

Mathematical Appendix

A.1 PROOF OF THE CENTRAL LIMIT THEOREM

We first need an important formula involving the Fourier transform of the probability density associated with the sum of any number of independent random variables. Let $S = X + Y + Z$, where X , Y , and Z are independent. From Eq. (1.51), we see that the probability distribution associated with S is

$$P_S(s) = \int \delta(s - x - y - z) P_X(x) P_Y(y) P_Z(z) dx dy dz \quad (A.1)$$

The Fourier transform of $P_S(s)$ is given by

$$\begin{aligned} \tilde{P}_S(k) &= \int e^{iks} P_S(s) ds \\ &= \int e^{iks} \delta(s - x - y - z) P_X(x) P_Y(y) P_Z(z) dx dy dz ds \\ &= \int e^{ik(x+y+z)} P_X(x) P_Y(y) P_Z(z) dx dy dz \\ &= \tilde{P}_X(k) \tilde{P}_Y(k) \tilde{P}_Z(k) \end{aligned} \quad (A.2)$$

The Fourier transform of the probability density is called the *characteristic function* associated with a random variable. Thus, for independent random variables, the characteristic function for their sum is the product of their characteristic functions. In the proof of the central limit theorem, the following easy generalization of this theorem will be used. The proof is left as an exercise for the reader.

Given N independent random variables x_1, x_2, \dots, x_N , with probability densities, P_1, P_2, \dots, P_N , if we define a random variable $T = \lambda(x_1 + \dots + x_N)$ where $\lambda > 0$, then

$$\tilde{P}_T(k) = \tilde{P}_1(\lambda k) \dots \tilde{P}_N(\lambda k) \quad (A.3)$$

We are now ready to prove the theorem. We consider an infinite sequence of independent random variables x_1, x_2, \dots with probability densities $P_1(x_1), P_2(x_2), \dots$. It is no serious restriction to assume that the average value of each of the separate variables vanishes.

$$\int P_n(x_n) x_n dx_n = 0 \quad (A.4)$$

For some positive integer N we define the random variable $T = (x_1 + \dots + x_N)/\sqrt{N}$. According to Eq. (A.3), the characteristic function associated with T is given by

$$\tilde{P}_T(k) = \tilde{P}_1(k/\sqrt{N}) \dots \tilde{P}_N(k/\sqrt{N}) \quad (A.5)$$

We must now derive a certain inequality involving $\tilde{P}_n(k)$. It is a theorem of calculus that there exists a positive constant C such that

$$|e^{i\theta} - (1 + i\theta - \frac{1}{2}\theta^2)| \equiv |R(\theta)| < C|\theta|^3 \quad (\text{A.6})$$

for any real number θ . Thus

$$e^{ikx} = 1 + ikx - \frac{1}{2}k^2x^2 + R(kx) \quad (\text{A.7})$$

where $|R(kx)| < C|k^3||x^3|$. Using this and Eq. (A.4) we see that

$$\begin{aligned} \tilde{P}_n(k) &= \int e^{ikx_n} P_n(x_n) dx_n \\ &= \int [1 + ikx_n - \frac{1}{2}k^2x_n^2 + R(kx_n)] P_n(x_n) dx_n \\ &= 1 - \frac{1}{2}k^2(\Delta x_n)^2 + r_n(k) \end{aligned} \quad (\text{A.8})$$

where $|r_n(k)| < C|k^3|\langle |x_n^3| \rangle$ and Δx_n is the uncertainty in the random variable x_n . From Eqs. (A.5) and (A.8) we find that

$$\begin{aligned} \log \tilde{P}_T(k) &= \sum_{n=1}^N \log \tilde{P}_n(k/\sqrt{N}) \\ &= \sum_{n=1}^N \log \left(1 - \frac{1}{2N} k^2 (\Delta x_n)^2 + r_n(k/\sqrt{N}) \right) \end{aligned} \quad (\text{A.9})$$

As $N \rightarrow \infty$ we can use the expansion $\log(1 + \epsilon) \approx \epsilon$.

$$\log \tilde{P}_T(k) \approx -\frac{k^2}{2} \left(\frac{1}{N} \sum (\Delta x_n)^2 \right) + \sum r_n(k/\sqrt{N}) \quad (\text{A.10})$$

We now make two assumptions regarding the sequence of random variables. They are that

$$\lim_{N \rightarrow \infty} \left(\frac{1}{N} \sum (\Delta x_n)^2 \right) \equiv a^2 < \infty \quad (\text{A.11})$$

and

$$\lim_{N \rightarrow \infty} \left(\frac{1}{N^{3/2}} \sum \langle |x_n^3| \rangle \right) = 0 \quad (\text{A.12})$$

Equation (A.12) guarantees that the remainder term can be ignored in the limit, giving, as $N \rightarrow \infty$

$$\log \tilde{P}_T(k) \rightarrow -\frac{1}{2}a^2k^2 \quad (\text{A.13})$$

or

$$\begin{aligned} P_T(t) &= \frac{1}{2\pi} \int \tilde{P}_T(k) e^{-ikt} dk \\ &\rightarrow \frac{1}{2\pi} \int e^{-\frac{1}{2}a^2k^2 - ikt} dk \\ &= \frac{e^{-t^2/2a^2}}{\sqrt{2\pi} a} \end{aligned} \quad (\text{A.14})$$

The average of the first N random variables [that is $X = (x_1 + \dots + x_N)/N$] is related to T by $X = T/\sqrt{N}$. The probability density associated with X is related to that associated with T by

$$P_X(x) dx = P_T(t) dt \quad (\text{A.15})$$

where $dx = dt/\sqrt{N}$. Thus, if N is large enough to allow the use of the asymptotic formula [Eq. (A.14)], then

$$\begin{aligned} P_X(x) &= \sqrt{N} P_T(\sqrt{N}x) \\ &= \sqrt{N/2\pi a^2} e^{-Nx^2/2a^2} \end{aligned} \tag{A.16}$$

which is the result we set out to prove.

