

PHY452 Problem Set 2

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Problem 1

(a) Consider N quantum harmonic oscillators whose energy is quantized by $\epsilon_i = \hbar\omega \left(n_i + \frac{1}{2}\right)$, where n_i is the quantum energy number of the i -th oscillator and $i = 1, \dots, N$ (hence ϵ_i is the internal energy of the i -th oscillator). The total energy of the system is then the addition of all indistinguishable energies, so we impose the constraint

$$E = \sum_{i=1}^N \hbar\omega n_i + \sum_{i=1}^N \frac{\hbar\omega}{2} = \sum_{i=1}^N \hbar\omega n_i + C \quad (1.1)$$

where C is a constant indicating a constant energy shift, which can be ignored (for now), since the total energy is relative between oscillators.

We begin by determining the discrete multiplicity $\Omega(E, N)$ which corresponds to the number of ways we can deposit $E' \equiv \frac{E}{\hbar\omega} = \sum_{i=1}^N n_i + \frac{C}{\hbar\omega}$ total energy into N oscillators, whose each deposition is n_i for $i = 1, \dots, N$.

We note that the oscillators themselves are distinguishable, but the distribution of the n_j are indistinguishable without exclusion (else each oscillator would receive an equal amount of energy).

We furthermore note that each oscillator obtains a constant amount of energy, $\frac{C'}{\hbar\omega N} = \frac{1}{2}$ for the ground state. This can be neglected as a constant then, since the energy distribution is truly just characterized by $\sum_{j=1}^N n_j$. We then ask how many ways can we choose E' out of $N + E' - 1$ total options to distribute $\hbar\omega$ quanta, that is,

$$\binom{N + E' - 1}{E'} = \frac{(N + E' - 1)!}{E'!(N - 1)!}. \quad (1.2)$$

As before, this is equivalently the multiplicity $\Omega(E', N)$ for the system. We determine the entropy by the definition

$$S(E', N) = k \log \Omega(E', N) \quad (1.3)$$

which becomes

$$S(E', N) = k [\log(N + E' - 1)! - \log E'! - \log(N - 1)!] \quad (1.3)$$

$$N, E' \gg 1 \rightarrow \approx k \left[(N + E' - 1) \log(N + E' - 1) - (N + E' - 1) - E' \log E' + E' - (N - 1) \log(N - 1) - (N - 1) \right] \quad (1.4)$$

$$= k [(N + E' - 1) \log(N + E' - 1) - E' \log E' - (N - 1) \log(N - 1)] \quad (1.5)$$

$$= k \left[E' \log \left(\frac{N + E' - 1}{E'} \right) + (N - 1) \log \left(\frac{N + E' - 1}{N - 1} \right) \right] \quad (1.6)$$

$$N \gg 1 \rightarrow \approx k \left[E' \log \left(\frac{N + E'}{E'} \right) + N \log \left(\frac{N + E'}{N} \right) \right] \quad (1.7)$$

where I have used the $N, E' \gg 1$ approximation twice: first in (1.4) to expand the factorials and second in (1.7) to send $N - 1 \approx N$. The total energy E is related to E' by $E' = \frac{E}{\hbar\omega}$, hence we can further write the entropy as

$$S(E, N) = k \left[\frac{E}{\hbar\omega} \log \left(\frac{N + E/(\hbar\omega)}{E/(\hbar\omega)} \right) + N \log \left(\frac{N + E/(\hbar\omega)}{N} \right) \right]. \quad (1.8)$$

