0.1　Homework 3

0.1.1　1-D Harmonic Oscillators

Derive

1. **an asymptotic expression for the number of ways in which a given energy E can be distributed among a set of N one-dimensional harmonic oscillators, the energy eigenvalues of the oscillators being $\left(n + \dfrac{1}{2}\right)\hbar\omega; n = 0, 1, 2, \cdots$;**

   The ground state energy for N oscillators is

   $$E_{\text{ground}} = N \cdot \frac{1}{2}\hbar\omega = \frac{N}{2}\hbar\omega.$$

   So the excitation energy above the ground state is

   $$E^* = E - E_{\text{ground}} = E - \frac{N}{2}\hbar\omega.$$

   So we need to distribute E^* among N oscillators, or

   $$\sum_{i=1}^{N} = M, \quad \text{where } M = \frac{E^*}{\hbar\omega} = \frac{E}{\hbar\omega} - \frac{N}{2}.$$

   So the number of ways, or the microstates, is given by the combinatorics

   $$\Omega = \binom{M + N - 1}{N - 1}$$

   With the Stirling approximation, we have

   $$\ln\Omega \approx (M + N)\ln(M + N) - M\ln M - N\ln N - \frac{1}{2}\ln(2\pi MN)$$

   $$\Omega \approx \frac{(M + N)^{M+N}}{M^M N^N}\sqrt{\frac{M + N}{2\pi MN}}$$

   Apply $M = \dfrac{E}{\hbar\omega} - \dfrac{N}{2}$ to the above equation, we have

   $$\Omega \approx \frac{\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)^{\frac{E}{\hbar\omega} + \frac{N}{2}}}{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)^{\frac{E}{\hbar\omega} - \frac{N}{2}} N^N}\sqrt{\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{2\pi\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)N}}$$

   If $\dfrac{E}{\hbar\omega} \gg N$, the number of states can be approximated as

   $$\Omega \approx \frac{1}{N!}\left(\frac{E}{\hbar\omega}\right)^N.$$

2. **and the corresponding expression for the "volume" of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor ω_0 is precisely h^N.**

   For a one-dimensinal harmonic oscillator with energy E_i, its Hamiltonian is a elliptic curve:

   $$H_i = \frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 x_i^2 = E_i$$

   So the phase space volume is given by the integral of the Hamiltonian over the energy surface:

   $$\Gamma_i = \iint H_i \mathrm{d}p_i \mathrm{d}x_i = \pi \cdot \sqrt{\frac{2E_i}{m}} \cdot m \cdot \frac{1}{\omega}\sqrt{\frac{2E_i}{m}} = \frac{2\pi E_i}{\omega}$$

So the total phase space volume is given by

$$\Gamma = \int_{\sum E_i \leq E} \prod_{i=1}^{N} \frac{2\pi E_i}{\omega} \mathrm{d}E_1 \cdots \mathrm{d}E_N = \frac{(2\pi/\omega)^N E^N}{N!} = \frac{1}{N!} \left(\frac{2\pi E}{\omega} \right)^N$$

The classical microstate is

$$\Omega = \frac{1}{N!} \left(\frac{E}{\hbar\omega} \right)^N = \frac{1}{N!} \left(\frac{2\pi E}{h\omega} \right)^N = \frac{1}{h^N} \Gamma$$

So we get

$$\boxed{\omega_0 = h^N}$$

3. **On the basis of Problem 1, derive the entropy and temperature. Comment on the result.**

