Quantum Monatomic Ideal Gas and the Classical Limit

- **Introduction:** Now that we have described the way identical particles are treated in quantum theory, we can look at the effects of quantum statistics on the equation of state for an ideal gas. If we start from the quantum partition function, we can write it as a series of terms in which the first one is the classical partition function (which will turn out to be a good approximation in the low-density and/or high-temperature limit) and the other ones are quantum corrections, that can be calculated systematically.

**Canonical Partition Function**

- **Setup:** Let us consider an ideal gas of $N$ identical structureless particles at temperature $T$. We will use the coordinate representation, with plane waves $\phi_\vec{k}(\vec{r})$ labelled by wave vectors $\vec{k}$ as basis for single-particle states, and associate an $N$-particle state $\psi_\{\vec{k}\}^{(N)}(\vec{r}_1, ..., \vec{r}_N) = \langle \vec{r}_1, ..., \vec{r}_N | \vec{k}_1, ..., \vec{k}_N \rangle$ to each permutation equivalence class $\{ \vec{k} \} = [\vec{k}_1, ..., \vec{k}_N]$ of $N$ wave vectors. Then we have to calculate

$$Z_\text{c}^{(qm)} = \text{tr} e^{-\beta \hat{H}} = \int_V d^3N \rho \langle \vec{r}_1, ..., \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1, ..., \vec{r}_N \rangle$$

$$= \sum_{\{ \vec{k} \}} \sum_{\{ \vec{k} \}'} \int_V d^3N \rho \langle \vec{r}_1, ..., \vec{r}_N | \vec{k}_1, ..., \vec{k}_N \rangle \langle \vec{k}_1, ..., \vec{k}_N | e^{-\beta \hat{H}} | \vec{k}_1, ..., \vec{k}_N \rangle \langle \vec{k}_1, ..., \vec{k}_N | \vec{r}_1, ..., \vec{r}_N \rangle$$

$$= \frac{1}{N!} \sum_{\{ \vec{k} \}} e^{-\beta E(\vec{k}_1, ..., \vec{k}_N)} \sum_{P,P',P_N} (\pm 1)^{\{P+P'\}} \int_V d^3N \rho \phi_{\vec{k}_1}(\vec{r}_{P_1}) \phi_{\vec{k}_N}(\vec{r}_{P_N}) \hat{\phi}_{\vec{k}_1}(\vec{r}_{P_1}) \hat{\phi}_{\vec{k}_N}(\vec{r}_{P_N}) \cdots$$

where we have used the completeness relation $\sum_{\{ \vec{k} \}} | \vec{k}_1, ..., \vec{k}_N \rangle < \vec{k}_1, ..., \vec{k}_N | = 1$, and the fact that $\langle \vec{k}_1, ..., \vec{k}_N |$ is an eigenstate of $\hat{H}$. In a rectangular box of size $V = L_1L_2L_3$ and with periodic boundary conditions, the allowed values for the $i$th component of each wave vector are $k_i = (2\pi/L_i)n$, where $n \in \mathbb{Z}$ is any integer. Therefore, an $N$-tuple of wave vectors is labelled by $3N$ integers $\vec{n}_i$, $i = 1, ..., N$.

- **Approximation:** We would like to replace the sum over $\vec{k}_i$'s by an integral, but that sum is over equivalence classes $\{ \vec{k} \}$ rather than sets of $N$ independent wave vectors. However, in the approximation in which the discrete set of values for $\vec{k}_i$ can be approximated by a continuous range of integration, each equivalence class $\{ \vec{k} \}$ corresponds to $N!$ distinct $N$-tuples (this would not be true for equivalence classes containing two or more equal $\vec{k}_i$s, but those are of measure zero in the continuum approximation). We can therefore replace

$$\sum_{\{ \vec{k} \}} (...) = \sum_{\{ \vec{n} \}} (...) \approx \frac{1}{N!} \int_{\mathbb{R}} d^3N n (...) = \frac{1}{N!} \left( \frac{V}{2\pi \hbar \pi} \right)^N \int_{\mathbb{R}} d^3N p (...) .$$

This approximation works well in the approximation of large box size and high temperature.