(b) We move forward by determining the energy and heat capacity as a function of the total energy E , where we invoke the thermodynamic relations $\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_N$ and $C = \frac{dE}{dT}$. We find

$$\frac{\partial S}{\partial E} \Big|_N = k \left[\frac{1}{\hbar\omega} \log \left(\frac{N + E/(\hbar\omega)}{E/(\hbar\omega)} \right) - \frac{E}{\hbar\omega} \frac{E/(\hbar\omega)}{N + E/(\hbar\omega)} \frac{N\hbar\omega}{E^2} + N \frac{N}{N + E/(\hbar\omega)} \frac{1}{N\hbar\omega} \right] \quad (1.9)$$

$$= \frac{k}{\hbar\omega} \log \left(\frac{N + E/(\hbar\omega)}{E/(\hbar\omega)} \right) - \frac{Nk}{\hbar\omega} \frac{1}{N + E/(\hbar\omega)} + \frac{Nk}{\hbar\omega} \frac{1}{N + E/(\hbar\omega)} \quad (1.10)$$

$$= \frac{k}{\hbar\omega} \log \left(\frac{N + E/(\hbar\omega)}{E/(\hbar\omega)} \right) \quad (1.11)$$

$$= \frac{1}{T} \quad (1.12)$$

$$\Rightarrow \exp \left[\frac{\hbar\omega}{kT} \right] = \frac{N + E/(\hbar\omega)}{E/(\hbar\omega)} \quad (1.13)$$

$$\Rightarrow N = \frac{E}{\hbar\omega} \left(\exp \left[\frac{\hbar\omega}{kT} \right] - 1 \right) \quad (1.14)$$

$$\Rightarrow E(T, N) = \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (1.15)$$

which is the energy as a function of temperature. As before, the heat capacity is equivalently

$$C(T, N) = \frac{dE}{dT} \quad (1.16)$$

$$= N\hbar\omega \frac{d}{dT} \left[\frac{1}{e^{\hbar\omega/kT} - 1} \right] \quad (1.17)$$

$$= N\hbar\omega \left(-\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \right) \left(-\frac{\hbar\omega}{kT^2} \right) \quad (1.18)$$

$$= \frac{N\hbar^2\omega^2}{kT^2} \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}. \quad (1.19)$$

(c) Next consider an arbitrary oscillator of the system, say the j -th out of N with quantum number n_j and energy $\epsilon_j = \hbar\omega \left(n_j + \frac{1}{2} \right)$ (the scaling of the total energy is unique up to a constant C as mentioned before, but this is not the case for an oscillator, as it's ground state energy must be

greater than zero). This (unconditional) probability of finding the j -th oscillator in the state $|n_j\rangle$ is then the ratio between the relative and total multiplicities:

$$\mathbb{P}(n_j) = \frac{\Omega(E - \epsilon_j, N - 1)}{\Omega(E, N)} \quad (1.20)$$

$$= \frac{(N + E' - n_j - 2)!}{(E' - n_j)!(N - 2)!} \frac{E'!(N - 1)!}{(N + E' - 1)!} \quad (1.21)$$

$$= \frac{(N + E' - n_j - 2)!}{(N + E' - 1)!} \frac{E'!}{(E' - n_j)!} \frac{(N - 1)!}{(N - 2)!} \quad (1.22)$$

This is difficult to simplify because n_j is unknown and can be much greater than one. I have also neglected ground state energies, hence $E' = \sum_{i=1}^N n_i$, and each oscillator always has a baseline energy of $\frac{\hbar\omega}{2}$. For instance, if we want to determine the probability of finding the j -th oscillator in its ground state, we have that

$$\mathbb{P}(0_j) = \frac{(N + E' - 2)!}{(N + E' - 1)!} \frac{E'!}{E'!} \frac{(N - 1)!}{(N - 2)!} \quad (1.23)$$

$$= \frac{N - 1}{N + E' - 1} \quad (1.24)$$

This can also be taken out similarly for $n_j = 1, 2, \dots$ just by cancelling the factorials.