A.2 STIRLING'S APPROXIMATION

$$\log N! = \log(1 \cdot 2 \cdots N) = \sum_{n=1}^N \log n \tag{A.17}$$

In Fig. A.1, two curves are superimposed. The discontinuous curve is a graph of $\log n$, with n ranging from 1 to 40. The smooth curve is the function $\log(x)$. $\log N!$ is given by the area under the discontinuous curve. Stirling's approximation to $\log N!$ is defined as the area under the smooth approximating curve.

$$\log N! \approx \int_1^N \log(x) dx = N \log N - N + 1 \tag{A.18}$$

Clearly, the ratio of the area under the smooth curve to the area under the discontinuous curve approaches one as $N \rightarrow \infty$. For large N , the 1 can be dropped. For more mathematically minded readers, the next section supplies a detailed evaluation of the error in Stirling's approximation and a generalization of the analysis to noninteger N .

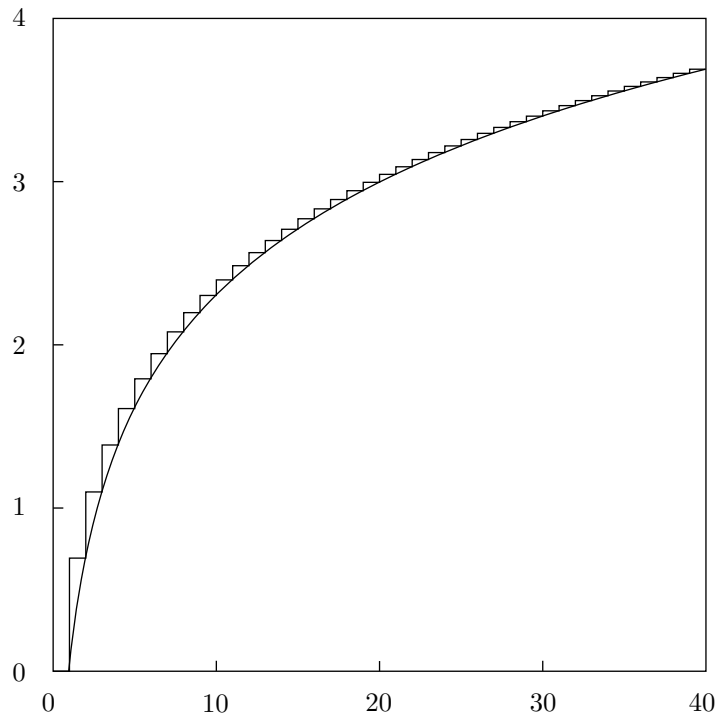


FIGURE A.2

A.3 THE GAMMA AND FACTORIAL FUNCTIONS

For any number N greater than -1 , the factorial function $N!$ and the gamma function $\Gamma(N + 1)$ are defined by

$$N! = \Gamma(N + 1) = \int_0^\infty e^{-x} x^N dx \tag{A.19}$$

By a partial integration, it can be seen that $N! = N(N - 1)!$ or, equivalently, $\Gamma(N + 1) = N\Gamma(N)$. For $N = 0$, the integral is easily done, giving $0! = 1$. Therefore, for any positive integer

$$N! = \Gamma(N + 1) = N(N - 1) \cdots 2 \times 1 \tag{A.20}$$

Another important case is $\Gamma(\frac{1}{2}) = \sqrt{\pi}$. From Eq. (A.19), we see that

$$N! = \int_0^\infty e^{g(x)} dx \tag{A.21}$$

where $g(x) = N \log x - x$. $g(x)$ is a function with a single maximum at $x = N$. The function approaches $-\infty$ at both limits of integration. The expansion to second order of $g(x)$ about its maximum yields

$$g(N + \xi) \approx N \log N - N - \xi^2/2N \tag{A.22}$$

which gives the following approximation for $N!$, valid for large N .

$$\begin{aligned} N! &\approx e^{N \log N - N} \int_{-N}^\infty e^{-\xi^2/2N} d\xi \\ &\approx e^{N \log N - N} (2\pi N)^{1/2} \end{aligned} \tag{A.23}$$

From this we can easily obtain the following four-term approximation to $\log N!$.

$$\log N! \approx N \log N - N + \frac{1}{2} \log N + \frac{1}{2} \log 2\pi \tag{A.24}$$

The use of the first two terms in this expansion is Stirling's approximation.

