change in z by adding up any set of changes in z that connect up from the initial and final state. The Dz_1 and Dz_2 values from steps 1 and 2, calculated above, connect from the initial state (1,1) to the final state (2,2) when added, thus,

$$\Delta z = \Delta z_1 + \Delta z_2 = 3 + 3 = 6$$

This can be verified directly, since we have an analytic for z in terms of x and y:

$$\Delta z = \Delta z(2,2) + \Delta z(1,1) = (2^2 + 2^2) - (1^2 + 1^2) = 8 - 2 - 6$$

2.17 Expressed as a single variable, the differential of z has a particularly simple form analogous to Equation 2.7:

$$dz = \frac{dz}{dr}dr = \frac{dr^2}{dr}dr = 2rdr$$

Note that for completeness, you might be tempted to include θ, the other variable in a two-dimensional polar coordinate system. The exact differential would, in general, look like this:

$$dz = \left(\frac{\partial z}{\partial r}\right)_\theta dr + \left(\frac{\partial z}{\partial \theta}\right)_r d\theta$$

However, for the paraboloid, the second term is zero because

$$\left(\frac{\partial z}{\partial \theta}\right)_r = \left(\frac{\partial r^2}{\partial \theta}\right)_r = r^2\left(\frac{\partial 1}{\partial \theta}\right)_r = 0$$

2.18 In this problem, the path is along an increasing radial line, with no change in the polar angle q. Thus, the integral can be written quite simply:

$$\Delta z = \int_{r_1}^{r_2} dz = \int_{r_1}^{r_2} 2rdr = \left.\frac{2r^2}{2}\right|_{r_1}^{r_2} = r_2^2 - r_1^2$$

The problem is that we have initial and final position in the x–y plane and we need to represent them as changes in r. This is done with the Pythagorean theorem:

$$r = \sqrt{x^2 + y^2}$$
$$r_1 = \sqrt{1^2 + 1^2} = \sqrt{2}$$
$$r_2 = \sqrt{2^2 + 2^2} = \sqrt{8}$$

Using these values of r_1 and r_2 in the integral for Δz above gives

$$\Delta z = \left.\frac{2r^2}{2}\right|_{\sqrt{2}}^{\sqrt{8}} = \sqrt{8}^2 - \sqrt{2}^2 = 8 - 2 = 6$$

This is the same value as was calculated above using Cartesian coordinates.

2.28 The F matrix for this problem is 31×2 ($n = 31$ data points, $m = 2$ parameters)

$$F = \begin{bmatrix} \frac{\partial f(x_1)}{\partial p_1} & \frac{\partial f(x_1)}{\partial p_2} \\ \frac{\partial f(x_2)}{\partial p_1} & \frac{\partial f(x_2)}{\partial p_2} \\ \vdots & \vdots \\ \frac{\partial f(x_{31})}{\partial p_1} & \frac{\partial f(x_{31})}{\partial p_2} \end{bmatrix}$$

Left-multiplying F by F^T by its transpose gives the 31×2 A matrix:

$$F^T F = \begin{bmatrix} \sum_{i=1}^{n} \left\{ \frac{\partial f(x_i)}{\partial p_1} \right\}^2 & \sum_{i=1}^{n} \left\{ \frac{\partial f(x_i)}{\partial p_1} \right\} \left\{ \frac{\partial f(x_i)}{\partial p_2} \right\} \\ \sum_{i=1}^{n} \left\{ \frac{\partial f(x_i)}{\partial p_1} \right\} \left\{ \frac{\partial f(x_i)}{\partial p_2} \right\} & \sum_{i=1}^{n} \left\{ \frac{\partial f(x_i)}{\partial p_2} \right\}^2 \end{bmatrix}$$

The determinant of this matrix (which is also the determinant of the transpose) is

$$\left|F^T F\right| = \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_1} \right)^2 \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_2} \right)^2 - \left\{ \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_1} \right) \left(\frac{\partial f(x_i)}{\partial p_2} \right) \right\}^2$$

Each of the cofactors (there are only three unique ones because $F^T F$ is symmetric is

$$cof(F^T F)_{1,1} = \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_2} \right)^2$$

$$cof(F^T F)_{2,2} = \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_1} \right)^2$$

$$cof(F^T F)_{1,2} = cof(F^T F)_{2,1} = \sum_{i=1}^{n} \left(\frac{\partial f(x_i)}{\partial p_1} \right) \left(\frac{\partial f(x_i)}{\partial p_2} \right)$$

Together, these three cofactor equations can be combined with the determinant equation to calculate the four elements of the covariance matrix V. For the variance term for parameter p_1,

$$v_{1,1} \propto \frac{cof_{1,1}(F^T F)}{\left|F^T F\right|} = \frac{\sum_{i=1}^{n} (\partial f(x_i)/\partial p_2)^2}{\sum_{i=1}^{n} (\partial f(x_i)/\partial p_1)^2 \sum_{i=1}^{n} (\partial f(x_i)/\partial p_2)^2 - \left\{ \sum_{i=1}^{n} (\partial f(x_i)/\partial p_1)(\partial f(x_i)/\partial p_2) \right\}^2}$$

