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:* Consider an ideal gas of N identical structureless, non-interacting 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 $\psi_{\{\vec k\}}(\vec r_1,...,\vec r_N) = \langle \vec r_1,...,\vec r_N|\vec k_1,...,\vec k_N\rangle$ to each permutation equivalence class $\{\vec k\} = [\vec k_1,...,\vec k_N]$ of N wave vectors. Then we have to calculate

$$\begin{aligned}
Z_{\rm c}^{\rm (qm)} &= {\rm tr}\,{\rm e}^{-\beta\hat H} = \int_V {\rm d}^{3N}r\,\langle \vec r_1,...,\vec r_N|\,{\rm e}^{-\beta\hat H}\,|\,\vec r_1,...,\vec r_N\rangle \\
&= \sum_{\{\vec k\}}\sum_{\{\vec k\}'}\int_V {\rm d}^{3N}r\,\langle \vec r_1,...,\vec r_N|\,\vec k_1,...,\vec k_N\rangle\,\langle \vec k_1,...,\vec k_N|\,{\rm e}^{-\beta\hat H}\,|\,\vec k'_1,...,\vec k'_N\rangle\,\langle \vec k'_1,...,\vec k'_N|\,\vec r_1,...,\vec r_N\rangle \\
&= \frac{1}{N!}\sum_{\{\vec k\}}{\rm e}^{-\beta E(k_1,...,k_N)}\sum_{P,P'\in\mathcal{P}_N}(\pm1)^{[P+P']}\int_V {\rm d}^{3N}r\,\phi_{\vec k_1}(\vec r_{P1})\cdots\phi_{\vec k_N}(\vec r_{PN})\,\phi^*_{\vec k_1}(\vec r_{P'1})\cdots\phi^*_{\vec k_N}(\vec r_{P'N})\;,
\end{aligned}$$

where we have used the completeness relation $\sum_{\{\vec k\}}|\vec k_1,...,\vec k_N\rangle\,\langle\vec k_1,...,\vec k_N| = \mathbf{1}$, and the fact that $|\vec k_1,...,\vec k_N\rangle$ 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 ith component of each wave vector are $k_i = (2\pi/L_i)\,n$, where $n\in\mathbf{Z}$ is any integer. Therefore, an N-tuple of wave vectors is labelled by $3N$ integers $\vec n_I$, $I = 1,...,N$. Notice that for both types of quantum statistics this does not equal $Z = Z_1^N/N!$, the value we would find using Boltzmann statistics.

• *Approximation:* We would like to replace the sum over the $\vec k_I$ by an integral, but the 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 replaced 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

$$\sum_{\{\vec k\}}(...) = \sum_{\{\vec n\}}(...) \approx \frac{1}{N!}\int_{\rm I\!R}{\rm d}^{3N}n\,(...) = \frac{1}{N!}\,\frac{V^N}{(2\pi\hbar)^{3N}}\int_{\rm I\!R}{\rm d}^{3N}p\,(...)\;.$$

This approximation works well in the large box size ($V\to\infty$) and high temperature ($T\to\infty$) limit.

• *Calculation:* The argument of the integral over the $\vec r_I$ in $Z_{\rm c}^{\rm (qm)}$ is a product of factors of the form

$$\phi_{\vec k_I}(\vec r_{PI})\,\phi^*_{\vec k_I}(\vec r_{P'I}) = \frac{1}{V}\,{\rm e}^{{\rm i}\,\vec k_I\cdot(\vec r_{PI}-\vec r_{P'I})}\;,$$

whose behavior is very different depending on whether $\vec r_{PI} = \vec r_{P'I}$ or not, so the result of the integration depends on how many factors have $\vec r_{PI} = \vec r_{P'I}$, 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 ${\rm d}^{3N}r = {\rm d}^{3N}Pr$),

$$\begin{aligned}
Z_{\rm c}^{\rm (qm)} &= \frac{1}{(N!)^2}\,\frac{V^N}{(2\pi\hbar)^{3N}}\int_{\rm I\!R}{\rm d}^{3N}p\;{\rm e}^{-\beta\,\Sigma_I p_I^2/2m}\sum_{P,P''\in\mathcal{P}_N}(\pm1)^{[P'']}\int_{V^N}{\rm d}^{3N}r\,\frac{1}{V^N}\prod_{I=1}^N{\rm e}^{{\rm i}\,\vec k_I\cdot(\vec r_I-\vec r_{P''I})} \\
&= \frac{1}{N!\,h^{3N}}\int_{\rm I\!R}{\rm d}^{3N}p\;{\rm e}^{-\beta\,\Sigma_I p_I^2/2m}\sum_{P''\in\mathcal{P}_N}(\pm1)^{[P'']}\int_{V^N}{\rm d}^{3N}r\,\prod_{I=1}^N{\rm e}^{{\rm i}\,\vec k_I\cdot(\vec r_I-\vec r_{P''I})} \\
&= \frac{1}{N!\,h^{3N}}\sum_{P''\in\mathcal{P}_N}(\pm1)^{[P'']}\prod_{I=1}^N\int_V{\rm d}^3r_I\int_{\rm I\!R}{\rm d}^3p_I\;\exp\big\{-\beta\,p_I^2/2m + {\rm i}\,\vec p_I\cdot(\vec r_I-\vec r_{P''I})/\hbar\big\}\;.
\end{aligned}$$