A.4 THE ERROR FUNCTION

The complementary error function is defined by the integral

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \tag{A.25}$$

For large values of x , the following expansion is useful.

$$\begin{aligned} \text{erfc}(x) &= \frac{e^{-x^2}}{\sqrt{\pi} x} \sum_{m=0}^\infty \frac{(-1)^m (2m)!}{m! (2x)^{2m}} \\ &= \frac{e^{-x^2}}{\sqrt{\pi} x} \left(1 - \frac{1}{2x^2} + \frac{3}{4x^4} - \cdots \right) \end{aligned} \tag{A.26}$$

A.5 LAGRANGE PARAMETERS

The following is Lagrange's method of calculating the stationary points of a function $f(\mathbf{x})$ when the N -dimensional variable \mathbf{x} is subjected to K constraints of the form $u_n(\mathbf{x}) = C_n$ ($n = 1, \dots, K$), where the u_n are K known functions, the C_n are K given constants, and $K < N$. What we seek is a point \mathbf{x}^o with the property that it satisfies the constraints and that for any infinitesimal $d\mathbf{x}$ satisfying $u_n(\mathbf{x}^o + d\mathbf{x}) = u_n(\mathbf{x}^o)$ ($n = 1, \dots, K$) it is also true that $f(\mathbf{x}^o + d\mathbf{x}) = f(\mathbf{x}^o)$. That is, the function f is stationary within the set of points defined by the constraint equations.

We define a function $g(\mathbf{x}, \lambda)$ of \mathbf{x} and the K Lagrange parameters $\lambda_1, \dots, \lambda_K$ by

$$g(\mathbf{x}, \lambda) = f(\mathbf{x}) + \sum_{n=1}^K \lambda_n u_n(\mathbf{x}) \quad (\text{A.27})$$

We next find the solution (or solutions) of the following system of $N + K$ equations in $N + K$ unknowns. We call the solution \mathbf{x}^o and λ^o .

$$\frac{\partial g(\mathbf{x}^o, \lambda^o)}{\partial x_k^o} = 0, \quad k = 1, \dots, N \quad (\text{A.28})$$

and

$$u_n(\mathbf{x}^o) = C_n, \quad n = 1, \dots, K \quad (\text{A.29})$$

By Eq. (A.28), we know that $g(\mathbf{x}^o + d\mathbf{x}, \lambda) = g(\mathbf{x}^o, \lambda)$ for any $d\mathbf{x}$. But, by the definition of $g(\mathbf{x}, \lambda)$, if we choose a $d\mathbf{x}$ that does not change the value of any of the constraint functions, then $f(\mathbf{x}^o + d\mathbf{x}) = f(\mathbf{x}^o)$. Thus \mathbf{x}^o is a solution of the constrained variational problem.

A.6 THE N-DIMENSIONAL SPHERE

The volume of an N -dimensional sphere of radius R is given by the integral

$$V_N(R) = \int \theta(R^2 - x^2) d^N x \quad (\text{A.30})$$

where $x^2 = \sum x_n^2$ and θ is the unit step function. Using the transformation of variables $y_n = x_n/R$ in Eq. (A.30) and making use of the fact that $\theta(\lambda x) = \theta(x)$ for any positive value of λ , one obtains

$$\int \theta(R^2 - x^2) d^N x = R^N \int \theta(1 - y^2) d^N y = R^N V_N(1) \quad (\text{A.31})$$

Differentiating Eq. (A.31) and using the fact that $d\theta(R^2 - x^2)/dR = 2R\delta(R^2 - x^2)$, where $\delta(x)$ is the Dirac delta function, gives

$$2R \int \delta(R^2 - x^2) d^N x = N V_N(1) R^{N-1} \quad (\text{A.32})$$

We now multiply both sides by $e^{-R^2} dR$ and integrate from 0 to ∞ to get

$$\begin{aligned} \int d^N x \int_0^\infty e^{-R^2} \delta(R^2 - x^2) dR^2 &= \int e^{-\sum x_n^2} d^N x \\ &= N V_N(1) \int_0^\infty e^{-R^2} R^{N-1} dR \end{aligned} \quad (\text{A.33})$$

The integral on the second line is easily calculated in terms of the factorial function. The integral on the right-hand side of the first line factors into a product of N simple Gaussian integrals, each having the value $\pi^{1/2}$. Thus

$$\pi^{N/2} = V_N(1)(N/2)! \quad (\text{A.34})$$

where, for odd N , the factorial function $(N/2)!$ is defined in terms of the gamma function. This formula for $V_N(1)$ implies that

$$V_N(R) = \frac{\pi^{N/2}}{(N/2)!} R^N \quad (\text{A.35})$$

The surface area of an N -dimensional sphere is the derivative with respect to R of its volume. Thus

$$S_N(R) = \frac{dV_N(R)}{dR} = \frac{N}{R} V_N(R) \quad (\text{A.36})$$

A.7 NORMAL MODES AND SMALL VIBRATIONS

We consider a classical system of N identical particles, each of mass m . The complete configuration of the system can be defined by $K = 3N$ scalar coordinates, $(x_1, x_2, \dots, x_K) \equiv (x)$. The potential energy of the system is some function of the coordinates, $V(x_1, x_2, \dots, x_K)$. Let $(x^o) = (x_1^o, x_2^o, \dots, x_K^o)$ be the configuration of minimum potential energy (the mechanical equilibrium configuration). Then

$$\frac{\partial V(x^o)}{\partial x_i} = 0, \quad i = 1, \dots, K \tag{A.37}$$

We introduce K new coordinates, $\xi_i = x_i - x_i^o$ ($i = 1, \dots, K$) that describe the displacement of the system particles from their equilibrium positions. If we restrict our analysis to small vibrations about the equilibrium configuration, then we can expand $V(x)$ in a Taylor expansion about the point (x^o) . Noting that the first derivatives all vanish at (x^o) , we get

$$V(x^o + \xi) = V(x^o) + \frac{1}{2} \sum_{i,j} V_{ij} \xi_i \xi_j \tag{A.38}$$

where $V_{ij} = \partial^2 V(x^o) / \partial x_i \partial x_j$. We are free to add any constant to the potential energy function without changing the equations of motion. We can thus assume that $V(x^o) = 0$. The Lagrangian function is defined as $T - V$. Therefore, for small vibrations,

$$L = \frac{1}{2} m \sum_{i=1}^K \dot{\xi}_i^2 - \frac{1}{2} \sum_{i,j} V_{ij} \xi_i \xi_j \tag{A.39}$$

