The Microcanonical Approach

1. Classical Harmonic Oscillators:

(a) The volume of accessible phase space for a given total energy is proportional to

$$\Omega = \frac{1}{h^N} \int_{\mathcal{H}=E} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N,$$

where the integration is carried out under the condition of constant energy,

$$E = \mathcal{H}\left(\{q_i, p_i\}\right) = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2}\right].$$

Note that Planck's constant h, is included as a measure of phase space volume, so as to make the final result dimensionless.

The surface of constant energy is an ellipsoid in 2N dimensions, whose area is difficult to calculate. However, for $N \to \infty$ the difference between volume and area is subleading in N, and we shall instead calculate the volume of the ellipsoid, replacing the constraint $\mathcal{H} = E$ by $\mathcal{H} \leq E$. The ellipsoid can be distorted into a sphere by a canonical transformation, changing coordinates to

$$q'_i \equiv \sqrt{m\omega}q_i, \quad \text{and} \quad p'_i \equiv \frac{p_i}{\sqrt{m\omega}}.$$

The Hamiltonian in this coordinate system is

$$E = \mathcal{H}(\{q'_i, p'_i\}) = \frac{\omega}{2} \sum_{i=1}^{N} \left(p'^2_i + q'^2_i\right).$$

Since the canonical transformation preserves volume in phase space (the Jacobian is unity), we have

$$\Omega \approx \frac{1}{h^N} \int_{\mathcal{H} \leq E} dq'_1 \cdots dq'_N dp'_1 \cdots dp'_N,$$

where the integral is now over the 2N-dimensional (hyper-) sphere of radius $R = \sqrt{2E/\omega}$. As the volume of a *d*-dimensional sphere of radius R is $S_d R^d/d$, we obtain

$$\Omega \approx \frac{2\pi^N}{(N-1)!} \cdot \frac{1}{2N} \left(\frac{2E}{h\omega}\right)^N = \left(\frac{2\pi E}{h\omega}\right)^N \frac{1}{N!}.$$

The entropy is now given by

$$S \equiv k_B \ln \Omega \approx N k_B \ln \left(\frac{2\pi eE}{Nh\omega}\right).$$

(b) From the expression for temperature,

$$\frac{1}{T} \equiv \left. \frac{\partial S}{\partial E} \right|_N \approx \frac{Nk_B}{E},$$

we obtain the energy

$$E = Nk_BT,$$

and the heat capacity

$$C = Nk_B.$$

(c) The single particle distribution function is calculated by summing over the undesired coordinates and momenta of the other N-1 particles. Keeping track of the units of h used to make phase space dimensionless, gives

$$p(p_1,q_1)dp_1dq_1 = \frac{\int_{(\mathcal{H} \le E_{N-1})} \frac{1}{h^{N-1}} dq_2 \cdots dq_N dp_2 \cdots dp_N}{\int_{(\mathcal{H} \le E)} \frac{1}{h^N} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N} \times \frac{dp_1 dq_1}{h}$$

where $E_{N-1} = E - p_1^2/2m - m\omega^2 q_1^2/2$. Using the results from part (a),

$$p(p_1, q_1) = \frac{\Omega \left(N - 1, E_{N-1}\right)}{h\Omega(N, E)}$$
$$= \frac{\left(\frac{2}{h\omega}\right)^{N-1} \frac{\pi^{N-1}}{(N-1)!} \left(E - \frac{p_1^2}{2m} - \frac{m\omega^2}{2} q_1^2\right)^{N-1}}{h\left(\frac{2}{h\omega}\right)^N \frac{\pi^N}{N!} E^N}$$
$$= \frac{\omega}{2\pi} \frac{N}{E} \left(1 - \frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2} q_1^2}{E}\right)^{N-1}.$$

Using the approximation $(N-1) \sim N$, for $N \gg 1$, and setting $E = Nk_BT$, we have

$$p(p_1, q_1) = \frac{\omega}{2\pi} \frac{N}{Nk_B T} \left(1 - \frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2} q_1^2}{Nk_B T} \right)^N$$
$$\approx \frac{\omega}{2\pi k_B T} \exp\left(-\frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2} q_1^2}{k_B T}\right).$$

Let us denote (p_1, q_1) by (p, q), then

$$p(p,q) = \frac{\omega}{2\pi k_B T} \exp\left(-\frac{p^2}{2mk_B T} - \frac{m\omega^2 q^2}{2k_B T}\right),$$

is a properly normalized product of two Gaussians. The mean kinetic energy is

$$\left\langle \frac{p^2}{2m} \right\rangle = \int p(p,q) \frac{p^2}{2m} dq dp = \frac{k_B T}{2},$$

while the mean potential energy is also

$$\left\langle \frac{m\omega^2 q^2}{2} \right\rangle = \int p(p,q) \frac{m\omega^2 q^2}{2} dq dp = \frac{k_B T}{2}$$

