School of Physics & Astronomy

PHS4200/4021 Statistical Mechanics

Lecture 2: The Microcanonical Ensemble

2.1 Introduction

As we noted in Lecture 1, the state of a system of N particles is described by a point in a $6N$-dimensional phase space (Γ-space). A microstate is represented by a set of coordinates in phase space:

$$(\boldsymbol{q},\boldsymbol{p}) \equiv (\{q_i\},\{p_i\}) = (q_1,q_2, \cdots ,q_{3N}; p_1,p_2, \cdots ,p_{3N}). \tag{2.1}$$

The classical dynamics of the system is described by the Hamiltonian, $H = H(\{q_i\},\{p_i\}) = H(\boldsymbol{q},\boldsymbol{p})$, with the concomitant equations of motion governed by Hamilton's equations (1.1). As the system evolves in time it traces out a path in Γ-space (see Fig. 2.1).
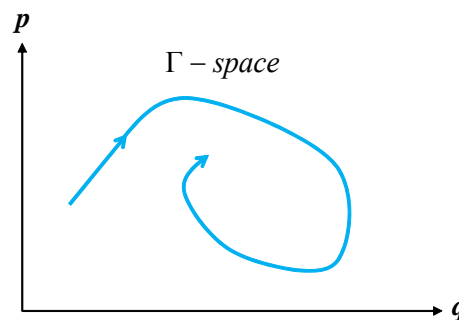

Figure 2.1: *The evolution of a system of N particles is described by a path in a 6N-dimensional phase space.*

If we specify the energy E of the system, the motion of N particles will be confined to a $(6N-1)$-dimensional hypersurface, given by:

$$E = H(\boldsymbol{q},\boldsymbol{p}). \tag{2.2}$$

The corresponding volume of phase space governed by Eq. (2.2) will be denoted by $\Gamma(E)$. Statistical mechanics is based on the postulate that for a closed system all the microstates of $\Gamma(E)$ have equal probability. However, for a non-closed system there will be microstates with a particular energy that are more likely than microstates with a different energy. In this case we introduce an energy-dependent weighting function $\rho = \rho(\boldsymbol{q},\boldsymbol{p},t)$. This density function represents the distribution of points in phase space (see Fig. 2.2), defined so that the number of points at $(\boldsymbol{q},\boldsymbol{p})$ contained in the volume element $d^{3N}q\,d^{3N}p$ at time t is given by:

$$\mathbb{N}(\boldsymbol{q},\boldsymbol{p},t) = \rho(\boldsymbol{q},\boldsymbol{p},t)d^{3N}q\,d^{3N}p. \tag{2.3}$$

A foundational concept in equilibrium statistical mechanics is the idea of an ensemble, where we consider, not a single system, but an infinite number of "copies" of that system. The ensemble is the collection of all possible microstates of the system (consistent with any constraints or conservation principles). The equilibrium macrostate of a system is then an ensemble average over all possible states in phase space.
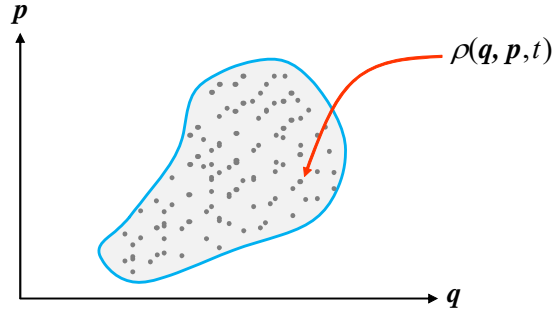
Figure 2.2: *The phase space distribution* ρ = ρ(*q*,*p*,*t*).

Consider a measurement of some macroscopic property of the system $f(q,p)$, carried out over a time interval $t_0 \le t \le t_0 + \tau$. During the measurement the point in phase space covers some part of $\Gamma(E)$. The measured value will be given by:

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} f(q,p)dt. \tag{2.4}$$

Since we are unable to determine the detailed dynamics of the point in phase space, we invoke the *ergodic hypothesis*, which posits that during the measurement the phase point will spend equal time intervals in all regions of $\Gamma(E)$. In this case we assert the equivalence of the time average and the ensemble average, whence:

$$\langle f \rangle = \int_{\Gamma(E)} \rho(q,p)f(q,p)d^{3N}q\,d^{3N}p. \tag{2.5}$$

This lecture will clarify these ideas and consider the microcanonical ensemble, in which the energy and number of particles of the system is fixed. In later lectures we will relax these constraints, whence the microcanonical ensemble is extended to the canonical ensemble and grand canonical ensemble.

Example 2.1: Construct the phase space for a one-dimensional simple harmonic oscillator, described by the classical Hamiltonian:

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}Kq^2,$$

where *m* is the mass of the oscillator and *K* is the spring constant.

Solution

In this case the phase space is two-dimensional and the constraint $H(q,p) = E$ gives rise to a phase space trajectory that is an ellipse - the one-dimensional "hypersurface" - whose semi-minor and semi-major axes are $a = \sqrt{2mE}$ and $b = \sqrt{2E/K}$, respectively. The phase space trajectory is shown in Fig. 2.3.
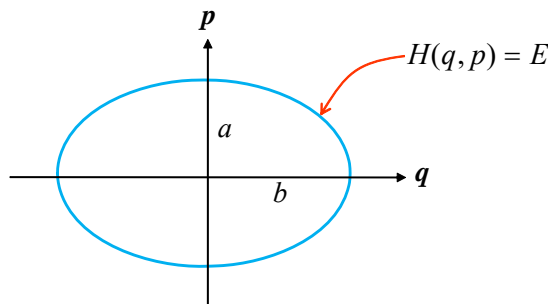

Figure 2.3: *Phase space for a one-dimensional simple harmonic oscillator. The "hypersurface"* H(*q*,*p*) = *E defines an ellipse.*

2.2   Liouville's Theorem

We now examine some of the general properties of phase space, in particular Liouville's theorem, which describes the "flow" of representative points in Γ-space. For a system in thermal equilibrium we would expect the phase space density to be time independent. However, for generality we will include an explicit time dependence and write $\rho = \rho(q,p,t)$. The total time derivative[1] of the phase space density is given by:

$$\frac{d\rho(q,p,t)}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial\rho}{\partial p_i}\frac{dp_i}{dt} \right). \tag{2.6}$$

Hamilton's equations allow us to relate $\dot{q}_i$ and $\dot{p}_i$ to the Hamiltonian of the system, i.e.,

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \quad and \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \quad (i = 1,2,3,...,3N) \tag{2.7}$$