The crucial part of this analysis is to realize that V_{ij} is a symmetric $K \times K$ matrix. It therefore has K orthogonal and normalized eigenvectors, with corresponding eigenvalues. That is, there are K nonzero solutions of the set of linear equations

$$\sum_{j=1}^K V_{ij} u_j^k = \lambda_k u_i^k, \quad i = 1, \dots, K \tag{A.40}$$

and those eigenvectors satisfy the orthogonality conditions

$$\sum_{i=1}^K u_i^k u_i^l = \delta_{kl} = \begin{cases} 0, & k \neq l \\ 1, & k = l \end{cases} \tag{A.41}$$

We now make another coordinate transformation, to K *normal-mode coordinates* Q_1, Q_2, \dots, Q_K , defined by

$$\xi_i = \sum_{k=1}^K u_i^k Q_k \tag{A.42}$$

and note that $\dot{\xi}_i = \sum u_i^k \dot{Q}_k$. Writing the Lagrangian in normal-mode coordinates, we see that

$$\begin{aligned} L &= \frac{1}{2} m \sum_{k,l,i} u_i^k u_i^l \dot{Q}_k \dot{Q}_l - \frac{1}{2} \sum_{k,l,i,j} V_{ij} u_j^k u_i^l Q_k Q_l \\ &= \frac{1}{2} m \sum_{k,l} \delta_{kl} \dot{Q}_k \dot{Q}_l - \frac{1}{2} \sum_{k,l,i} \lambda_k u_i^k u_i^l Q_k Q_l \\ &= \frac{1}{2} \sum_k \dot{Q}_k^2 - \frac{1}{2} \sum_k \lambda_k Q_k^2 \end{aligned} \tag{A.43}$$

The momentum canonical to the normal-mode coordinate Q_k is

$$P_k = \frac{\partial L}{\partial \dot{Q}_k} = m \dot{Q}_k \tag{A.44}$$

Writing the Hamiltonian function in terms of the normal-mode coordinates and momenta gives

$$H = T + V = \sum_{k=1}^K \left(\frac{P_k^2}{2m} + \frac{1}{2} \lambda_k Q_k^2 \right) \quad (\text{A.45})$$

This is exactly the Hamiltonian for a system composed of K noninteracting harmonic oscillators with angular frequencies $\omega_1, \omega_2, \dots, \omega_K$ given by

$$\omega_k = \sqrt{\frac{\lambda_k}{m}} \quad (\text{A.46})$$

The assumption that the configuration (x^o) gives a minimum for the potential energy $V(x)$ guarantees that all the eigenvalues λ_k , are nonnegative and, therefore, that all the angular frequencies are real.

A.8 THE TRANSFORMATION OF MULTIPLE INTEGRALS

Consider the two-dimensional integral of a function $f(x_1, x_2)$ over some region R in the x_1 - x_2 plane.

$$I = \int_R f(x_1, x_2) dx_1 dx_2 \quad (\text{A.47})$$

In this section we will describe how to express the integral I in terms of two new variables, y_1 and y_2 , that are related to the original variables by some known transformation equations, $y_1(x_1, x_2)$ and $y_2(x_1, x_2)$.

1. First we must express the function $f(x_1, x_2)$ in terms of the new variables. We do that by defining a new function $F(y_1, y_2)$ by

$$F(y_1, y_2) = f(x_1(y_1, y_2), x_2(y_1, y_2)) \quad (\text{A.48})$$

2. Next we must transform the region of integration. The region of integration in the y_1 - y_2 plane can be defined by

$$(y_1, y_2) \in Q \quad \text{iff} \quad (x_1(y_1, y_2), x_2(y_1, y_2)) \in R \quad (\text{A.49})$$

3. Finally the volume element $dx_1 dx_2$ must be transformed into the new volume element $dy_1 dy_2$. That is done by the replacement

$$dx_1 dx_2 \rightarrow |J(y_1, y_2)| dy_1 dy_2 \quad (\text{A.50})$$

where the *Jacobian determinant* J is the determinant of the partial derivatives.

$$J(y_1, y_2) = \begin{vmatrix} \partial x_1 / \partial y_1 & \partial x_2 / \partial y_1 \\ \partial x_1 / \partial y_2 & \partial x_2 / \partial y_2 \end{vmatrix} \quad (\text{A.51})$$

The final result is

$$I = \int_Q F(y_1, y_2) |J(y_1, y_2)| dy_1 dy_2 \quad (\text{A.52})$$

The generalization to three or more variables is very simple. Steps (1) and (2) are unchanged, except for the fact that they involve three or more variables. The only change in step (3) is that, for a transformation involving N variables $(x_1, x_2, \dots, x_N) \rightarrow (y_1, y_2, \dots, y_N)$, the Jacobian determinant becomes an $N \times N$ determinant.

$$J = \begin{vmatrix} \partial x_1 / \partial y_1 & \cdots & \partial x_N / \partial y_1 \\ \cdots & \cdots & \cdots \\ \partial x_1 / \partial y_N & \cdots & \partial x_N / \partial y_N \end{vmatrix} \quad (\text{A.53})$$