   Since the number of microstates Ω is given by

   $$\Omega \approx \frac{(\frac{E}{\hbar\omega} + \frac{N}{2})^{\frac{E}{\hbar\omega} + \frac{N}{2}}}{(\frac{E}{\hbar\omega} - \frac{N}{2})^{\frac{E}{\hbar\omega} - \frac{N}{2}} N^N} \sqrt{\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{2\pi(\frac{E}{\hbar\omega} - \frac{N}{2})N}},$$

   we can calculate the entropy S using the Boltzmann entropy formula with Stirling approximation:

   $$\boxed{S = k_B \left[\left(\frac{E}{\hbar\omega} + \frac{N}{2} \right) \ln \left(\frac{E}{\hbar\omega} + \frac{N}{2} \right) - \left(\frac{E}{\hbar\omega} - \frac{N}{2} \right) \ln \left(\frac{E}{\hbar\omega} - \frac{N}{2} \right) - N \ln N \right]}$$

   With the thermodynamic connection $\frac{1}{T} = \frac{\partial S}{\partial E}$, we have

   $$\frac{1}{T} = \frac{k_B}{\hbar\omega} \ln \left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}} \right)$$

   $$\Rightarrow \boxed{T = \frac{\hbar\omega}{k_B} \left[\ln \left(\frac{E + \frac{N}{2}\hbar\omega}{E - \frac{N}{2}\hbar\omega} \right) \right]^{-1}}$$

   Comments:

   - Role of Zero-Point Energy: The derived expressions explicitly include the zero-point energy $\frac{1}{2}\hbar\omega$ per oscillator, a quantum mechanical feature absent in classical treatments. This ensures that the total energy E cannot drop below $\frac{N\hbar\omega}{2}$, even at absolute zero, preserving the quantum ground state. The entropy and temperature formulas inherently account for this residual energy, distinguishing them from classical results.

   - High-Temperature Classical Limit: At high energies $E \gg \frac{N\hbar\omega}{2}$, the zero-point energy becomes negligible. The entropy and temperature expressions reduce to classical results, aligning with the correspondence principle. For instance, the logarithmic terms simplify, leading to a linear relationship between E and T, consistent with the classical equipartition theorem.

   - Phase Space Quantization: The phase space volume $\Gamma \propto \left(\frac{E}{\omega} \right)^N$ and its conversion to quantum states via h^N underscores Planck's constant h as the fundamental unit of phase space volume. This bridges classical and quantum descriptions, emphasizing h^N as the natural measure for counting microstates in quantum systems.

   - Validity of Approximations: The use of Stirling's approximation assumes $N \gg 1$, which is valid for macroscopic systems. The derived entropy S exhibits logarithmic scaling with energy, characteristic of systems with extensive degrees of freedom. This ensures consistency with thermodynamic expectations for large N.

   - Temperature-Energy Relationship: The inverse logarithmic dependence of T on E reflects how energy distribution among oscillators governs thermal behavior. At low energies, quantum effects dominate, while high energies recover classical proportionality between E and T.

0.1.2 Helmholtz Free Energy

Making use of the fact that the Helmholtz free energy $A(N, V, T)$ of a thermodynamic system is an extensive property of the system, show that

$$N \left(\frac{\partial A}{\partial N} \right)_{V,T} + V \left(\frac{\partial A}{\partial V} \right)_{N,T} = A$$

[Note that this result implies the well-known relationship: $N\mu = A + PV (\equiv G)$.]

Since the Helmholtz free energy $A(N, V, T)$ satisfies the scaling relation

$$A(\lambda N, \lambda V, T) = \lambda A(N, V, T) \quad \text{for any } \lambda > 0,$$

so $A(N, V, T)$ is homogeneous of degree 1 in N and V. So apply the Euler theorem for homogeneous functions to show that

$$N \left(\frac{\partial A}{\partial N} \right)_{V,T} + V \left(\frac{\partial A}{\partial V} \right)_{N,T} = A(N, V, T).$$

Since the chemical potential μ is defined as $\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$, and the pressure P is defined as $P = - \left(\frac{\partial A}{\partial V} \right)_{N,T}$, so we have the relation between the Helmholtz free energy and the chemical potential and pressure:

$$N\mu + V(-P) = A \Rightarrow N\mu = A + PV \equiv G.$$

0.1.3 Dilute Hard Sphere Gas

Assume there's a dilute hard sphere system, where exists N hard spheres with radius a, or volume $\omega_e = \frac{4}{3}\pi(2a)^3$. The system is at thermal equilibrium at temperature T. The total energy is E, and the system is in a container with volume V. Derive