Substituting Eq. (2.7) into Eq. (2.6) we obtain:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right)$$
$$= \frac{\partial\rho}{\partial t} + \{\rho,H\}, \tag{2.8}$$

where the Poisson bracket (see Appendix A) is defined as:

$$\{\rho,H\} = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right). \tag{2.9}$$

Liouville's theorem asserts that the phase space density vanishes along a path in Γ-space, i.e.,

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{\rho,H\} = 0. \tag{2.10}$$

For a system in thermodynamic equilibrium the phase space density cannot depend explicitly on time (i.e., $\partial\rho/\partial t = 0$), hence we $\{\rho,H\} = 0$. This latter result follows from Equation (2.9), since:

$$\{\rho,H\} = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right) = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial H}\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial H}\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} \right) = 0. \tag{2.11}$$

Liouville's theorem ensures that a volume element in phase space moves to another volume element in such a manner that no points are lost or gained. The distribution of points in Γ-space "flows" like an incompressible "fluid". To see this, consider a volume ω defined by:

$$\omega = \int_{H(q,p)\leq E} d\omega = \int_{H(q,p)\leq E} d^{3N}q\,d^{3N}p, \tag{2.12}$$

where $H(q,p) \leq E$ is the volume bounded by the energy hypersurface $\sigma = \partial\omega$. The rate at which points in phase space flow out of the volume ω is equal to the flux through the boundary hypersurface $\sigma = \partial\omega$ (see Fig. 2.4):

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[1] The total time derivative of a function $f = f(x,y,z,...,t) = f(R,t)$ is given by:

$$\frac{df(x,y,z,...,t)}{dt} = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt} + \frac{\partial f}{\partial z}\frac{dz}{dt} + \ldots + \frac{\partial f}{\partial t} = \nabla_R f \cdot \frac{dR}{dt} + \frac{\partial f}{\partial t}.$$

$$\frac{\partial}{\partial t}\int_{\Gamma(E)} \rho\, d^{3N}q\, d^{3N}p \;=\; \frac{\partial}{\partial t}\int_\omega \rho\, d\omega \;=\; -\oint_{\sigma=\partial\omega} \rho\boldsymbol{u}\cdot\hat{\boldsymbol{n}}\, d\sigma, \tag{2.13}$$

where the $6N$-dimensional "velocity" vector is $\boldsymbol{u} = (\dot{\boldsymbol{q}},\dot{\boldsymbol{p}}) = (\dot{q}_1,\dot{q}_2,...,\dot{q}_{3N};\dot{p}_1,\dot{p}_2,...,\dot{p}_{3N})$ and $\hat{\boldsymbol{n}}$ is an outward directed normal to the hypersurface σ. We can invoke the divergence theorem[2] (in $6N$ dimensions) to re-write Eq. (2.13) as:

$$\frac{\partial}{\partial t}\int_\omega \rho\, d\omega \;=\; -\oint_{\sigma=\partial\omega} \rho\boldsymbol{u}\cdot\hat{\boldsymbol{n}}\, d\sigma \;=\; -\int_\omega \nabla\cdot(\rho\boldsymbol{u})\, d\omega. \tag{2.14}$$

Hence we have:

$$\int_\omega \left(\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{u}) \right) d\omega \;=\; 0 \quad\Rightarrow\quad \frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{u}) \;=\; 0. \tag{2.15}$$

Equation (2.15) is the continuity equation, which describes the "flow" of points in phase space as an incompressible "fluid".
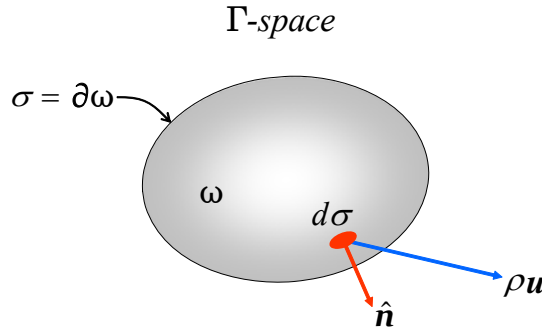
<p style="text-align:center;">Γ-space</p>

Figure 2.4: *Flux of ρ**u** in phase space.*

We now show that Eq. (2.15) leads directly to Liouville's theorem (2.10). We begin by noting that the gradient operator in $6N$-dimensional phase space is:

$$\begin{aligned}
\nabla\cdot(\rho\boldsymbol{u}) &= \sum_{i=1}^{3N}\left(\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i} \right) \\
&= \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \rho\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\rho}{\partial p_i}\dot{p}_i + \rho\frac{\partial\dot{p}_i}{\partial p_i} \right) \\
&= \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i \right) + \sum_{i=1}^{3N}\rho\left(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i} \right).
\end{aligned} \tag{2.16}$$

Using Hamilton's equations (2.7) allows Eq. (2.16) to be re-written as:

$$\nabla\cdot(\rho\boldsymbol{u}) = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right) + \sum_{i=1}^{3N}\rho\left(\frac{\partial^2 H}{\partial q_i\partial p_i} - \frac{\partial^2 H}{\partial p_i\partial q_i} \right). \tag{2.17}$$

It is evident that the last term in Eq. (2.17) vanishes, which allows the $6N$-dimensional gradient operator to be written as:

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[2] Recall that Gauss's divergence theorem for a vector field A in three space dimensions is written as:

$$\oint_{S=\partial\mathbb{R}^3} \boldsymbol{A}\cdot\hat{\boldsymbol{n}}\, dS \;=\; \int_{\mathbb{R}^3} \nabla\cdot A\, d^3\boldsymbol{r}.$$

$$\nabla\cdot(\rho\boldsymbol{u}) = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = \{\rho,H\}. \tag{2.18}$$

Substituting Eq. (2.18) into the continuity equation (2.15) we obtain:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{u}) = 0 \quad \Rightarrow \quad \frac{\partial\rho}{\partial t} + \{\rho,H\} = 0. \tag{2.19}$$

Equation (2.19) leads immediately to Liouville's theorem, since:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{\rho,H\} = 0. \tag{2.20}$$

This shows that ρ is a constant of the motion, i.e., it is a conserved quantity.