A simple but important example is the transformation of an integral involving the coordinates of two equal-mass particles

$$I = \int_o^L dx_1 \int_o^L dx_2 f(x_1, x_2) \quad (\text{A.54})$$

to center-of-mass and relative coordinates, defined by

$$y_1 = (x_1 + x_2)/2 \quad \text{and} \quad y_2 = x_1 - x_2 \quad (\text{A.55})$$

The inverse transformation is

$$x_1 = y_1 + y_2/2 \quad \text{and} \quad x_2 = y_1 - y_2/2 \tag{A.56}$$

1. The new function is

$$F(y_1, y_2) = f(y_1 + y_2/2, y_1 - y_2/2) \tag{A.57}$$

2. The vertices of the rectangle in the x_1 - x_2 plane are $(x_1, x_2) = (0, 0)$, $(L, 0)$, $(0, L)$, and (L, L) . These are transformed into $(y_1, y_2) = (0, 0)$, $(L/2, L)$, $(L/2, -L)$, and $(L, 0)$. (See Fig. A.2.)

3. The Jacobian determinant is

$$\begin{vmatrix} \partial x_1 / \partial y_1 & \partial x_2 / \partial y_1 \\ \partial x_1 / \partial y_2 & \partial x_2 / \partial y_2 \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ 1/2 & -1/2 \end{vmatrix} = -1 \tag{A.58}$$

and therefore

$$dx_1 dx_2 \rightarrow |-1| dy_1 dy_2 = dy_1 dy_2 \tag{A.59}$$

which completes the transformation

$$\int_0^L dx_1 \int_0^L dx_2 f(x_1, x_2) = \int \int_{R'} F(y_1, y_2) dy_1 dy_2 \tag{A.60}$$

A.9 INTEGRALS WITH LARGE EXPONENTS

We want to develop an approximation to the integral

$$I = \int_a^b e^{\lambda f(x)} dx \tag{A.61}$$

that is valid for large values of λ . We assume that the function $f(x)$ has a single maximum at $x = X$ and that $a < X < b$. For very large λ , the ratio $e^{\lambda f(x)} / e^{\lambda f(X)}$ is extremely small if $x \neq X$. Thus, the integral is dominated by the values of the integrand close to $x = X$. We may therefore extend the range of integration from (a, b) to $(-\infty, \infty)$ and expand $f(x)$ about its maximum, retaining only the first two nonvanishing terms. [The linear term vanishes because $f(x)$ is stationary at X .]

$$f(x) \approx f(X) - \frac{1}{2} a \xi^2 \tag{A.62}$$

where $\xi = x - X$ and $a = -\partial^2 f(X) / \partial X^2$. a must be positive, since $f(x)$ has a *maximum* at $x = X$. Therefore, for large λ ,

$$\begin{aligned} I &\approx e^{\lambda f(X)} \int_{-\infty}^{\infty} e^{-\frac{1}{2} \lambda a \xi^2} d\xi \\ &= \left(\frac{2\pi}{a\lambda} \right)^{1/2} e^{\lambda f(X)} \end{aligned} \tag{A.63}$$

where the Gaussian integral can be found in the Table of Integrals.

A.10 THE CLASSICAL LIMIT

We want to show that, in the limit $\hbar \rightarrow 0$, the number of N -particle quantum states with energy less than E approaches the phase-space volume enclosed by the classical energy surface $\omega(E)$ divided by $h^K N!$. This is a difficult theorem, particularly for any reader who is not secure in the mathematics of quantum mechanics. Therefore, to simplify the analysis slightly, we will treat a system of N one-dimensional particles. Nothing really depends in any important way on the dimensionality of the system; treating a one-dimensional system simply allows us to avoid a number of shifts, back and forth, between scalar coordinates (x_1, \dots, x_K) and vector coordinates $(\mathbf{r}_1, \dots, \mathbf{r}_N)$. In fact, in this section we will use boldface letters to distinguish operators, rather than vectors, from ordinary scalars.

The Hamiltonian operator for the system is

$$\mathbf{H} = \mathbf{T} + \mathbf{V} = \sum_1^N \frac{\mathbf{P}_i^2}{2m} + V(x_1, \dots, x_N) \quad (\text{A.64})$$

where the coordinates and momenta satisfy the Heisenberg commutation relations

$$x_i \mathbf{p}_j - \mathbf{p}_j x_i = i\hbar \delta_{ij} \quad (\text{A.65})$$

We are interested in the classical limit of the function $\sum_n \theta(E - E_n)$. However, it will help if we first determine the classical limit of a simpler function, namely $F(\alpha) = \sum_n \exp(\alpha E_n)$, where α is any (possibly complex) constant. First we recall a few facts from quantum mechanics. 1. The exponential of any operator is the operator defined by the power series expansion,

$$e^{\mathbf{A}} = 1 + \mathbf{A} + \frac{1}{2} \mathbf{A}^2 + \dots \quad (\text{A.66})$$

2. If $|\psi\rangle$ is an eigenfunction of \mathbf{A} with eigenvalue a , then

$$e^{\mathbf{A}} |\psi\rangle = e^a |\psi\rangle \quad (\text{A.67})$$

This is easy to verify, using the expansion of $e^{\mathbf{A}}$. 3. The *trace* of an operator, written $\text{tr}(\mathbf{A})$, is defined as the sum of its diagonal elements with respect to any complete set of functions.

$$\text{tr}(\mathbf{A}) = \sum_n \langle \phi_n | \mathbf{A} | \phi_n \rangle \quad (\text{A.68})$$