- **Calculation:** The argument of the integral over the $\vec{r}_i$ in $Z_\text{c}^{(qm)}$ is a product of factors of the form

$$\phi_{\vec{k}_i}^{(P)}(\vec{r}_{P_i}) \phi_{\vec{k}_i}^{(P')}^{(P)}(\vec{r}_{P_{P_i}}) = V^{-1} e^{i \vec{k}_i \cdot (\vec{r}_{P_i} - \vec{r}_{P_{P_i}})} ,$$

whose behavior is very different depending on whether $\vec{r}_{P_i} = \vec{r}_{P_{P_i}}$ or not, so the result of the integration depends on how many factors have $\vec{r}_{P_i} = \vec{r}_{P_{P_i}}$, i.e., how different the two permutations $P$ and $P'$ are. So, if we introduce a relative permutation $P''$ by setting $P'' := PP'$, the argument of the sum turns out to depend only on $P''$ and the sum over $P$ simply produces a factor $N!$ (since $[2P + P''] = [P'']$ and $d^3N \rho = d^3N P''$),

$$Z_\text{c}^{(qm)} = \frac{1}{(N!)^2} \left( \frac{V}{2\pi \hbar \pi} \right)^N \int_{\mathbb{R}} d^3N p e^{-\beta \sum (\vec{r}^2)/2m} \sum_{P,P'' \in P_N} (\pm 1)^{\{P''\}} \int_V d^3N \rho \prod_{i=1}^{N} \frac{1}{V N} \sum_{P,P'' \in P_N} (\pm 1)^{\{P''\}} \int_V d^3N \rho \prod_{i=1}^{N} e^{i \vec{k}_i \cdot (\vec{r}_i - \vec{r}_{P_{P_i}})}$$

$$= \frac{1}{N! \hbar^{3N}} \int_{\mathbb{R}} d^3N p e^{-\beta \sum (\vec{r}^2)/2m} \sum_{P,P'' \in P_N} (\pm 1)^{\{P''\}} \int_V d^3N \rho \prod_{i=1}^{N} e^{i \vec{k}_i \cdot (\vec{r}_i - \vec{r}_{P_{P_i}})}$$

$$= \frac{1}{N! \hbar^{3N}} \sum_{P,P'' \in P_N} (\pm 1)^{\{P''\}} \prod_{i=1}^{N} \int_{\mathbb{R}} d^3r_i \int_{\mathbb{R}} d^3p_i \exp\{-\beta \vec{p}^2_i/2m + i \vec{p}_i \cdot (\vec{r}_i - \vec{r}_{P_{P_i}}) / \hbar \} .$$
Now “complete the square” in the exponent inside the last integral to get, for each $i$, three Gaussian integrals that evaluate to $(2\pi mk_B T)^{3/2}$ and an extra factor $\exp\left(-\frac{m/2\hbar^2}{(r_i - r_j_{\infty})^2}\right)$. Renaming $P^\prime$, the result is

$$Z_c^{(qm)} = \frac{1}{N!\lambda^{3N}} \sum_{P \in \mathcal{P}_N} (\pm 1)^{|P|} \prod_{i=1}^{N} \int_{V} d^3r_i \ f(r_i - r_{P_i}) , \quad f(r) := e^{-\frac{m/2\hbar^2}{r^2}} = e^{-\pi r^2/\lambda^2} ,$$

where $\lambda := h/\sqrt{2\pi mk_B T}$, as in the classical case, and $f$ is a fast decreasing function of the magnitude of $\vec{r}$.