(d) We can lastly consider a chain of N classical harmonic oscillators with Hamiltonian

$$\mathcal{H}_i = \frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2 \quad (1.25)$$

whose momentum and coordinate pairs live in a $2N$ -dimensional phase space, assuming the oscillators are one-dimensional as in the quantum case. The multiplicity of the system is then the volume in the phase space under the constraint of energy conservation,

$$\Omega(E, N) = \int \prod_{i=1}^N dq_i \prod_{j=1}^N dp_j \delta \left(E - \sum_{k=1}^N \left[\frac{p_k^2}{2m} + \frac{1}{2}m\omega^2 q_k^2 \right] \right). \quad (1.26)$$

We proceed by performing a change of variables to reduce the integral into a form which we can impose the constraint. Letting $y_k = \frac{p_k}{\sqrt{2mE}}$ and $x_k = \sqrt{\frac{m\omega^2}{2E}} q_k$, the Jacobian of the transformation is

$$\det D(y_k, x_k) = \det \begin{pmatrix} \sqrt{2mE} & 0 \\ 0 & \sqrt{\frac{2E}{m\omega^2}} \end{pmatrix} \quad (1.27)$$

$$= \frac{2E}{\omega} \quad (1.28)$$

which must be multiplied N times for N variable changes:

$$\prod_{i=1}^N dq_i \prod_{j=1}^N dp_j \longrightarrow \left(\frac{2E}{\omega} \right)^N \prod_{i=1}^N dy_i \prod_{j=1}^N dx_j. \quad (1.29)$$

The reduction of the integral then becomes the surface area of a $2N$ -dimensional sphere of unit radius in both variables (you could perform a second change of variables into polar coordinates by letting $r_i^2 = x_i^2 + y_i^2$ to solve this, but I'll just apply the formula from class)

$$\Omega(E, N) = \left(\frac{2E}{\omega}\right)^N \int \prod_{i=1}^N dy_i \prod_{j=1}^N dx_j \delta\left(1 - \sum_{k=1}^N y_k^2 + x_k^2\right) \quad (1.30)$$

$$= \left(\frac{2E}{\omega}\right)^N \cdot \frac{2N\pi^{2N/2}}{\left(\frac{2N}{2}\right)!} (1)^{2N-1} \quad (1.31)$$

$$= \left(\frac{2\pi E}{\omega}\right)^N \frac{2N}{N!} \quad (1.32)$$

$$= \left(\frac{2\pi E}{\omega}\right)^N \frac{2}{(N-1)!}. \quad (1.33)$$

We can then again calculate the entropy

$$S(E, N) = k \log \Omega(E, N) \quad (1.34)$$

$$= k \left[\log \left(\frac{2\pi E}{\omega}\right)^N + \log 2 + \log N - \log(N!) \right] \quad (1.35)$$

$$= k \left[N \log \left(\frac{2\pi E}{\omega}\right) + \log(N) - N \log N + N \log e + \cancel{\log 2}^0 \right] \quad (1.36)$$

$$= k \left[N \log \left(\frac{2\pi e E}{N}\right) + \log N \right] \quad (1.37)$$

$$= k \log \left[N \left(\frac{2\pi e E}{N}\right)^N \right]. \quad (1.38)$$

Since we desire to calculate the heat capacity, which is $\frac{dE}{dT}$, we first must again find $E(T)$, given that $\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_N$:

$$\frac{\partial S}{\partial E} \Big|_N = k \left(\frac{N}{2\pi e E}\right)^N \frac{1}{N} \cdot N^2 \left(\frac{2\pi e E}{N}\right)^{N-1} \left(\frac{2\pi e}{N}\right) \quad (1.39)$$

$$= k \frac{N^2}{2\pi e E} \left(\frac{N}{2\pi e E}\right)^{N-1} \cdot \frac{2\pi e E}{N} \left(\frac{2\pi e E}{N}\right)^{N-1} \quad (1.40)$$

$$= \frac{Nk}{E} \quad (1.41)$$

$$\implies E = NkT. \quad (1.42)$$

The heat capacity is then simply $C(T) = Nk$, which is constant if N is constant. In comparison to the quantum system, given in equation (1.19), we observe something interesting in the high-temperature limit as $\frac{\hbar\omega}{kT} \rightarrow 0$ (I will re-parametrize this as $x(T)$):