The value of $\text{tr}(\mathbf{A})$ does not depend on the set of functions used to evaluate it. Using these facts, we can see that

$$\begin{aligned} \text{tr}(e^{\alpha \mathbf{H}}) &= \sum_n \langle E_n | e^{\alpha \mathbf{H}} | E_n \rangle \\ &= \sum_n \langle E_n | E_n \rangle e^{\alpha E_n} \\ &= \sum_n e^{\alpha E_n} \\ &= F(\alpha) \end{aligned} \quad (\text{A.69})$$

In the limit $\hbar \rightarrow 0$, the right hand side of Eq. (A.65) can be neglected. Then \mathbf{T} and \mathbf{V} can be treated as commuting operators. Thus in that limit

$$e^{\alpha \mathbf{H}} = e^{\alpha \mathbf{T} + \alpha \mathbf{V}} \approx e^{\alpha \mathbf{V}} e^{\alpha \mathbf{T}} \quad (\text{A.70})$$

Because the trace of an operator is independent of the set of functions that is used to evaluate it, we can, in evaluating the trace of $e^{\alpha \mathbf{H}}$, use the set of eigenfunctions of \mathbf{T} rather than \mathbf{H} . The reason why we do this is that the eigenfunctions of the kinetic energy are known, simple functions, while those of the complete Hamiltonian are usually not known for a system of interacting particles. In writing the kinetic energy eigenfunctions we will temporarily ignore any symmetry requirements on the wave functions (Bose–Einstein or Fermi–Dirac). Then, if we assume that the system is in a periodic box of length L , a correctly normalized kinetic energy eigenfunction can be constructed by choosing any N allowed momentum values, p_1, \dots, p_N , and writing the N -particle plane wave function

$$|p_1, \dots, p_N\rangle = L^{-N/2} \exp\left(\frac{i}{\hbar}(p_1 x_1 + \dots + p_N x_N)\right) \quad (\text{A.71})$$

With this function

$$\mathbf{T} |p_1, p_2, \dots, p_N\rangle = \sum_1^N \frac{\mathbf{P}_i^2}{2m} |p_1, p_2, \dots, p_N\rangle = \left(\sum_1^N p_i^2 / 2m\right) |p_1, p_2, \dots, p_N\rangle \quad (\text{A.72})$$

and

$$e^{\alpha \mathbf{V}} e^{\alpha \mathbf{T}} |p_1, p_2, \dots, p_N\rangle = \exp\left[\alpha \sum p_i^2/2m + \alpha V\right] |p_1, p_2, \dots, p_N\rangle \quad (\text{A.73})$$

Using these functions to evaluate the trace, we get

$$\begin{aligned} F(\alpha) &= \sum_{\{p\}} \langle p_1, p_2, \dots, p_N | e^{\alpha \mathbf{H}} | p_1, p_2, \dots, p_N \rangle \\ &= L^{-N} \sum_{\{p\}} \int d^N x e^{-(i/\hbar) \sum p_i x_i} \left(\exp\left[\alpha \sum p_i^2/2m + \alpha V\right] \right) e^{(i/\hbar) \sum p_i x_i} \\ &= L^{-N} \sum_{\{p\}} \int d^N x e^{\alpha \sum p_i^2/2m + \alpha V} \end{aligned} \quad (\text{A.74})$$

The sum, indicated by $\{p\}$, is over all allowed values of p_1, p_2, \dots, p_N . Each sum over momentum eigenvalues can be converted to an integral by using the fact that, in a periodic box of length L , the density of momentum eigenvalues is L/h (see Fig. 2.5). $F(\alpha)$ may then be written as

$$F(\alpha) = \frac{1}{h^N} \int d^N p \int d^N x e^{\alpha H(x,p)} \quad (\text{A.75})$$

where $H(x, p)$ is the classical Hamiltonian function $\sum p_i^2/2m + V(x)$. We must now correct for the fact that we have ignored the wave function symmetry. First we notice that, in the classical limit, the density of momentum eigenvalues L/h becomes greater and greater, while the number of particles N remains fixed. Therefore, the cases in which two or more momenta are equal become a smaller and smaller fraction of the sum over all N momentum values and can be ignored. If the N momenta p_1, p_2, \dots, p_N are different, then the correction we need to make is simple. We have overcounted the number of momentum eigenstates by a factor of $N!$ and so we must divide the result in Eq. (A.75) by $N!$ in order to obtain the trace only over properly symmetrized states. This gives

$$F(\alpha) = \frac{1}{N! h^N} \int d^N p \int d^N x e^{\alpha H(x,p)} \quad (\text{A.76})$$

To get the classical limit for $\sum \theta(E - E_n)$ we use the fact that any function $f(x)$ can be written in terms of its Fourier transform $\tilde{f}(k)$.

$$f(x) = \int dk e^{ikx} \tilde{f}(k) \quad (\text{A.77})$$

Then

$$\begin{aligned} \sum_n f(E_n) &= \int dk \sum_n e^{ikE_n} \tilde{f}(k) \\ &\xrightarrow{\hbar \rightarrow 0} \frac{1}{N! h^N} \int d^N x d^N p \int dk e^{ikH(x,p)} \tilde{f}(k) \\ &= \frac{1}{N! h^N} \int d^N x d^N p f(H(x,p)) \end{aligned} \quad (\text{A.78})$$

Specializing this result to the function $f(x) = \theta(E - x)$ gives the result we need.

$$\sum_n \theta(E - E_n) = \frac{1}{N! h^N} \int \theta(E - H(x,p)) d^N x d^N p \quad (\text{A.79})$$