1. **entropy $S(E, V)$. [Hint: For an n-dimensional sphere with radius R, its $(n-1)$-dimensional sphere area $S^{(n-1)}$ is Area $= \dfrac{2\pi^{n/2}}{\Gamma(n/2)} R^{n-1} s$]**

   The number of microstates is given by

   $$\Omega(E, V, N) = \frac{1}{N! h^{3N}} \int_{\mathcal{D}} \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, \delta \left(E - \sum_{i=1}^{N} \frac{p_i^2}{2m} \right), \quad \text{where } \mathcal{D} : |\vec{q}_i - \vec{q}_j| \geq 2a, \quad \forall i < j.$$

   At dilute gas limit, the free volume can be consideres as the rest volume:

   $$V_{\text{free}} \approx V - \frac{N\omega_e}{2}.$$

   So for the real space integral part, we have

   $$\int_{\mathcal{D}} \mathrm{d}^{3N}q \approx \left(V - \frac{N\omega_e}{2} \right)^N.$$

   Since the energy consists of the kinetic energy only, as

   $$E = \sum_{i=1}^{N} \frac{p_i^2}{2m},$$

   the momentum integral part can be calculated:

   $$\int \mathrm{d}^{3N}p \, \delta \left(E - \sum_{i=1}^{N} \frac{p_i^2}{2m} \right) = \int \mathrm{d}\Omega_{3N} \int_0^{\infty} \mathrm{d}p \, p^{3N-1} \delta(E - \frac{p^2}{2m}), \quad p = \sqrt{\sum_{i=1}^{3N} p_i^2}$$

where $\mathrm{d}\Omega_{3N}$ is the angle interal part of the $3N$-dimensional sphere. As the hint gives, we have

$$S_{3N-1}(R) = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} R^{3N-1}$$

Let $R = \sqrt{2mE}$, and remember that $\delta(E - \frac{p^2}{2m}) = \frac{m}{p}\delta(p - \sqrt{2mE})$, we have

$$\int \mathrm{d}^{3N}p\,\delta\left(E - \sum_{i=1}^{N}\frac{p_i^2}{2m}\right) \propto (2mE)^{3N/2-1}$$

So the number of microstates is given by

$$\Omega(E,V,N) \approx \frac{1}{N!h^{3N}}\left(V - \frac{N\omega_e}{2}\right)^N \frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1}$$

So the Boltzmann entropy is given by

$$S(E,V,N) = k_B\left\{-\ln N! - 3N\ln h + N\ln\left(V - \frac{N\omega_e}{2}\right) + \left(\frac{3N}{2} - 1\right)\ln E + \frac{3N}{2}\ln(2\pi m) - \ln\Gamma\left(\frac{3N}{2}\right)\right\}$$

With thermodynamic limit $N \to \infty$ and Stirling approximation $\ln N! \approx N\ln N - N$, we have

$$S(E,V,N) \sim Nk_B\ln\left(V - \frac{N\omega_e}{2}\right) + \frac{3N}{2}k_B\ln E + \cdots$$

2. **guess the equation of state.**

   Since only the volume changed from V to $V - \dfrac{N\omega_e}{2}$, the state equation can be compared with the ideal gas one:

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

3. **calculate the equation of state.**

   With the thermodynamic relation $\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial E}\right)_{V,N}$ and $\dfrac{P}{T} = \left(\dfrac{\partial S}{\partial V}\right)_{E,N}$, we have

   $$S(E,V,N) \sim NK_B\ln\left(V - \frac{N\omega_e}{2}\right) + \cdots$$
   $$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \sim \frac{Nk_B}{V - \frac{N\omega_e}{2}}\cdots$$

   So we have the equation of state for the dilute hard sphere system:

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