$$\lim_{T \rightarrow \infty} C(T, N) = \lim_{x \rightarrow 0} Nk \frac{x^2 e^x}{(e^x - 1)^2} \quad (1.43)$$

$$\xrightarrow{\text{L'Hopital}} = Nk \lim_{x \rightarrow 0} \frac{2xe^x + x^2e^x}{2(e^x - 1)e^x} \quad (1.44)$$

$$= \lim_{x \rightarrow 0} \frac{2x + x^2}{2(e^x - 1)} \quad (1.45)$$

$$\xrightarrow{\text{L'Hopital}} = Nk \lim_{x \rightarrow 0} \frac{2 + 2x}{2e^x} \quad (1.46)$$

$$= Nk \frac{2}{2} \quad (1.47)$$

$$= Nk \quad (1.48)$$

which is equivalent to the classical heat capacity as found above for a classical chain of N harmonic oscillators. The difference therefore between the classical and quantum system of oscillators is that they behave differently at low temperatures than at high temperatures. This implies that, at low energies, the quantized system more accurately models the behaviour of the oscillators, while the classical system does not.

Problem 2

(a) The macrostate of this system is characterized by the statistical variables $M = (E, N, V)$, and the microstate μ characterized by the Hamiltonian $\mathcal{H}(\mu) = \sum_{k=1}^N \frac{p_k^2}{2m}$, where we neglect the particle-particle hard-hitting interaction potential U_{ij} . We determine the entropy of the system $S(E, N)$ by first determining the volume of density of states in phase space, given by

$$\Omega(E, N) = \int \prod_{i=1}^N d^3 q_i \prod_{j=1}^N d^3 p_j \delta \left(E - \sum_{k=1}^N \frac{p_k^2}{2m} \right). \quad (2.1)$$

We first note that the particles can explore a volume V and are non-interacting, which implies that the integral in $\prod_{j=1}^N d^3 p_j$, whose integrand is the delta function, corresponds to the surface area of a sphere of radius $\sqrt{2mE}$ in $3N$ dimensions whose coordinates are specified by the 3 components of momentum for each particle ($j = 1, \dots, N$). If we recall, the surface area for an n -dimensional sphere of radius r is given by

$$S_n(r) = \frac{2\pi^{n/2}}{\left(\frac{n}{2} - 1\right)!} r^{n-1} \quad (2.2)$$

hence the multiplicity becomes

$$\Omega(E, N) = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (2mE)^{\frac{3N-1}{2}} \int \prod_{i=1}^N d^3 q_i. \quad (2.3)$$

The spatial volume integral becomes more complicated, as the particles of volume b are under the constraint of volume exclusion, thus we should approximate the integral discretely. For a free particle which can explore a volume V , the spatial integral is just V . The next particle, however, can also explore the same volume V but minus the volume b from particle 1. We work our way up to the N -th particle, which must obey the volume exclusion of the $N - 1$ particles before it, making it's volume element $V - (N - 1)b$. We then multiply all of these terms together to obtain the approximation of the integral, which is

$$\int \prod_{i=1}^N d^3 q_i \approx \prod_{i=1}^N (V - (i - 1)b). \quad (2.4)$$

Our goal now is to simplify the product and impose an approximation for large N . For simplicity, let $a \equiv i - 1$ rescale the index, so that the spatial component of the multiplicity becomes

$$\prod_{a=0}^{N-1} (V - ab). \quad (2.5)$$

This product arranges volume elements in ascending order, $(V)(V - b)(V - 2b) \dots (V - (N - 1)b)$ but we can also write the same product in descending order by recognizing that $V = (V - (N - 1 - (N - 1))b)$, so we can write the same product in descending order as

$$\prod_{a=0}^{N-1} (V - (N - a - 1)b) = (V - (N - 1)b)(V - (N - 2)b) \dots (V - b)(V). \quad (2.6)$$

by the commutivity of multiplication. Thus we can square the initial product and write

$$\left(\prod_{i=1}^N (V - (i-1)b) \right)^2 = \prod_{a=0}^{N-1} (V - ab)(V - (N-a-1)b). \quad (2.7)$$