A.11 A THEOREM IN ELECTROSTATICS

The relationship between the electric field \mathbf{E} and the polarization field \mathbf{P} within a dielectric is

$$\nabla \cdot \left(\mathbf{E} + \frac{1}{\epsilon_0} \mathbf{P} \right) = \rho_{\text{free}} \quad (\text{A.80})$$

where ρ_{free} is the density of free charge. Thus, if ρ_{free} is kept fixed but $\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ are changed to $\mathbf{E}(\mathbf{r}) + \Delta\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r}) + \Delta\mathbf{P}(\mathbf{r})$, then

$$\nabla \cdot \left(\Delta\mathbf{E} + \frac{1}{\epsilon_o} \Delta\mathbf{P} \right) = 0 \quad (\text{A.81})$$

Since $\nabla \times \mathbf{E} = 0$, we can express \mathbf{E} in terms of a scalar potential by $\mathbf{E} = -\nabla\phi(\mathbf{r})$. The needed steps in transforming the integral $\epsilon_o \int \mathbf{E} \cdot \Delta\mathbf{E} d^3\mathbf{r}$ are explained following the equation.

$$\begin{aligned} \epsilon_o \int_{E_3} \mathbf{E} \cdot \Delta\mathbf{E} d^3\mathbf{r} &= -\epsilon_o \int_{E_3} \nabla\phi \cdot \Delta\mathbf{E} d^3\mathbf{r} \\ &= -\epsilon_o \int_{E_3} \nabla \cdot (\phi\Delta\mathbf{E}) d^3\mathbf{r} + \epsilon_o \int_{E_3} \phi \nabla \cdot (\Delta\mathbf{E}) d^3\mathbf{r} \\ &= \epsilon_o \int_{E_3} \phi \nabla \cdot (\Delta\mathbf{E}) d^3\mathbf{r} \\ &= - \int_{E_3} \phi \nabla \cdot (\Delta\mathbf{P}) d^3\mathbf{r} \\ &= - \int_{E_3} \nabla \cdot (\phi\Delta\mathbf{P}) d^3\mathbf{r} + \int_{E_3} \nabla\phi \cdot \Delta\mathbf{P} d^3\mathbf{r} \\ &= - \int_{V_S} \mathbf{E} \cdot \Delta\mathbf{P} d^3\mathbf{r} \end{aligned} \quad (\text{A.82})$$

In going from line 1 to line 2, the vector identity $\nabla \cdot (\phi\mathbf{A}) = \nabla\phi \cdot \mathbf{A} + \phi\nabla \cdot \mathbf{A}$ was used. The first term in line 2 is zero by Gauss's theorem. Line 3 \rightarrow line 4 uses Eq. (A.81). Line 4 \rightarrow line 5 uses the vector identity again, and line 6 follows from Gauss's theorem and the fact that $\mathbf{P} = 0$ in free space.

A.12 A THEOREM IN MAGNETOSTATICS

The relationship between the magnetic field \mathbf{B} and the magnetization field \mathbf{M} within any substance is

$$\nabla \times (\mathbf{B} - \mu_o\mathbf{M}) = \mu_o(\mathbf{J} + \nabla \times \mathbf{M}_{\text{ext}}) \quad (\text{A.83})$$

where \mathbf{J} is the electric current density and \mathbf{M}_{ext} is the magnetization of any fixed external magnets. If \mathbf{J} and \mathbf{M}_{ext} are kept fixed but \mathbf{B} and \mathbf{M} are changed by the amounts $\Delta\mathbf{B}(\mathbf{r})$ and $\Delta\mathbf{M}(\mathbf{r})$, then

$$\nabla \times (\Delta\mathbf{B} - \mu_o\Delta\mathbf{M}) = 0 \quad (\text{A.84})$$

Since $\nabla \cdot \mathbf{B} = 0$, we can express \mathbf{B} in terms of a vector potential by $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$. The needed steps in transforming the integral $\mu_o^{-1} \int \mathbf{B} \cdot \Delta\mathbf{B} d^3\mathbf{r}$ are explained following the equation.

$$\begin{aligned} \frac{1}{\mu_o} \int_{E_3} \mathbf{B} \cdot \Delta\mathbf{B} d^3\mathbf{r} &= \frac{1}{\mu_o} \int_{E_3} (\nabla \times \mathbf{A}) \cdot \Delta\mathbf{B} d^3\mathbf{r} \\ &= \frac{1}{\mu_o} \int_{E_3} \nabla \cdot (\mathbf{A} \times \Delta\mathbf{B}) d^3\mathbf{r} + \frac{1}{\mu_o} \int_{E_3} \mathbf{A} \cdot \nabla \times (\Delta\mathbf{B}) d^3\mathbf{r} \\ &= \int_{E_3} \mathbf{A} \cdot \nabla \times (\Delta\mathbf{M}) d^3\mathbf{r} \\ &= \int_{E_3} (\nabla \times \mathbf{A}) \cdot \Delta\mathbf{M} d^3\mathbf{r} - \int_{E_3} \nabla \cdot (\mathbf{A} \times \Delta\mathbf{M}) d^3\mathbf{r} \\ &= \int_{V_S} \mathbf{B} \cdot \Delta\mathbf{M} d^3\mathbf{r} \end{aligned} \quad (\text{A.85})$$

Line 1 \rightarrow line 2 uses the vector identity $\nabla \cdot (\mathbf{A} \times \mathbf{B}) = (\nabla \times \mathbf{A}) \cdot \mathbf{B} - \mathbf{A} \cdot (\nabla \times \mathbf{B})$. Line 2 \rightarrow line 3 uses Gauss's theorem and Eq. (A.84). Line 3 \rightarrow line 4 uses the vector identity again and line 4 \rightarrow line 5 uses Gauss's theorem and the fact that $\Delta\mathbf{M} = 0$ outside the sample.