2. Quantum Harmonic Oscillators:

(a) The total energy of the set of oscillators is

$$E = \hbar \omega \left(\sum_{i=1}^{N} n_i + \frac{N}{2} \right).$$

Let us set the sum over the individual quantum numbers to

$$M \equiv \sum_{i=1}^{N} n_i = \frac{E}{\hbar\omega} - \frac{N}{2}.$$

The number of configurations $\{n_i\}$ for a given energy (thus for a given value of M) is equal to the possible number of ways of distributing M energy units into N slots, or of partitioning M particles using N - 1 walls. This argument gives to the number of states as

$$\Omega = \frac{(M+N-1)!}{M! \ (N-1)!},$$

and a corresponding entropy

$$S = k_B \ln \Omega \approx k_B \left[(M+N-1) \ln \left(\frac{M+N-1}{e}\right) - M \ln \frac{M}{e} - (N-1) \ln \left(\frac{N-1}{e}\right) \right].$$

(b) The temperature is calculated by

$$\frac{1}{T} \equiv \left. \frac{\partial S}{\partial E} \right|_N \approx \frac{k_B}{\hbar \omega} \ln \left(\frac{M + N - 1}{M} \right) = \frac{k_B}{\hbar \omega} \ln \left(\frac{\frac{E}{\hbar \omega} + \frac{N}{2} - 1}{\frac{E}{\hbar \omega} - \frac{N}{2}} \right) \approx \frac{k_B}{\hbar \omega} \ln \left(\frac{E + \frac{N}{2} \hbar \omega}{E - \frac{N}{2} \hbar \omega} \right).$$

By inverting this equation, we get the energy

$$E = \frac{N}{2}\hbar\omega \frac{\exp\left(\hbar\omega/k_BT\right) + 1}{\exp\left(\hbar\omega/k_BT\right) - 1} = N\hbar\omega \left[\frac{1}{2} + \frac{1}{\exp\left(\hbar\omega/k_BT\right) - 1}\right],$$

and a corresponding heat capacity

$$C \equiv \left. \frac{\partial E}{\partial T} \right|_{N} = N k_{B} \left(\frac{\hbar \omega}{k_{B}T} \right)^{2} \frac{\exp\left(\hbar \omega / k_{B}T \right)}{\left[\exp\left(\hbar \omega / k_{B}T \right) - 1 \right]^{2}}.$$

(c) The probability that a particular oscillator is in its nth quantum level is given by summing the joint probability over states for all the other oscillators, i.e.

$$\begin{split} p(n) &= \sum_{\{n_{i\neq 1}\}} p(n_{i}) = \frac{\sum_{(E-(n+1/2)\hbar\omega)} 1}{\sum_{(E)} 1} = \frac{\Omega\left(N-1, E-(n+\frac{1}{2})\hbar\omega\right)}{\Omega(N,E)} \\ &= \frac{\left[(M-n)+N-2\right]!}{(M-n)! \cdot (N-2)!} \cdot \frac{M! \cdot (N-1)!}{(M+N-1)!} \\ &\approx \frac{M(M-1) \cdots (M-n+1) \cdot N}{(M+N-1)(M+N-2) \cdots (M+N-n-1)} \\ &\approx N(M+N)^{-n-1} M^{n}, \end{split}$$

where the approximations used are of the from $(I-1) \approx I$, for $I \gg 1$. Hence,

$$p(n) = N \left(\frac{E}{\hbar\omega} - \frac{N}{2} + N\right)^{-n-1} \left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)^n$$
$$= \frac{N}{\frac{E}{\hbar\omega} + \frac{N}{2}} \left(\frac{\frac{E}{\hbar\omega} - \frac{N}{2}}{\frac{E}{\hbar\omega} + \frac{N}{2}}\right)^n,$$

which using

$$\frac{1}{T} = \frac{k_B}{\hbar\omega} \ln\left(\frac{E + \frac{N\hbar\omega}{2}}{E - \frac{N\hbar\omega}{2}}\right), \quad \Longrightarrow \quad \left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}}\right)^n = \exp\left(-\frac{n\hbar\omega}{k_BT}\right),$$

leads to the probability

$$p(n) = \exp\left(-n\frac{\hbar\omega}{k_BT}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{k_BT}\right)\right].$$

(d) As found in part (b),

$$C_{quantum} = Nk_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_BT}\right) - 1\right]^2}.$$