- **Expansion**: Given a permutation $P$ in the final expression for $Z_c^{(qm)}$, for each $i$ such that $P_i = i$ the value of the integral $\int d^3r_i \ f(r_i - r_{P_i}) = \int d^3r_i = V$, so the identity permutation contributes a term $V^N$ to the sum. The next simplest permutations only switch two positions $i$ and $j$, for which the integrals are

$$\int_{V} d^3r_i \int_{V} d^3r_j \ f^2(r_i - r_j) = \int_{V} d^3r_i \int_{V} d^3r_j \ e^{-2\pi(r_i - r_j)^2/\lambda^2} \approx V \int_{\mathbb{R}^3} d^3r e^{-2\pi r^2/\lambda^2} = \frac{V\lambda^3}{2\sqrt{2}} .$$

Since there are $\binom{N}{2}$ such permutations, together they contribute a term $\pm \binom{N}{2} V^{N-2} (V\lambda^3)^{2-3/2}$, proportional to $(N-1)V^N (\rho\lambda^3)$, to the overall sum over $P \in \mathcal{P}_N$. In general, terms with more $f_{ij}$'s in the expansion

$$Z_c^{(qm)} = \frac{1}{N!\lambda^{3N}} \int_{V} d^3r \left[ 1 \pm \sum_{i<j} f(r_i - r_j) f(r_j - r_i) + \sum_{i<j<k} f(r_i - r_j) f(r_j - r_k) f(r_k - r_i) \pm \ldots \right]$$

contribute terms with higher powers of the degeneracy parameter $\delta := N\lambda^3/V = \rho\lambda^3$ to the sum. Since the approximations made assume that this parameter is small, we can expand $Z_c^{(qm)}$ in powers of $\delta$. These are related to the number of $f_{ijk}$'s in the sum over permutations, so we already have the two leading terms,

$$Z_c^{(qm)} = \frac{V^N}{N!\lambda^{3N}} + \frac{1}{N!\lambda^{3N}} \binom{N}{2} V^{N-2} \frac{V\lambda^3}{2^{3/2}} + \ldots = Z_c^{(cm)} \left( 1 \pm \frac{N-1}{2^{5/2}} \rho\lambda^3 + \ldots \right) .$$

The first term, arising from the identity permutation, is the classical partition function, including the $N!$ in the denominator, and the first quantum correction, arising from 2-particle exchanges, becomes increasingly important at large densities and low temperatures.

**Quantum Corrections to Ideal-Gas Thermodynamics**

- **Idea**: The physical meaning of the first quantum correction can be seen either by deriving an effective statistical interparticle potential (see the P&B book, for example), or by looking at the $p$ equation of state.

- **Free energy**: All thermodynamic quantities are evaluated using $F$, so we start with

$$F = -k_B T \ln Z_c^{(qm)} = -k_B T \ln \left[ Z_c^{(cm)} \left( 1 \pm \frac{N-1}{2^{5/2}} \rho\lambda^3 + \ldots \right) \right] = F^{(cm)} - k_B T \ln \left( 1 \pm \frac{N-1}{2^{5/2}} \rho\lambda^3 + \ldots \right) \approx F^{(cm)} + k_B T \frac{N-1}{2^{5/2}} \rho\lambda^3 = F^{(cm)} + \frac{N(N-1)}{2} \left( \frac{\pi}{m} \right)^{3/2} \frac{\hbar^3}{V^{2} k_B T} ,$$

- **Pressure equation of state**: From the general expression for $p$ in terms of $F$,

$$p = \left. \frac{\partial F}{\partial V} \right|_{T,N} = p^{(cm)} + \frac{N(N-1)}{2} \left( \frac{\pi}{m} \right)^{3/2} \frac{\hbar^3}{V^{2} k_B T} + \ldots = k_B T \left( 1 \pm \frac{\lambda^3 N}{2^{5/2} V} + \ldots \right) ,$$

from which we can read off the second virial coefficient $B_2(T) = \mp \lambda^3/2^{5/2}$, and we see that bosons have a negative quantum correction to the pressure and fermions have a positive one, purely as a consequence of quantum statistics and even in the absence of interactions.

**Reading**

- **Pathria & Beale**: Ch 5.
- **Other texts**: Halley, Ch 5; Plischke & Bergersen, Sec 2.4; Reif, Sec 9.8; Schwabl, Secs 4.2–4.3.