Now "complete the square" in the exponent inside the last integral to get, for each I, three Gaussian integrals that evaluate to $(2\pi m k_{\rm B} T)^{3/2}$ and an extra factor $\exp\{-(m/2\beta\hbar^2)(\vec r_I - \vec r_{P''I})^2\}$. Renaming P'', the result is

$$Z_{\rm c}^{\rm (qm)} = \frac{1}{N!\,\lambda^{3N}} \sum_{P\in\mathcal{P}_N} (\pm 1)^{[P]} \prod_{I=1}^N \int_V {\rm d}^3 r_I\, f(\vec r_I - \vec r_{PI})\;, \qquad f(\vec r) := {\rm e}^{-(m/2\beta\hbar^2)\, r^2} = {\rm e}^{-\pi r^2/\lambda^2}\;,$$

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

• *Expansion:* The sum over P includes the identity permutation ($PI = I$ for all I), permutations in which only two labels I and J are switched ($PI = J$ and $PJ = I$), and ones in which more labels are changed. For each P, any label that is not involved give rise to $f(\vec r_I - \vec r_{PI}) = f(\vec r_I - \vec r_I) = f(0) = 1$, so

$$Z_{\rm c}^{\rm (qm)} = \frac{1}{N!\,\lambda^{3N}} \int_{V^N} {\rm d}^{3N} r \left[1 \pm \sum_{I<J} f(\vec r_I - \vec r_J)\, f(\vec r_J - \vec r_I) + \sum_{I<J<K} f(\vec r_I - \vec r_J)\, f(\vec r_J - \vec r_K)\, f(\vec r_K - \vec r_I) \pm ...\right] .$$

The first term contributes a term V^N to the sum. The next term contains $\binom{N}{2}$ integrals of the form

$$\int_V {\rm d}^3 r_I \int_V {\rm d}^3 r_J\, f^2(\vec r_I - \vec r_J) = \int_V {\rm d}^3 r_I \int_V {\rm d}^3 r_J\, {\rm e}^{-2\pi(\vec r_I - \vec r_J)^2/\lambda^2} \approx V \int_{{\rm I\!R}^3} {\rm d}^3 r\, {\rm e}^{-2\pi r^2/\lambda^2} = \frac{V\lambda^3}{2^{3/2}}\;.$$

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 fs in the expansion contribute terms with higher powers of the degeneracy parameter $\delta := N\lambda^3/V = \rho\lambda^3$ to the sum. Since the approximations we made assume that this parameter is small we can expand $Z_{\rm c}^{\rm (qm)}$ in powers of δ, and we have already calculated the two leading terms,

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

The first term, which came from the identity permutation, is the classical partition function, including the $N!$ in the denominator from Boltzmann state counting, 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

$$\begin{aligned} F = -k_{\rm B} T \ln Z_{\rm c}^{\rm (qm)} &= -k_{\rm B} T \ln\left[Z_{\rm c}^{\rm (cm)} \left(1 \pm \frac{N-1}{2^{5/2}}\, \rho\lambda^3 + ...\right)\right] = F^{\rm (cm)} - k_{\rm B} T \ln\left(1 \pm \frac{N-1}{2^{5/2}}\, \rho\lambda^3 + ...\right) \\ &\approx F^{\rm (cm)} \mp k_{\rm B} T\, \frac{N-1}{2^{5/2}}\, \rho\lambda^3 = F^{\rm (cm)} \mp \frac{N(N-1)}{2} \left(\frac{\pi}{m}\right)^{3/2} \frac{\hbar^3}{V\sqrt{k_{\rm B} T}}\;. \end{aligned}$$

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

$$p = -\frac{\partial F}{\partial V}\bigg|_{T,N} = p^{\rm (cm)} \mp \frac{N(N-1)}{2} \left(\frac{\pi}{m}\right)^{3/2} \frac{\hbar^3}{V^2\sqrt{k_{\rm B} T}} + ... = k_{\rm B} T\, \frac{N}{V} \left(1 \mp \frac{\lambda^3}{2^{5/2}}\, \frac{N}{V} + ...\right) ,$$

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 (degeneracy pressure), purely as a consequence of quantum statistics and even in the absence of interactions.

Reading

• *Course textbook:* Kennett's book does not cover this topic.

• *Other texts:* Halley, Ch 4 & 5; Kardar, § 7.2; Pathria & Beale, Ch 5; Plischke & Bergersen, § 2.4; Reichl, § 5.3; Reif, § 9.8; Schwabl, §§ 4.2–4.3.