A similar formula (with differentiation by p_1 in the numerator instead of p_2) is obtained for $v_{2,2}$. The two covariance elements are given by

$$v_{1,2} \propto \frac{cof_{1,2}(F^T F)}{\left|F^T F\right|} = \frac{\sum_{i=1}^{n} (\partial f(x_i)/\partial p_1)(\partial f(x_i)/\partial p_2)}{\sum_{i=1}^{n} (\partial f(x_i)/\partial p_1)^2 \sum_{i=1}^{n} (\partial f(x_i)/\partial p_2)^2 - \left\{ \sum_{i=1}^{n} (\partial f(x_i)/\partial p_1)(\partial f(x_i)/\partial p_2) \right\}^2}$$

2.32 The mode of the distribution (that is, the peak) can be found by differentiating with respect to χ^2 and setting the result to zero:

$$\frac{dP_{\chi^2}}{d\chi^2} = 2^{\nu/2}\Gamma(\nu/2)\left\{\frac{d}{d\chi^2}(\chi^2)^{(\nu-2)/2}e^{-\chi^2/2}\right\}$$
$$= 2^{\nu/2}\Gamma(\nu/2)\left\{\frac{(\nu-2)(\chi^2)^{(\nu-4)/2}e^{-\chi^2/2}}{2} - \frac{(\chi^2)^{(\nu-2)/2}e^{-\chi^2/2}}{2}\right\}$$
$$= \frac{2^{\nu/2}\Gamma(\nu/2)}{2}e^{-\chi^2/2}\left\{(\nu-2)(\chi^2)^{(\nu-4)/2} - (\chi^2)^{(\nu-2)/2}\right\} = 0$$

The zero in the equation above has to come from the term in the curly braces, since all of the multiplying terms outside the braces are everywhere positive. This means

$$(\nu-2)(\chi^2)^{(\nu-4)/2} - (\chi^2)^{(\nu-2)/2} = 0$$

Rearranging gives

$$\nu - 2 = (\chi^2)^{\frac{(\nu-2)}{2}-\frac{(\nu-4)}{2}}$$
$$= (\chi^2)^{\frac{\nu}{2}-1-\frac{\nu}{2}+2}$$
$$\nu - 2 = (\chi^2)^{\frac{(\nu-2)}{2}-\frac{(\nu-4)}{2}}$$
$$= (\chi^2)^{\frac{\nu}{2}-1-\frac{\nu}{2}+2}$$

Cancelling the exponents gives the value of χ^2 at the critical point,

$$\chi^2 = \nu - 2$$

Based on the shape of the probability distribution, it is clearly a maximum. This can be confirmed by a second derivative test, but the exponential from the third line above needs to be included in the differentiation.

2.33 The normalization condition means that

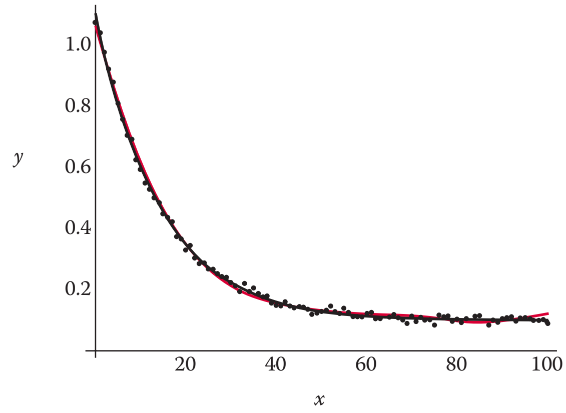
$$\int_0^\infty P_{\chi^2} d\chi^2 = 1$$

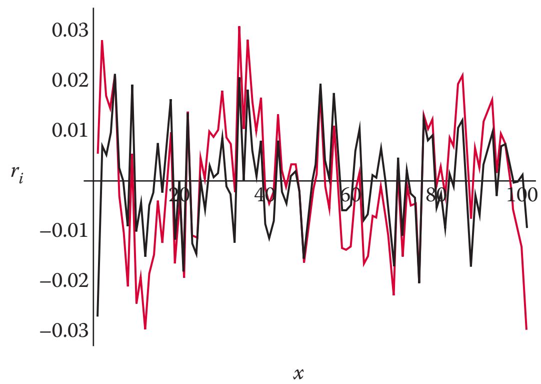
The integral on the left-hand-side of the distribution can be broken into two parts, or "complements":

$$\int_0^{\chi^2_{obs}} P_{\chi^2} d\chi^2 + \int_{\chi^2_{obs}}^\infty P_{\chi^2} d\chi^2 = 1$$

This is a result of the fundamental theorem of calculus, but it may be easier to see by thinking about the integrals as area under the curve. Rearranging the equation above gives the desired equality.