When we consider the large N limit, $N-1 \approx N$ which implies that we can impose the (poor) approximation that $(V - ab)(V - (N-a)b) \approx \left(V - \frac{Nb}{2} \right)^2$ and thus, when taking the square root, yields

$$\prod_{i=1}^N (V - (i-1)b) \approx \prod_{a=0}^N \left(V - \frac{Nb}{2} \right) = \left(V - \frac{Nb}{2} \right)^N. \quad (2.8)$$

We therefore have the multiplicity under such approximation (and the $N \gg 1$ limit),

$$\Omega(E, N) \approx \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} (2mE)^{\frac{3N}{2}} \left(V - \frac{Nb}{2} \right)^N \quad (2.9)$$

and hence the entropy $S(E, N) = k \log \Omega(E, N)$:

$$S(E, N) = k \left[\log 2^{\approx 0} + \frac{3N}{2} \log \pi - \log \left(\frac{3N}{2} \right)! + \frac{3N}{2} \log(2mE) + N \log \left(V - \frac{Nb}{2} \right) \right] \quad (2.10)$$

$$\approx k \left[\frac{3N}{2} \log \pi - \frac{3N}{2} \log \left(\frac{3N}{2} \right) + \frac{3N}{2} \log e + \frac{3N}{2} \log(2mE) + N \log \left(V - \frac{Nb}{2} \right) \right] \quad (2.11)$$

$$= k \left[\frac{3N}{2} \log \left(\frac{4\pi emE}{3N} \right) + N \log \left(V - \frac{Nb}{2} \right) \right] \quad (2.12)$$

$$= kN \log \left[\left(V - \frac{Nb}{2} \right) \left(\frac{4\pi emE}{3N} \right)^{3/2} \right] \quad (2.13)$$

Where we have imposed the logarithm rules to simplify the expression.

(b) We now determine the equation of state from the entropy found in (2.13). We return to the first law of thermodynamics,

$$dE = dQ + dW \quad (2.14)$$

$$= TdS - PdV \quad (2.15)$$

from which, at fixed energy and particle number N , we have that $\frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{E, N}$. Taking the derivative of $S(E, N)$ in (2.13) by V implies

$$\frac{\partial S}{\partial V} \Big|_{E, N} = \frac{kN}{\left(V - \frac{Nb}{2} \right) \left(\frac{4\pi emE}{3N} \right)^{3/2}} \cdot \left(\frac{4\pi emE}{3N} \right)^{3/2} \quad (2.16)$$

$$= \frac{kN}{V - \frac{Nb}{2}} \quad (2.17)$$

$$= \frac{P}{T} \quad (2.18)$$

and therefore the equation relating P, T and V altogether is

$$P \left(V - \frac{Nb}{2} \right) = NkT \quad (2.17)$$

which obeys the ideal gas limit as $b \rightarrow 0$.

(c) We lastly consider the isothermal compressibility of the gas $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$ from the previous equation of state. At fixed T (and N), the volume as a function of P is given by

$$V = \frac{NkT}{P} + \frac{Nb}{2} \quad (2.18)$$

from (2.17). The change in volume with respect to pressure is then $\frac{\partial V}{\partial P} = -\frac{NkT}{P^2}$, which is always negative since $N, k, T, P^2 > 0$. This implies that as the pressure of the gas increases, the volume should decrease to keep T and N constant. But this altogether implies that the isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T \quad (2.19)$$

$$= \frac{NkT}{P^2 V} \quad (2.20)$$

which is always a positive quantity. This is equivalently the same compressibility as that of an ideal gas, and refers to the instantaneous volume change in response to any change in pressure, which makes sense because as the gas is compressed it's volume wants to increase.