2.3   The Microcanonical Ensemble

The ensemble average defined by Eq. (2.5) requires that we know $\rho = \rho(\boldsymbol{q},\boldsymbol{p},t)$. For a closed system in thermodynamic equilibrium with a given fixed energy E, volume V and particle number N, we postulate equal *a priori* probability, whence the phase space density is:

$$\rho(\boldsymbol{q},\boldsymbol{p}) \propto \delta(E - H(\boldsymbol{q},\boldsymbol{p})), \tag{2.21}$$

where the constant of proportionality is a normalisation factor, related to the area of the constant energy hypersurface. The Dirac δ– function (see Appendix B) guarantees that only points on this hypersurface contribute to the probability density. The resulting ensemble described by Eq. (2.21) is known as the *microcanonical ensemble.* Since it is awkward to deal with the delta function, we relax the constraint $H(\boldsymbol{q},\boldsymbol{p}) = E$, and re-define Eq. (2.21) to allow for a small energy range, i.e.,

$$\rho(\boldsymbol{q},\boldsymbol{p}) = \begin{cases} C & (E \le H(\boldsymbol{q},\boldsymbol{p}) \le E+\Delta E) \\ 0 & \textit{otherwise.} \end{cases} \tag{2.22}$$

The constant C is determined via the normalisation condition:

$$\int_\omega \rho(\boldsymbol{q},\boldsymbol{p})d\omega = \int_{\Gamma(E)} \rho(\boldsymbol{q},\boldsymbol{p})d^{3N}q\,d^{3N}p = C\int_{E\le H(\boldsymbol{q},\boldsymbol{p})\le E+\Delta E} d^{3N}q\,d^{3N}p = 1. \tag{2.23}$$

Before proceeding to explicitly determine the constant C, let us first clarify some aspects of how we describe phase space. First we consider phase space as being partitioned into volume elements (cells), each of size $d^{3N}q\,d^{3N}p$. Noting that $dq\,dp$ has dimensions of action (i.e., angular momentum), we sub-divide phase space into cells each having a volume h^{3N} (see Fig. 2.5). The choice of the symbol h is suggestive of Planck's constant, which is consistent with a treatment of quantum statistical mechanics; however, in classical statistical mechanics we consider h^{3N} to be the smallest volume element corresponding to each microstate in phase space. For the microcanonical ensemble the number of microstates (see Sec. 1.4) is related to the area of the energy hypersurface, i.e.,

$$\Omega(E,V,N) \propto \int_{H(\boldsymbol{q},\boldsymbol{p}) = E} d\sigma = \sigma(E,N,V), \tag{2.24}$$

where $d\sigma$ denotes the surface element (see Fig. 2.4). Equation (2.24) is difficult to calculate as it involves high dimensional surfaces. We therefore consider an alternate approach. Define the volume of Γ-space enclosed by the energy hypersurface as:

$$\omega(E) = \int_{H(\boldsymbol{q},\boldsymbol{p}) \le E} d\omega = \int_{H(\boldsymbol{q},\boldsymbol{p}) \le E} d^{3N}q\,d^{3N}p. \tag{2.25}$$
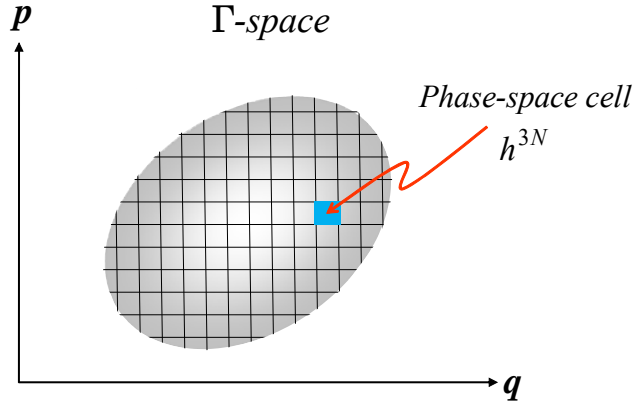
Figure 2.5: *Subdivision of phase space into cells of volume* h^{3N}.

Taylor expanding Eq. (2.25) we obtain an expression for the volume between two energy hypersurfaces with energy E and $E + \Delta E$:

$$\Delta\omega = \omega(E+\Delta E) - \omega(E) = \left(\frac{\partial\omega}{\partial E}\right)_{N,V}\Delta E + \frac{1}{2!}\left(\frac{\partial^2\omega}{\partial E^2}\right)_{N,V}(\Delta E)^2 + \ldots \qquad (2.26)$$

For $\Delta E \ll E$, Eq. (2.26) becomes:

$$\Delta\omega = \left(\frac{\partial\omega}{\partial E}\right)_{N,V}\Delta E = \sigma(E)\Delta E \quad \Rightarrow \quad \sigma(E) = \frac{\partial\omega(E)}{\partial E}. \qquad (2.27)$$

where $\sigma(E)$ is the density of states at energy E. From Eq. (2.24) we have:

$$\Omega(E,V,N) \propto \frac{\partial\omega}{\partial E}. \quad or \quad \Omega(E,V,N) = \frac{1}{\sigma_0}\frac{\partial\omega}{\partial E}. \qquad (2.28)$$

The thermodynamic properties of the system do not depend on the constant of proportionality σ_0^{-1}.

Exercise 2.1: *Construct the phase space for a one-dimensional simple harmonic oscillator, described by the classical Hamiltonian in Example 2.1, with energy lying between E and $E + \Delta E$. Using Eq. (2.27) show that $\Delta\omega = (2\pi/\omega_0)\Delta E$. In this case $\sigma(E) = (2\pi)/\omega_0$, where the angular frequency of the oscillator is $\omega_0 = \sqrt{K/m}$.*

We can now evaluate the constant in Eqs. (2.22) and (2.23) to obtain:

$$C \int_{E \le H(q,p) \le E+\Delta E} d^{3N}q\,d^{3N}p = C\Omega(E,V,N) = 1 \quad \Rightarrow \quad C = \frac{1}{\Omega(E,V,N)}. \qquad (2.29)$$

There are two important caveats to our discussion of phase space. First it is common to include the factor h^{3N} in the defining relations [e.g., Eq. (2.23)], which ensures that the phase space density is a dimensionless quantity. The second modification is to include the Gibbs factor[3] to correctly account for the fact that the particles are indistinguishable (see Sec. 2.3.2). This means that in the case of N particles, there are $N!$ ways to enumerate them, so that the phase space volume element $d^{3N}q\,d^{3N}p$ overestimates the number of microstates by a factor of $N!$ Including both these refinements, we write the normalisation condition and ensemble average as:

$$\frac{1}{N!h^{3N}}\int_{\Gamma(E)}\rho(q,p)d^{3N}q\,d^{3N}p = 1, \qquad (2.30)$$

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[3] This is also known as correct Boltzmann counting, see e.g., J. R. Ray, Eur. J. Phys. **5**, 219 (1984).

and

$$\langle f \rangle = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\boldsymbol{q},\boldsymbol{p}) f(\boldsymbol{q},\boldsymbol{p}) d^{3N}q \, d^{3N}p. \tag{2.31}$$

2.3.1 Entropy and Thermodynamics

The entropy of a system is defined (up to an additive constant) in terms of the number of microstates (2.24) as:

$$S = S(E,V,N) = k_B \ln \Omega(E,V,N) + S_0 \tag{2.32}$$

Since only entropy differences are measured, it is usual to absorb the constant S_0 into the definition of entropy. The thermodynamic quantities are calculated from Eq. (2.32) as follows:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} \quad and \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N} \right)_{E,V}. \tag{2.33}$$

Unfortunately, for practical situations it is difficult to use this formalism to calculate $\Omega(E,V,N)$. To illustrate this point, in Example 2.2, we calculate the entropy of an ideal gas using the methods of Sec. 2.3. In subsequent lectures we will formulate alternative ways of evaluating the thermodynamic properties of system (e.g., using the canonical ensemble).