2.34 To carry out this test, we need to start with fits using both models. The fit for the exponential decay model (we will call it model 2) is shown in Figure 2.17. For the cubic model, the fit is shown in below.

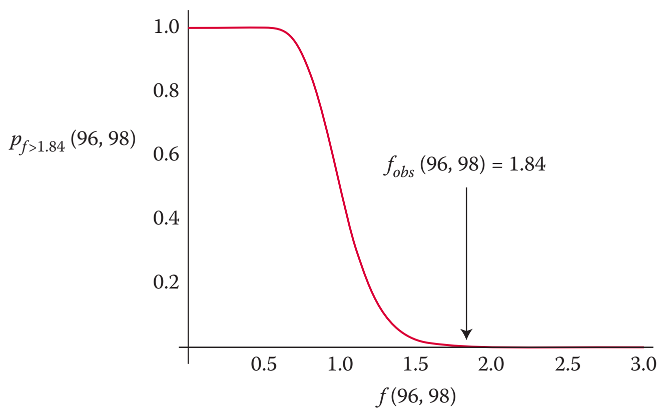




As can be seen from the residuals, the quartic model does not fit as well as the exponential (this may not be a surprise, since we used an exponential model to generate the data). Using the SSR values for the two fits, we can calculate the f_{obs} ratio as

$$f_{obs}(\nu_{quartic},\ \nu_{\exp}) = \frac{SSR_{quartic}/\nu_{quartic}}{SSR_{\exp}/\nu_{\exp}} = \frac{0.0165/(101-5)}{0.00902/(101-3)} = 1.848$$

The f-ratio distribution, given the degrees of freedom ν_1=96, ν_2=98, is shown below:



As indicated by the arrow, there is very little of getting an f-ratio value of 1.84 or higher from statistically equivalent models with 96 and 98 degrees of freedom. The exact probability can be calculated by solving the equation

$$p_{f>1.848} = \int_{1.848}^{\infty} p_f df = 0.00137$$

(easiest done with the `CDF[FRatioDistribution…]` command in Mathematica). In other words, it is pretty unlikely (about one in a thousand) that you would get this f-value from two statistically equivalent models. Compared to the exponential model, SSR is unexpectedly high for the quartic model. We can certainly reject the model at the 95% confidence level.

CHAPTER 3

3.4 Starting with equation

$$dV = -\kappa_T V dp + \alpha V dT + \bar{V} dn$$

Substituting the ideal gas results $\kappa_T = p^{-1}$, $\alpha = T^{-1}$, and the single-component molar volume definition $\bar{V} = V/n$ gives

$$dV = \frac{Vdp}{p} + \frac{VdT}{T} + \frac{Vdn}{n}$$

Dividing by V separates variables:

$$\frac{dV}{V} = \frac{dp}{p} + \frac{dT}{T} + \frac{dn}{n}$$

We need to integrate this expression from starting values V_i, T_i, p_i, and n_i, to general values p, V, T, and n. Using the ideas developed in Chapter 2, we can integrate in three steps, first changing V at constant T and n, next changing T at constant V and n, and finally changing n at constant V and T. Each of these will lead to a change in p, which can be added to get the total change in pressure.

3.5 Assuming the ideal gas law,

$$T_i = \frac{pV_i}{nR} = \frac{2.27\times10^5\ \text{Pa}\times0.0005\ \text{m}^3}{0.05\ \text{mol}\times8.315\ \text{J}\cdot\text{mol}^{-1}\text{K}^{-1}} = 273\ \text{K}$$

$$T_f = \frac{pV_f}{nR} = \frac{2.27\times10^5\ \text{Pa}\times0.002\ \text{m}^3}{0.05\ \text{mol}\times8.315\ \text{J}\cdot\text{mol}^{-1}\text{K}^{-1}} = 1092\ \text{K}$$

As described above, to maintain the pressure throughout the expansion, the temperature increases.

3.9 To calculate the work done on the polymer (you can think of it as the system), integrate Equation 3.17. A nice way to do this is with a single limit of $x = 0$ end-to-end separation, giving work as an analytical function of of x:

$$\begin{aligned} w &= -\int_0 F dx \\ &= \frac{k_B T}{L_p}\int_0 \left[\frac{1}{4(1-x/L_c)^2} - \frac{1}{4} + \frac{x}{L_c}\right]dx \\ &= \frac{k_B T}{L_p}\left[\frac{L_c}{4(1-x/L_c)} - \frac{x}{4} + \frac{x^2}{2L_c}\right]\Bigg|_0 \\ &= \frac{k_B T}{4L_p}\left\{\frac{L_c^2}{L_c - x} - x + \frac{2x^2}{L_c}\right\}\Bigg|_0 \end{aligned}$$