A.13 EXPANSIONS OF FERMI-DIRAC INTEGRALS

We want to obtain a power series expansion in the temperature $\tau = kT$ of an integral of the form

$$I = \int_o^\infty \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/\tau} + 1} d\varepsilon \tag{A.86}$$

At $\tau = 0$ the integral has the value

$$I_o = \int_o^\mu g(\varepsilon) d\varepsilon \tag{A.87}$$

The difference between I and I_o , which we call I_1 , may be written as

$$I_1 = I - I_o = \int_o^\infty \left[\frac{1}{e^{(\varepsilon-\mu)/\tau} + 1} - \theta\left(\frac{\mu - \varepsilon}{kT}\right) \right] g(\varepsilon) d\varepsilon \tag{A.88}$$

We now make a transformation from the variable ε to a variable $x = (\varepsilon - \mu)/\tau$, noting that $d\varepsilon = \tau dx$.

$$I_1 = kT \int_{-\mu/kT}^\infty \left(\frac{1}{e^x + 1} - \theta(-x) \right) g(\mu + kTx) dx \tag{A.89}$$

The function $[(e^x + 1)^{-1} - \theta(-x)]$ becomes exponentially small if $|x|$ is much larger than one. Therefore the lower limit of integration, for small T , may be extended to $-\infty$. The function, $g(\mu + kTx)$ can be expanded in a power series in the small quantity kTx , giving

$$I_1 = \sum_{n=0}^\infty (kT)^{n+1} \frac{d^n g(\mu)}{d\mu^n} J_n \tag{A.90}$$

where

$$J_n = \int_{-\infty}^\infty \left[\frac{1}{e^x + 1} - \theta(-x) \right] x^n dx \tag{A.91}$$

If we let $f(x) = (e^x + 1)^{-1} - \theta(-x)$, then it is easy to see that, for $x > 0$,

$$f(-x) = \frac{1}{e^{-x} + 1} - 1 = -\frac{1}{e^x + 1} = -f(x) \tag{A.92}$$

Thus the factor in large parentheses is an odd function of x . This implies that $J_n = 0$ for even n and, for odd n ,

$$J_n = 2 \int_o^\infty \frac{x^n}{e^x + 1} dx = 2(1 - 2^{-n})n!\zeta(n + 1) \tag{A.93}$$

where $\zeta(x)$ is the Riemann zeta function. Using the special values of ζ given in the Table of Integrals, we get the following expansion.

$$I = \int_o^\mu g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} g'(\mu)(kT)^2 + \frac{7\pi^4}{360} g'''(\mu)(kT)^4 + \dots \tag{A.94}$$

A.14 TABLE OF INTEGRALS

$$\int_0^\infty e^{-ax^2} x^{2n} dx = \frac{1 \times 3 \cdots (2n-1)}{2^{n+1} a^{(2n+1)/2}} \sqrt{\pi}$$

$$\int_0^\infty e^{-ax^2} x^{2n+1} dx = \frac{n!}{2a^{n+1}}$$

$$\int_0^\infty \frac{x^s}{e^x - 1} dx = s! \zeta(s+1) \quad s > 0$$

$$\int_0^\infty \frac{x^s}{e^x + 1} dx = (1 - 2^{-s}) s! \zeta(s+1)$$

$$\int_0^\infty \frac{dx}{e^x + 1} = \log 2$$

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

Special Values of the Riemann Zeta Function and the Gamma Function

$$\zeta(1) = \infty \qquad \zeta(2) = \frac{\pi^2}{6} \qquad \zeta(3) = 1.202 \qquad \zeta(4) = \frac{\pi^4}{90}$$

$$\zeta(5) = 1.037 \qquad \zeta(6) = \frac{\pi^6}{945} \qquad \zeta(3/2) = 2.612 \qquad \zeta(5/2) = 1.341$$

$$\Gamma(u+1) = u\Gamma(u) \qquad \Gamma(N) = (N-1)! \qquad \Gamma(1/2) = \sqrt{\pi}$$

A.15 PHYSICAL CONSTANTS AND CONVERSIONS

c	2.998×10^8	m/s	Speed of light
e	1.602×10^{-19}	C	Electronic charge
\hbar	1.055×10^{-34}	J s	Planck's constant
h	6.626×10^{-34}	J s	Planck's constant
k	1.381×10^{-23}	J/K	Boltzmann's constant
u	1.661×10^{-27}	kg	Atomic mass unit
m_e	9.1095×10^{-31}	kg	Electron mass
N_A	6.022×10^{23}		Avogadro's number
R	8.314	J/mol K	Molar gas constant
ϵ_o	8.854×10^{-12}	F/m	Permittivity of vacuum
μ_o	$4\pi \times 10^{-7}$	H/m	Permeability of vacuum
Å	10^{-10}	m	Ångstrom

Energy 1 cal = 4.186 J
 1 eV = 1.602×10^{-19} J

Pressure 1 atm = 1.013×10^5 N/m²
 1 bar = 10^5 N/m²
 1 mm Hg = 1.333×10^5 N/m²

Temperature 0° C = 273.15 K

STP = 0° C and 1 atm $n(\text{STP}) = 2.69 \times 10^{25}$ part./m³

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