Example 2.2: Calculate the entropy of a classical ideal gas using the microcanonical ensemble.

Solution

We follow the derivation in Ref. [1] and start with the Hamiltonian for N non-interacting monoatomic gas atoms, each of mass m, confined to a volume V in 3-space:

$$H(\boldsymbol{q},\boldsymbol{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$$

The corresponding phase space volume (2.25) is:

$$\omega(E,V,N) = \int_{H(\boldsymbol{q},\boldsymbol{p}) \le E} d^{3N}q \, d^{3N}p,$$

where we have omitted the factor h^{3N} and the Gibbs correction factor $N!$ In Sec. 2.3.2 we will discuss the consequences of not accounting for the fact the gas atoms are indistinguishable. The integration over the coordinates $\boldsymbol{q} = (q_1, q_2, ..., q_{3N})$ is trivial and gives V^N, hence:

$$\omega(E,V,N) = V^N \int_{H(\boldsymbol{q},\boldsymbol{p}) \le E} d^{3N}p,$$

The integration over the momentum coordinates corresponds to the volume of a $3N$-dimensional sphere of radius $R = \sqrt{2mE}$. This follows directly from the equation:

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m} = E \quad \Rightarrow \quad \sum_{i=1}^{3N} p_i^2 = 2mE = R^2,$$

which defines a hypersphere in $3N$ dimensions. The volume of a sphere of radius R in D dimensions is given by (see Appendix C):

$$V_D(R) = \frac{\pi^{D/2}}{\frac{D}{2}\Gamma\left(\frac{D}{2}\right)} R^D,$$

where $\Gamma(z)$ denotes the gamma function.[4] Using the expression for $V_D(R)$, we write the phase space volume as:

$$\omega(E,V,N) = V^N \int_{H(q,p)\leq E} d^{3N}p = \frac{(\pi)^{3N/2}(2mE)^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} V^N.$$

From Eq. (2.28) we obtain:

$$\Omega(E,V,N) = \frac{1}{\sigma_0}\frac{\partial\omega(E,V,N)}{\partial E} = \frac{1}{\sigma_0}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}(2m)^{3N/2}E^{3N/2-1}V^N.$$

Finally, we calculate the entropy of the gas using Eq. (2.32), i.e.,

$$S(E,V,N) = k_B \ln\Omega(E,V,N) = k_B\ln\left\{\frac{1}{\sigma_0}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}(2m)^{3N/2}E^{3N/2-1}V^N\right\}$$

The expression for entropy can be simplified by noting that $N \gg 1$, whence $E^{3N/2-1} \approx E^{3N/2}$, and Stirling's approximation (see Appendix B, Lecture 1) is exploited to write the gamma function as:

$$\Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2}-1\right)! \approx \left(\frac{3N}{2}\right)! \implies \ln\Gamma\left(\frac{3N}{2}\right) \approx \ln\left(\frac{3N}{2}\right)! \approx \left(\frac{3N}{2}\right)\ln\left(\frac{3N}{2}\right) - \frac{3N}{2},$$

where we have implicitly assumed that $3N/2$ is an integer. With these approximations, the entropy of an ideal classical gas is now given by:

$$S(E,V,N) = k_B\ln\left\{\frac{1}{\sigma_0}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}(2m)^{3N/2}E^{3N/2-1}V^N\right\}$$

$$= -k_B\ln\Gamma\left(\frac{3N}{2}\right) + k_B\ln\left\{(2\pi mE)^{3N/2}\left(\frac{V}{\sigma_0^{1/N}}\right)^N\right\}$$

$$= -k_B\left(\frac{3N}{2}\right)\ln\left(\frac{3N}{2}\right) + k_B\left(\frac{3N}{2}\right) + k_B\ln\left\{(2\pi mE)^{3N/2}\left(\frac{V}{\sigma_0^{1/N}}\right)^N\right\}$$

$$= Nk_B\left[\frac{3}{2} + \ln\left\{\left(\frac{4\pi mE}{3N}\right)^{3/2}\left(\frac{V}{\sigma}\right)\right\}\right] \qquad (where\ \sigma = \sigma_0^{1/N}).$$

Example 2.3: Based on the results in Example 2.2, determine the internal energy and the equation of state for an ideal monoatomic gas.

Solution

Using Eq. (2.33) with the entropy defined in Example 2.2, we obtain:

[4] See Appendix B, Lecture 1 or https://en.wikipedia.org/wiki/Gamma_function

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}\frac{Nk_B}{E} \quad\Rightarrow\quad E \equiv U = \frac{3}{2}Nk_BT.$$

and

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk_B}{V} \quad\Rightarrow\quad pV = Nk_BT = nRT,$$

where n is the number of moles of gas and $R = N_Ak_B$ is the ideal gas constant (see Lecture 1). It is noteworthy that the internal energy is what the equipartition theorem[5] would predict, since each degree of freedom contributes $\frac{1}{2}k_BT$ to the energy of the gas, and in this case we have $3N$ degrees of freedom.

2.3.2 The Gibbs Paradox

There is a problem with the entropy as calculated in Example 2.2. To illustrate this problem, we consider the Gibbs paradox, in which a system comprising two ideal gases (A and B) are confined to a container, with an impermeable partition separating the gases (see Fig. 2. 6). The internal energy E, temperature T and pressure p of the two gases are equal, but they occupy different volumes and have different numbers of atoms. The entropy of each gas is given by:

$$S(E,V_i,N_i) = N_ik_B\left[\frac{3}{2} + \ln\left\{\left(\frac{V_i}{\sigma}\right)\left(\frac{4\pi mE)}{3N_i}\right)^{3/2}\right\}\right] \quad (i = A, B). \tag{2.34}$$

or

$$S(T,V_i,N_i) = N_ik_B\left[\frac{3}{2} + \ln\left\{\left(\frac{V_i}{\sigma}\right)(2\pi mk_BT))^{3/2}\right\}\right] \quad (E = \frac{3}{2}N_ik_BT). \tag{2.35}$$

Gas A	Gas B
N_A, V_A	N_B, V_B
T, p	T, p

Figure 2.6: *A container comprising two ideal gases (A and B), each at temperature T and pressure p. The two gases are separated by an impermeable partition.*

When the partition is removed the two gases mix. Since this is clearly an irreversible process, the entropy change must be positive.