In the high temperature limit, $\hbar \omega / (k_B T) \ll 1$, using the approximation $e^x \approx 1 + x$ for $x \ll 1$, gives

$$C_{quantum} = Nk_B = C_{classical}.$$

At low temperatures, the quantized nature of the energy levels of the quantum oscillators becomes noticeable. In the limit $T \to 0$, there is an energy gap between the ground state and the first excited state. This results in a heat capacity that goes to zero exponentially, as can be seen from the limit $\hbar\omega/(k_B T) \gg 1$,

$$C_{quantum} = Nk_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(-\frac{\hbar\omega}{k_BT}\right)$$

3. Hard Sphere Gas:

(a) The available phase space for N identical particles is given by

$$\Omega = \frac{1}{N!h^{3N}} \int_{H=E} d^3 \vec{q}_1 \cdots d^3 \vec{q}_N d^3 \vec{p}_1 \cdots d^3 \vec{p}_N,$$

where the integration is carried out under the condition,

$$E = \mathcal{H}(\vec{q}_i, \vec{p}_i) = \sum_{i=1}^{N} \frac{p_i^2}{2m}, \quad \text{or} \quad \sum_{i=1}^{N} p_i^2 = 2mE.$$

The momentum integrals are now performed as in an ideal gas, yielding

$$\Omega = \frac{(2mE)^{3N/2-1}}{N!h^{3N}} \cdot \frac{2\pi^{3N}}{\left(\frac{3N}{2} - 1\right)!} \cdot \int d^3\vec{q_1} \cdots d^3\vec{q_N}.$$

The joint integral over the spacial coordinates with excluded volume constraints is best performed by introducing particles one at a time. The first particle can explore a volume V, the second $V - \omega$, the third $V - 2\omega$, etc., resulting in

$$\int d^3 \vec{q_1} \cdots d^3 \vec{q_N} = V(V - \omega)(V - 2\omega) \cdots (V - (N - 1)\omega)$$

Using the approximation $(V - a\omega)(V - (N - a)\omega) \approx (V - N\omega/2)^2$, we obtain

$$\int d^3 \vec{q_1} \cdots d^3 \vec{q_N} \approx \left(V - \frac{N\omega}{2}\right)^N.$$

Thus the entropy of the system is

$$S = k_B \ln \Omega \approx N k_B \ln \left[\frac{e}{N} \left(V - \frac{N\omega}{2} \right) \left(\frac{4\pi m E e}{3Nh^2} \right)^{3/2} \right]$$

(b) We can obtain the equation of state by calculating the expression for the pressure of the gas,

$$\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} \approx \frac{Nk_B}{V - \frac{N\omega}{2}},$$

which is easily re-arranged to,

$$P\left(V - \frac{N\omega}{2}\right) = Nk_BT.$$

Note that the joint effective excluded volume that appears in the above expressions is one half of the total volume excluded by N particles.

(c) The isothermal compressibility is calculated from

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T,N} = \frac{Nk_B T}{P^2 V} > 0,$$

and is explicitly positive, as required by stability constraints.

4. Interacting Rod-Molecules:



(a) Including both forms of entropy, translational and rotational, leads to

$$S = k_{\rm B} \ln \left[\frac{1}{N!} \left(V - \frac{N\Omega(\theta)}{2} \right)^N A(\theta)^N \right] \approx N k_{\rm B} \left[\ln \left(n^{-1} - \frac{\Omega(\theta)}{2} \right) + 1 + \ln A(\theta) \right].$$

(b) The extremum condition $\partial S/\partial \theta = 0$ is equivalent to

$$\frac{\Omega'}{2n^{-1} - \Omega} = \frac{A'}{A},$$

where primes indicate derivatives with respect to θ . Solving for the density gives

$$n = \frac{2A'}{\Omega A' + \Omega' A}.$$

(c) Elementary geometry yields

$$\Omega = l^2 \left(\theta + \sin \theta\right),\,$$

so that the equilibrium condition becomes

$$n = f(\theta) = \frac{2}{l^2} \left[\theta \left(2 + \cos \theta \right) + \sin \theta \right]^{-1},$$

with the function $f(\theta)$ plotted below:



(d) At high densities, $\theta \ll 1$ and the equilibrium condition reduces to

$$N \approx \frac{V}{2\theta l^2};$$

the angle θ is as open as allowed by the close packing. The equilibrium value of θ increases as the density is decreased, up to its "optimal" value $\theta_{\rm c}$ at $n_{\rm c}$, and $\theta (n < n_{\rm c}) = \theta_{\rm c}$. The transition occurs at the minimum of $f(\theta)$, whence $\theta_{\rm c}$ satisfies

$$\frac{d}{d\theta} \left[\theta \left(2 + \cos \theta \right) + \sin \theta \right] = 0,$$

i.e.

$$2\left(1 + \cos\theta_{\rm c}\right) = \theta_{\rm c}\sin\theta_{\rm c}$$
