Homework 1

Statistical Mechanics, by D. A. McQuarrie, is an excellent textbook with a more chemical emphasis. In our notation $Q \to Z$, $A \to F$, $\Omega \to W$, etc. for both McQuarrie and our textbook. These 5 problems are taken from McQuarrie.

1–58. One often encounters the gamma function in statistical thermodynamics. It was introduced by Euler as a function of x, which is continuous for positive values of x and which reduces to $n!$ when $x = n$, an integer. The gamma function $\Gamma(x)$ is defined by

$$\Gamma(x) = \int_0^\infty e^{-t} t^{x-1}\, dt$$

First show by integrating by parts that

$$\Gamma(x+1) = x\Gamma(x)$$

Using this, show that $\Gamma(n+1) = n!$ for n an integer. Show that

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi}$$

Evaluate $\Gamma(\frac{3}{2})$ using the recurrence formula $\Gamma(x+1) = x\Gamma(x)$. Lastly show that

$$\Gamma\left(n + \frac{1}{2}\right) = \frac{1 \cdot 3 \cdots (2n-1)}{2^n} \Gamma\left(\frac{1}{2}\right)$$

$$= \frac{(2n)!}{2^{2n} n!} \sqrt{\pi}$$

For a discussion of the gamma function, see G. Arfken, *Mathematical Methods for Physicists*, 2nd ed. (New York: Academic, 1970).

1–59. We can derive Stirling's approximation from an asymptotic approximation to the gamma function $\Gamma(x)$. From the previous problem

$$\Gamma(N+1) = N! = \int_0^\infty e^{-x} x^N\, dx$$

$$= \int_0^\infty e^{Ng(x)}\, dx$$

where $g(x) = \ln x - x/N$. If $g(x)$ possesses a maximum at some point, say x_0, then for large N, $\exp(Ng(x))$ will be extremely sharply peaked at x_0. Under this condition, the integral for $N!$ will be dominated by the contribution of the integrand from the point x_0. First show that $g(x)$ does, in fact, possess at maximum at the point $x_0 = N$. Expand $g(x)$ about this point, keeping terms only up to and including $(x - N)^2$ to get

$$g(x) \approx g(N) - \frac{(x-N)^2}{2N^2} + \cdots$$

Why is there no linear term in $(x - N)$? Substitute this expression for $g(x)$ into the integral for $N!$ and derive the asymptotic formula

$$\ln N! \approx N \ln N - N + \ln(2\pi N)^{1/2}$$

1-63. Another function that occurs frequently in statistical mechanics is the Riemann zeta function, defined by

$$\zeta(s) = \sum_{k=1}^{\infty} k^{-s}$$

First show that $\zeta(1) = \infty$, but that $\zeta(s)$ is finite for $s > 1$. Show that another definition of $\zeta(s)$ is

$$\zeta(s) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}\, dx}{(e^x - 1)}$$

that is, show that this is identical to the first definition. In addition, show that

$$\eta(s) = \sum_{k=1}^{\infty} (-1)^{k-1} k^{-s} = (1 - 2^{1-s})\zeta(s)$$

$$\lambda(s) = \sum_{k=0}^{\infty} (2k+1)^{-s} = (1 - 2^{-s})\zeta(s)$$

The evaluation of $\zeta(s)$ for integral s can be done using Fourier series, and some results are $\zeta(2) = \pi^2/6$ and $\zeta(4) = \pi^4/90$.
For a discussion of the Riemann zeta function, see G. Arfken, *Mathematical Methods for Physicists*, 2nd ed. (New York: Academic, 1970).

1-24. We need to know the volume of an N-dimensional sphere in order to derive Eq. (1-36). This can be determined by the following device. Consider the integral

$$I = \int_{-\infty}^{\infty} \cdots \int e^{-(x_1^2 + x_2^2 + \cdots + x_N^2)}\, dx_1\, dx_2 \cdots dx_N$$

First show that $I = \pi^{N/2}$. Now one can formally transform the volume element $dx_1\, dx_2 \cdots dx_N$ to N-dimensional spherical (hyperspherical) coordinates to get

$$\int_{\text{angles}} dx_1\, dx_2 \cdots dx_N \rightarrow r^{N-1} S_N\, dr$$

where S_N is the factor that arises upon integration over the angles. Show that $S_2 = 2\pi$ and $S_3 = 4\pi$. S_N can be determined for any N by writing I in hyperspherical coordinates:

$$I = \int_0^\infty e^{-r^2} r^{N-1} S_N\, dr$$

Show that $I = S_N \Gamma(N/2)/2$, where $\Gamma(x)$ is the gamma function (see Problem 1-58). Equate these two values for I to get

$$S_N = \frac{2\pi^{N/2}}{\Gamma(N/2)}$$

Show that this reduces correctly for $N = 2$ and 3. Lastly now, convince yourself that the volume of an N-dimensional sphere of radius a is given by

$$V_N = \int_0^a S_N r^{N-1}\, dr = \frac{\pi^{N/2}}{\Gamma\left(\frac{N}{2} + 1\right)} a^N$$

and show that this reduces correctly for $N = 2$ and 3.

1–61. An integral that appears often in statistical mechanics and particularly in the kinetic theory of gases is

$$I_n = \int_0^\infty x^n e^{-ax^2}\, dx$$

This integral can be readily generated from two basic integrals. For even values of n, we first consider

$$I_0 = \int_0^\infty e^{-ax^2}\, dx$$

The standard trick to evaluate this integral is to square it, and then transform the variables into polar coordinates.

$$I_0{}^2 = \int_0^\infty \int_0^\infty e^{-ax^2} e^{-ay^2}\, dx\, dy$$

$$= \int_0^\infty \int_0^{\pi/2} e^{-ar^2} r dr d\theta$$

$$= \frac{\pi}{4a}$$

$$I_0 = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$$

Using this result, show that for even n

$$I_n = \frac{1 \cdot 3 \cdot 5 \cdots (n-1)}{2(2a)^{n/2}}\left(\frac{\pi}{a}\right)^{1/2} \qquad n \text{ even}$$

For odd values of n, the basic integral I_1 is easy. Using I_1, show that

$$I_n = \frac{\Gamma\left(\dfrac{n+1}{2}\right)}{2a^{(n+1)/2}} \qquad n \text{ odd}$$