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[5] The equipartition theorem can be written more generally for position and momentum as:

$$\left\langle q_i\frac{\partial H}{\partial q_i}\right\rangle = k_BT \quad and \quad \left\langle p_i\frac{\partial H}{\partial p_i}\right\rangle = k_BT.$$

For a Hamiltonian that depends quadratically on the generalised coordinates and momenta, the equipartition theorem gives (for each degree of freedom):

$$\langle H\rangle \equiv U = \frac{1}{2}k_BT.$$

A derivation of the generalised equipartition theorem can be found in Huang, K. *Statistical Mechanics* (2nd Edition, John Wiley and Sons, 1987), pp. 136 - 138.

The mixing entropy is calculated from:

$$\Delta S_{mix} = S_{final} - S_{initial},$$ (2.36)

where

$$S_{initial} = S_A(T,V_A,N_A) + S_B(T,V_B,N_B),$$ (2.37)

and

$$S_{final} = S_A(T,V_A+V_B,N_A) + S_B(T,V_A+V_B,N_B).$$ (2.38)

Substituting Eq. (2.35) into Eqs. (2.36) - (2.38) we have:

$$
\begin{aligned}
\Delta S_{mix} &= S_{final} - S_{initial} \\
&= N_A k_B \left[\frac{3}{2} + \ln\left\{ \left(\frac{V_A+V_B}{\sigma} \right) (2\pi m k_B T)^{3/2} \right\} \right] + N_B k_B \left[\frac{3}{2} + \ln\left\{ \left(\frac{V_A+V_B}{\sigma} \right) (2\pi m k_B T)^{3/2} \right\} \right] \\
&\quad - N_A k_B \left[\frac{3}{2} + \ln\left\{ \left(\frac{V_A}{\sigma} \right) (2\pi m k_B T)^{3/2} \right\} \right] - N_B k_B \left[\frac{3}{2} + \ln\left\{ \left(\frac{V_B}{\sigma} \right) (2\pi m k_B T)^{3/2} \right\} \right].
\end{aligned}
$$ (2.39)

Upon simplifying Eq. (2.39) we obtain the mixing entropy:

$$\Delta S_{mix} = N_A k_B \ln\left(\frac{V_A+V_B}{V_A} \right) + N_B k_B \ln\left(\frac{V_A+V_B}{V_B} \right).$$ (2.40)

Note that ΔS_{mix} does not depend on the factor $\sigma = \sigma_0^{1/N}$. Since $V_A + V_B > V_{A,B}$, the mixing entropy $\Delta S_{mix} > 0$, as one would expect from an irreversible process. However, a problem arises if we now consider the two gases to be identical. In this case Eq. (2.38) becomes:

$$S_{final} = S(T,V_A+V_B,N_A+N_B).$$ (2.41)

However, the mixing entropy calculated from Eqs. (2.36), (2.37) and (2.41) still increases; but this cannot be correct, as in this latter situation the process is reversible and we expect $\Delta S_{mix} = 0$. It is easy to see why the process is reversible, because the partition has no effect if the two gases are the same. Indeed after mixing we can re-insert the partition and recover the original configuration! So what is missing in the analysis leading to the entropy defined by Eq. (2.34) or Eq. (2.35)? In fact we have assumed that the atoms comprising the ideal gas are distinguishable. Quantum mechanically this is untenable, as the atoms are indistinguishable. Consequently, a permutation of the N atoms does not gives rise to a different macrostate. To account for this we use the Gibbs factor and reduce the number of microstates by $N!$ so that the entropy is given by:

$$
\begin{aligned}
S(E,V,N) &= k_B \ln\left(\frac{1}{N!} \Omega(E,V,N) \right) \\
&= k_B \ln\Omega(E,V,N) - k_B \ln N! \\
&= N k_B \left[\frac{3}{2} + \ln\left\{ \left(\frac{V}{\sigma} \right) \left(\frac{4\pi m E)}{3N} \right)^{3/2} \right\} \right] - k_B \ln N!
\end{aligned}
$$ (2.42)

For $N \gg 1$ we exploit Stirling's approximation (see Appendix B, Lecture 1):

$$S(E,V,N) = Nk_B\left[\frac{3}{2} + \ln\left\{\left(\frac{V}{\sigma}\right)\left(\frac{4\pi mE)}{3N}\right)^{3/2}\right\}\right] - k_B\ln N!$$

$$Nk_B\left[\frac{3}{2} + \ln\left\{\left(\frac{V}{\sigma}\right)\left(\frac{4\pi mE)}{3N}\right)^{3/2}\right\}\right] - k_B N\ln N + Nk_B \tag{2.43}$$

$$Nk_B\left[\frac{5}{2} + \ln\left\{\frac{1}{\sigma}\left(\frac{V}{N}\right)\left(\frac{4\pi mE)}{3N}\right)^{3/2}\right\}\right].$$

Note that the appearance of the ratios V/N and E/N in Eq. (2.43) means that the entropy is now an extensive (additive) thermodynamic quantity as required (see Lecture 1). Using the equation of state, we can also write Eq. (2.43) as:

$$S(T,V,N) = Nk_B\left[\frac{5}{2} + \ln\left\{\frac{1}{\sigma}\left(\frac{V}{N}\right)(2\pi mk_BT)^{3/2}\right\}\right] \qquad (E = \frac{3}{2}Nk_BT). \tag{2.44}$$

We now repeat the calculation of the mixing entropy when the two gases are the same. Using Eqs. (2.37), (2.41) and (2.44) we have:

$$\Delta S_{mix} = S_{final} - S_{initial}$$

$$= (N_A + N_B)k_B\left[\frac{5}{2} + \ln\left\{\frac{1}{\sigma}\left(\frac{V_A + V_B}{N_A + N_B}\right)(2\pi mk_BT)^{3/2}\right\}\right]$$

$$- N_A k_B\left[\frac{5}{2} + \ln\left\{\frac{1}{\sigma}\left(\frac{V_A}{N_A}\right)(2\pi mk_BT)^{3/2}\right\}\right] \tag{2.45}$$

$$- N_B k_B\left[\frac{5}{2} + \ln\left\{\frac{1}{\sigma}\left(\frac{V_B}{N_B}\right)(2\pi mk_BT)^{3/2}\right\}\right].$$

However, during the mixing process, the temperature and pressure do not change, hence we have:

$$\frac{N_A}{V_A} = \frac{N_B}{V_B} = \frac{N_A + N_B}{V_A + V_B}. \tag{2.46}$$

Using Eq. (2.46) in Eq. (2.45) we see that indeed the mixing entropy for this process is zero, i.e., $\Delta S_{mix} = 0$.

