DS 3:
The Microcanonical and Canonical Ensembles

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Important formulae

- **Surface area of $d-$dimensional hypersphere of radius R**

$$S_d(R) = \frac{2\pi^{d/2}}{\Gamma(d/2)} R^{d-1}. \tag{1}$$

- **Gamma function definitions**

$$\begin{aligned} \Gamma(z) &= \int_0^\infty \mathrm{d}u\ u^{z-1} e^{-u} \\ \Gamma(z) &= \int_{-\infty}^\infty \mathrm{d}u\ u^{2z-1} e^{-u^2} = 2\int_0^\infty \mathrm{d}u\ u^{2z-1} e^{-u^2} \end{aligned} \tag{2}$$

- **Gamma function of half-integers**

  It is easy to show that

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}. \tag{3}$$

  We can use this to find the value at other half-integers using

$$\Gamma(z+1) = z\Gamma(z). \tag{4}$$

  For example,

$$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2}. \tag{5}$$

- **Derivatives with respect to T and β**

$$\frac{\partial}{\partial\beta} = -T^2\frac{\partial}{\partial T} \qquad \text{and} \qquad \frac{\partial}{\partial T} = -\beta^2\frac{\partial}{\partial\beta} \tag{6}$$

1 The microcanonical and canonical approaches

1.1 Calculating quantities using a microcanonical approach

In order to calculate quantities in the microcanonical ensemble, the general procedure is as follows:

- First, find the Hamiltonian of a single microstate in terms of the different x_i and p_i present in the problem, writing
$$H(x,p) \equiv H(x_1, x_2, \ldots, x_{3N}, p_1, p_2, \ldots, p_{3N}). \tag{7}$$

- Next, determine the accessible volume of phase space (subject to energy conservation) and calculate the number of states in this volume:
$$\Omega(E,V,N) = \frac{1}{h^{3N}} \int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p\, \delta(E - H(x,p)) = \underbrace{\int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p}_{E<H(x,p)<E+\Delta E}. \tag{8}$$

- If the particles are indistinguishable, add an ad-hoc $N!$ in the denominator:
$$\Omega^{\text{indist}}(E,V,N) = \frac{1}{N!\, h^{3N}} \int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p\, \delta(E - H(x,p)) = \underbrace{\int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p}_{E<H(x,p)<E+\Delta E}. \tag{9}$$

- From $\Omega(E,V,N)$, compute the entropy using
$$S(E,V,N) = \ln \Omega(E,V,N). \tag{10}$$

- From the entropy, thermodynamic quantities can be extracted using
$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \qquad \text{and} \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}} \tag{11}$$

- Using the above equations, we can compute the "thermodynamic" energy in terms of the thermodynamic quantities, writing
$$U = \langle H \rangle = E(S,V,N). \tag{12}$$

- Once we have U, T, and S, we can compute different thermodynamic potentials through Legendre Transformations:
$$\begin{aligned} F(T,V,N) &= U - TS, \\ H(S,P,N) &= U + PV, \\ G(T,P,N) &= U + PV - TS. \end{aligned} \tag{13}$$

1.2 Calculating quantities using a canonical approach

In order to calculate quantities in the canonical ensemble for a system in contact with a thermal heat-bath at some temperature T, the general procedure is as follows:

- First, find the Hamiltonian of a single microstate in terms of the different x_i and p_i present in the problem, writing
$$H(x,p) \equiv H(x_1, x_2, \ldots, x_{3N}, p_1, p_2, \ldots, p_{3N}). \tag{14}$$

- Next, weight every point in phase space (no restrictions) and the Partition Function $Z(T,V,N)$

$$Z(T,V,N) = \frac{1}{h^{3N}} \int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p e^{-\beta H(x,p)} \tag{15}$$

- If the particles are indistinguishable, add an ad-hoc $N!$ in the denominator:

$$Z(T,V,N) = \frac{1}{N!\, h^{3N}} \int \mathrm{d}^{3N}x \int \mathrm{d}^{3N}p e^{-\beta H(x,p)} \tag{16}$$

- From $Z(T,V,N)$, compute the free energy

$$F = -T \ln Z(T,V,N). \tag{17}$$

- From the free energy, thermodynamic quantities can be extracted using

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \text{and} \quad \mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V}} \tag{18}$$

- From the probability distribution

$$\mathcal{P}_m \equiv \frac{e^{-\beta E_m}}{Z}, \tag{19}$$

  we can find other ensemble quantities like

$$U = \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z. \tag{20}$$

- Again, using these quantities we can compute other thermodynamic potentials like H and G, if necessary.
- We can also use the probability distribution to compute the variance in the energy, σ_E^2, which gives us

$$\sigma_E^2 = T^2 C_V. \tag{21}$$

  We could also compute C_V using

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T^2}. \tag{22}$$

2 Lattice of harmonic oscillators

Consider a square lattice of N identical 3-D harmonic oscillators with the same mass m and spring constant k. We will attempt to solve this system statistically.

2.1 A microcanonical approach

(a) Begin by computing the energy of a single microstate.

(b) Constrain the energy and compute $\Omega(E,V,N)$ for this lattice system.

(c) Find the entropy of this system, and use it to determine its temperature and pressure.

(d) Find the equation of state.

(e) Find C_V.

2.2 A canonical approach

(a) As before, begin by computing the energy of a single microstate.

(b) By weighting the integral over phase space, compute $Z(T,V,N)$ for this lattice system.

(c) Find the free-energy of this system, and use it to determine its entropy and pressure.

(d) Find the equation of state.

(e) Find C_V.