Exercise 2.2: *Show that Eq. (2.35) predicts the incorrect mixing entropy for two identical gases.*

2.3.3 Entropy in the Microcanonical Ensemble

The ensemble average of a function $f(q,p)$ is defined in Eq. (2.31) as:

$$\langle f \rangle = \frac{1}{N!h^{3N}} \int_{\Gamma(E)} \rho(q,p)f(q,p)d^{3N}qd^{3N}p, \tag{2.47}$$

where $\rho(q,p)$ is the phase space density for the relevant ensemble. For the microcanonical ensemble:

$$\rho(q,p) = \begin{cases} \dfrac{1}{\Omega(E,V,N)} & (E \le H(q,p) \le E + \Delta E) \\ 0 & otherwise. \end{cases} \tag{2.48}$$

In statistical mechanics the entropy is formally defined in terms of an ensemble average as:

$$S(E,V,N) = -\langle k_B \ln\rho(\boldsymbol{q},\boldsymbol{p})\rangle = \frac{1}{N!h^{3N}} \int_{\Gamma(E)} \rho(\boldsymbol{q},\boldsymbol{p})\big(-k_B\ln\rho(\boldsymbol{q},\boldsymbol{p})\big)d^{3N}q d^{3N}p. \tag{2.49}$$

Substituting for the microcanonical phase space density $\rho(\boldsymbol{q},\boldsymbol{p})$ from Eq. (2.48) we obtain:

$$\begin{aligned}
S(E,V,N) &= \frac{1}{N!h^{3N}} \int_{E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E} \frac{1}{\Omega(E,V,N)} \left[-k_B\ln\left(\frac{1}{\Omega(E,V,N)}\right)\right] d^{3N}q d^{3N}p \\
&= \frac{1}{N!h^{3N}} \int_{E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E} \frac{1}{\Omega(E,V,N)} \big(+k_B\ln\Omega(E,V,N)\big) d^{3N}q d^{3N}p.
\end{aligned} \tag{2.50}$$

Since the energy is constant on the energy shell $E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E$, we can remove $\Omega(E,V,N)$ from the integrand in Eq. (2.50) and write:

$$\begin{aligned}
S(E,V,N) &= \frac{1}{N!h^{3N}} \int_{E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E} \frac{1}{\Omega(E,V,N)} \big(+k_B\ln\Omega(E,V,N)\big) d^{3N}q d^{3N}p \\
&= \frac{1}{N!h^{3N}} \frac{k_B\ln\Omega(E,V,N)}{\Omega(E,V,N)} \int_{E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E} d^{3N}q d^{3N}p.
\end{aligned} \tag{2.51}$$

Finally, we note that the remaining integral is just the number of microstates in the phase space volume $\Gamma(E)$, i.e.,

$$\frac{1}{N!h^{3N}} \int_{E \leq H(\boldsymbol{q},\boldsymbol{p}) \leq E+\Delta E} d^{3N}q d^{3N}p = \Omega(E,V,N), \tag{2.52}$$

Hence Eq. (2.51) reduces to:

$$S(E,V,N) = \frac{k_B\ln\Omega(E,V,N)}{\Omega(E,V,N)} \cdot \Omega(E,V,N) = k_B\ln\Omega(E,V,N). \tag{2.53}$$

As one would expect, this is consistent with our earlier definition of entropy [see Eq. (2.32)]. In subsequent lectures we will use other ensembles (e.g., the canonical ensemble) to calculate entropy; however, in all cases entropy is defined as the ensemble average:

$$S(E,V,N) = -\langle k_B\ln\rho(\boldsymbol{q},\boldsymbol{p})\rangle, \tag{2.54}$$

where $\rho(\boldsymbol{q},\boldsymbol{p})$ is phase space density of the relevant ensemble.

Appendix A: Poisson Brackets

Consider two functions of the N generalised coordinates and N conjugate momenta, $A = A(\boldsymbol{q},\boldsymbol{p})$. and $B = B(\boldsymbol{q},\boldsymbol{p})$. The Poisson bracket of A and B is defined as:

$$\{A,B\} = \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right). \tag{A2.1}$$

When the function A is the Hamiltonian $H = H(\boldsymbol{q},\boldsymbol{p})$, the Poisson bracket plays an important role in classical mechanics [2]. For example, the time dependence of an observable $A = A(\boldsymbol{q},\boldsymbol{p},t)$, which includes an explicit time dependence, is written in terms of the Poisson bracket, i.e.,

$$\begin{aligned}
\frac{dA}{dt} &= \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial A}{\partial p_i} \frac{dp_i}{dt} \right) \\
&= \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \\
&= \frac{\partial A}{\partial t} + \{A,H\}.
\end{aligned} \tag{A2.2}$$

where we have exploited Hamilton's equations (2.7). Poisson brackets anticommute, so that $\{A,B\} = -\{B,A\}$, and they have the following properties:

$$\{q_i,q_j\} = \{p_i,p_j\} = 0 \quad and \quad \{q_i,p_j\} = \delta_{ij}. \tag{A2.3}$$

Equation (A2.3) provided Dirac with a route to quantum mechanics [3], in which the Poisson bracket is replaced by a commutator according to the following prescription:

$$\{q_i,p_j\} \rightarrow [\hat{Q}_i,\hat{P}_j] = i\hbar\delta_{ij}, \tag{A2.4}$$

where $\hat{Q}_i$ and $\hat{P}_j$ now represent position and momentum operators. In quantum mechanics the time evolution of an operator $\hat{A}$ in the Heisenberg picture is given by:

$$\frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + \frac{1}{i\hbar}[\hat{A},\hat{H}]. \tag{A2.5}$$

Appendix B: The Dirac Delta Function

The Dirac δ-function can be thought of as a generalisation of the discrete Kronecker delta function δ_{ij}. However, the δ-function is not a function at all, rather it is an example of what mathematicians call a distribution. From an intuitive point of view we consider the δ-function as the limit of a proper function. For example, Fig. B.1 shows how the function $rect(x)$ approaches a δ-function as $\varepsilon \rightarrow 0$.

The δ-function has the following properties:

$$\delta(x) = 0 \quad for \ x \neq 0, \tag{B2.1}$$

and

$$\int_{-\infty}^{+\infty} \delta(x)dx = 1 \tag{B2.2}$$

One of the key properties of the Dirac δ-function is its *sifting property*, defined for an arbitrary function $f(x)$ as:

$$\int_{-\infty}^{+\infty} f(x)\delta(x - x')dx = f(x'),$$ (B2.3)

As long as the δ-function is manipulated within an integral you should not encounter problems!

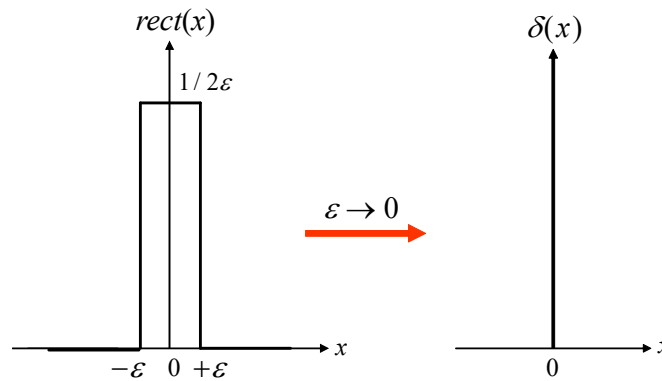**Figure B.1:** *The δ-function defined as the limit* $\lim_{\varepsilon \to 0} rect(x)$.

The physicists' view of the Dirac δ-function does not do justice to the subtleties of distribution theory, which was developed by Schwartz and independently by Gelfand[6]. In order to define the δ-function (really the δ-distribution) more precisely we consider a class of suitably smooth (proper) functions, called *test functions,* $\varphi(x)$, which have the following properties:

    (i) $\varphi(x)$ is infinitely differentiable, that is it has derivatives of all orders at each point $x \in \mathbb{R}$. We say that $\varphi(x)$ is a C^{∞} function.

    (ii) $\varphi(x)$ has compact support, which means that it vanishes outside the interval (a,b).

We also need a definition of convergence for a sequence of test functions $\{\varphi_n(x)\}$, which are elements of a vector space. We say that $\varphi_n(x) \to 0$ as $n \to \infty$, if:

    (i)   The test functions $\varphi_n(x)$ and all its derivatives $\partial_m\varphi_n(x)$ tend to zero, uniformly in both x and m.

    (ii) There is an interval (a,b) containing the support of all the test functions $\varphi_n(x)$.

The action of an integrable function $f(x)$ on the test function $\varphi(x)$ is given by:

$$\langle f,\varphi\rangle = \int_{-\infty}^{+\infty} f(x)\varphi(x)dx.$$ (B2.4)

Equation (B2.4) may be regarded as describing a linear map from the vector space of test functions to $\mathbb{R}$, satisfying:

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[6] A discussion of the theory of distributions, including the Dirac distribution, can be found at:

http://en.wikipedia.org/wiki/Distribution_(mathematics)
http://en.wikipedia.org/wiki/Dirac_delta_function

$$\langle f,\ a\varphi_1 + b\varphi_2 \rangle\ =\ a\langle f,\ a\varphi_1 \rangle\ +\ b\langle f,\ \varphi_2 \rangle \quad (a,b \in \mathbb{R}). \tag{B2.5}$$

A distribution **D** is defined as a continuous linear map from the space of test functions to $\mathbb{R}$, i.e.,

$$\mathbf{D}:\ \varphi \ \rightarrow\ \langle \mathbf{D},\varphi \rangle \in \mathbb{R}. \tag{B2.6}$$

The Dirac distribution $\delta(x)$ is but one example, albeit an important one, of a distribution. It is defined as:

$$\langle \delta,\varphi \rangle\ =\ \varphi(0). \tag{B2.7}$$

Note that this definition is consistent with Eq. (B2.3). There are many examples of suitable test functions. Figure 1.4 shows a sequence of Gaussian test functions, defined by:

$$\varphi_\sigma(x)\ =\ \frac{1}{\sqrt{\pi}\sigma}e^{-x^2/\sigma^2}. \tag{B2.8}$$

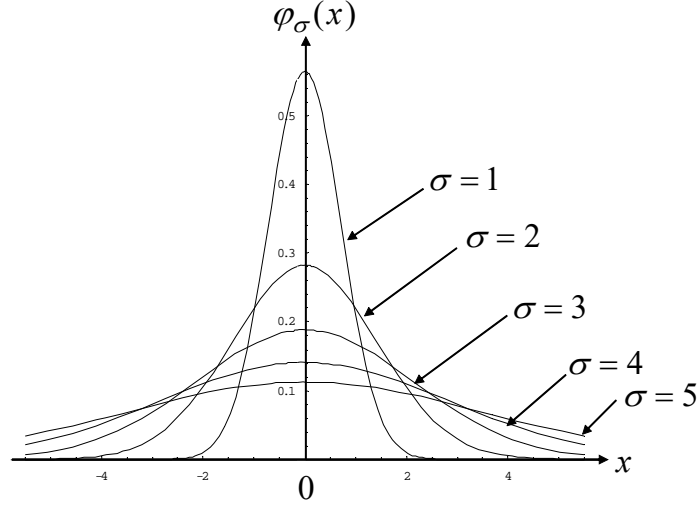**Figure B.2:** *The sequence of Gaussian test functions* $\varphi_\sigma(x)$ $(\sigma\ =\ 1,2,...,5)$.

The Dirac δ-function can be expressed as the limit

$$\delta(x)\ =\ \lim_{\sigma \to 0}\frac{1}{\sqrt{\pi}\sigma}e^{-x^2/\sigma^2}. \tag{B2.9}$$

We recover the sifting property (B2.3) by noting that:

$$\int_{-\infty}^{+\infty}\varphi_\sigma(x)f(x)dx\ =\ \int_{-\infty}^{+\infty}\frac{1}{\sqrt{\pi}\sigma}e^{-x^2/\sigma^2}f(x)dx\ \cong\ f(0)\int_{-\infty}^{+\infty}\frac{1}{\sqrt{\pi}\sigma}e^{-x^2/\sigma^2}dx\ =\ f(0). \tag{B2.10}$$

where we have used the standard Gaussian integral:

$$\int_{-\infty}^{+\infty}e^{-\alpha x^2}dx\ =\ \sqrt{\frac{\pi}{\alpha}}. \tag{B2.11}$$

Taking the limit, Eq. (B2.10) gives:

$$\lim_{\sigma \to 0}\int_{-\infty}^{+\infty}\varphi_\sigma(x)f(x)dx\ =\ \lim_{\sigma \to 0}\int_{-\infty}^{+\infty}\frac{1}{\sqrt{\pi}\sigma}e^{-x^2/\sigma^2}f(x)dx\ =\ \int_{-\infty}^{+\infty}\delta(x)f(x)dx\ =\ f(0). \tag{B2.12}$$

Alternative representations of the Dirac δ-function are:

$$\delta(x) = \lim_{\varepsilon \to 0} \frac{\varepsilon}{\pi(x^2 + \varepsilon^2)} \quad (Lorentzian)$$

$$\delta(x) = \lim_{\tau \to 0} \frac{1}{\tau} sinc\left(\frac{x}{\tau}\right) \quad (sinc).$$

(B2.13)

The δ-function has the following properties:

$$\delta(-x) = \delta(x)$$

$$\delta(ax) = \frac{1}{|a|}\delta(x)$$

$$\delta[(x - a)(x - b)] = \frac{1}{|a - b|}[\delta(x - a) + \delta(x - b)]$$

$$\int_{-\infty}^{+\infty} f(x)\delta'(x - a)dx = -f'(a) = -\left[\frac{df}{dx}\right]_{x=a}$$

$$\delta(f(x)) = \sum_i \frac{1}{\left|\frac{df(x)}{dx}\right|_{x=x_i}}\delta(x - x_i) \quad (where \; f(x_i) = 0).$$

(B2.14)

The Fourier transform of the δ-function is given by:

$$\delta(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\delta(x - x')e^{-ikx}dx = \frac{1}{\sqrt{2\pi}}e^{-ikx'}.$$

(B2.15)

The inverse transform is given by:

$$\delta(x - x') = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\delta(k)e^{ikx}dk = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\frac{1}{\sqrt{2\pi}}e^{-ikx'}e^{ikx}dk = \frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{ik(x-x')}dk.$$

(B2.16)

In three dimensions the δ-function becomes:

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x')\delta(y - y')\delta(z - z').$$

(B2.17)

The sifting property in three dimensions is given by:

$$\int_{\mathbb{R}^3} f(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')d^3r = f(\mathbf{r}').$$

(B2.18)

The Fourier transform of the three-dimensional δ-function is:

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3}\int_{k-space} e^{ik(\mathbf{r} - \mathbf{r}')}d^3k.$$

(B2.19)

Finally, the Heaviside step function $\theta(x)$ is defined as (see Fig. B.3):

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0. \end{cases}$$

(B2.20)

This is related to the Dirac δ-function via:

$$\frac{d\theta(x)}{dx} = \delta(x).$$ (B2.21)

Equation (B2.21) only makes sense within the context of the theory of distributions.
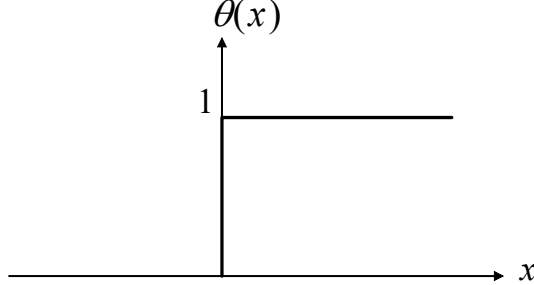

Figure B.3: *The Heaviside step function.*

Appendix C: Volume of a Sphere in D Dimensions

In Example 2.2 we required the volume of a sphere of radius R in D dimensions, which is defined as:

$$V_D(R) = \int\limits_{\substack{\sum_{i=1}^{D} x_i^2 \leq R^2}} \cdots \int dx_1 dx_2 \ldots dx_D.$$ (C2.1)

Letting $\xi_i = x_i/R$, Eq. (C2.1) becomes:

$$V_D(R) = R^D \int\limits_{\substack{\sum_{i=1}^{D} \xi_i^2 \leq 1}} \cdots \int d\xi_1 d\xi_2 \ldots d\xi_D = C_D R^D.$$ (C2.2)

Since $dV_D(R) = C_D D R^{D-1} dR,$ the volume (C2.2) can also be expressed as an integral over hyperspherical shells:

$$V_D(R) = C_D \int_0^R D R^{D-1} dR.$$ (C2.3)

It remains to calculate the constant C_D, which depends only on the dimensionality of the space. To proceed we note that:

$$\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} e^{-(x_1^2 + \ldots + x_D^2)} dx_1 dx_2 \ldots dx_D = \prod_{i=1}^{D} \int_{-\infty}^{+\infty} e^{-x_i^2} dx_i = \pi^{D/2}.$$ (C2.4)

where we have used a standard Gaussian integral[7]. Using Eq. (C2.3) we can write Eq. (C2.4) as:

$$\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} e^{-(x_1^2 + \ldots + x_D^2)} dx_1 dx_2 \ldots dx_D = C_D \int_0^{\infty} e^{-R^2} D R^{D-1} dR = \pi^{D/2}.$$ (C2.5)

---

[7] The standard real-valued Gaussian integral is defined as:

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\alpha x^2} dx = \sqrt{\frac{2\pi}{\alpha}}.$$

Making the following substitution:

$$t = R^2 \quad \Rightarrow \quad dt = 2RdR,$$ (C2.6)

allows us to express Eq. (C2.5) in terms of the gamma function, i.e.,

$$C_D \int_0^\infty e^{-R^2} D R^{D-1} dR = C_D D \int_0^\infty e^{-t} t^{(D-1)/2} \frac{1}{2t^{1/2}} dt$$

$$= C_D \frac{D}{2} \int_0^\infty e^{-t} t^{D/2-1} dt$$ (C2.7)

$$= C_D \frac{D}{2} \Gamma\left(\frac{D}{2}\right),$$

where $\Gamma(z)$ denotes the gamma function. Equating (C2.7) with (C2.5) and re-arranging, we obtain an expression for the constant C_D:

$$C_D = \frac{\pi^{D/2}}{\dfrac{D}{2}\Gamma\left(\dfrac{D}{2}\right)}.$$ (C2.8)

Finally, from Eq. (C2.2) we obatin an expression for the volume of a hypersphere in D dimensions, i.e.,

$$V_D(R) = \frac{\pi^{D/2}}{\dfrac{D}{2}\Gamma\left(\dfrac{D}{2}\right)} R^D,$$ (C2.9)

Exercise C1.1: *Show that the formula for the volume of a hypersphere of radius R, reproduces the expected results for $V_D(R)$, when D = 1, 2, 3.*

References

[1] Huang, K., *Statistical Mechanics* (2nd Edition, John Wiley and Sons, 1987). Chapter 6.
[2] Goldstein, H., *Classical Mechanics* (2nd Edition, Addison-Wesley, 1980). Chapter 9.
[3] Dirac, P. A. M., *The Principles of Quantum Mechanics* (4th Edition, Oxford University Press, 1970). Chapter IV, Sec. 21.