First Order Virial Correction to the Equation of State of an Ideal Quantum Gas

Pranav Murugan
Massachusetts Institute of Technology Department of Physics,
77 Massachusetts Ave., Cambridge, MA 02139-4307
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We develop the formalism of second quantization and quantum statistical mechanics to derive the equations of state of an ideal quantum gas with both Fermi and Bose statistics. In the high-temperature limit, we compare the quantum and classical equations of state for dilute gases. We also discuss the divergence in behavior for fermions and bosons as density increases, and motivate the existence of Bose-Einstein condensates.

I. INTRODUCTION

The equation of state of an ideal gas has been well-understood for hundreds of years. Simply, it relates macroscopic properties of noninteracting classical particles – the pressure, P, and volume V, are related to the temperature of the gas T via the relationship

$$PV = Nk_BT \tag{1}$$

where N is the number of particles and k_B is the Boltzmann constant. However, this model breaks down outside the ideal gas limit; when particles have non-negligible pairwise interactions, the equation of state instead is better approximated as

$$P = \frac{Nk_BT}{V}\left[1 - a\frac{N}{Vk_BT}\right] \tag{2}$$

where the second term $B \equiv -a\frac{N}{Vk_BT}$ is the first *virial correction* to the ideal gas pressure, and a is some constant dependent on the properties of the gas under study [1]. In principle, the multiplicative term in the RHS of (2) can be an infinite series in the density $\rho = \frac{N}{V}$; however, these second- and higher-order corrections play a much smaller role than the first virial correction and are not necessary to describe experimental data well unless in extreme regimes [2].

In particular, Figure 1 shows the agreement between the ideal gas law and the first virial correction for large volumes (which correspond to the low-density limit). We can observe the divergence of the two approximations at smaller volumes, where the intermolecular interactions are nontrivial. The first virial correction (2) is clearly nonphysical as the pressure becomes negative for volumes approaching zero; inclusion of the finite size of gas particles avoids this nonphysicality, and results in the Van der Waal's equation of state [1, 3].

The above results hold well for particles in the classical regime, but quantum particles exhibit qualitatively different behavior [4]. We can similarly define a quantum gas as a population of quantum particles without a pairwise potential. While again in the dilute limit the dynamics resemble those of a classical ideal gas (1), the first order virial correction is qualitatively different to (2) and must be obtained with care.

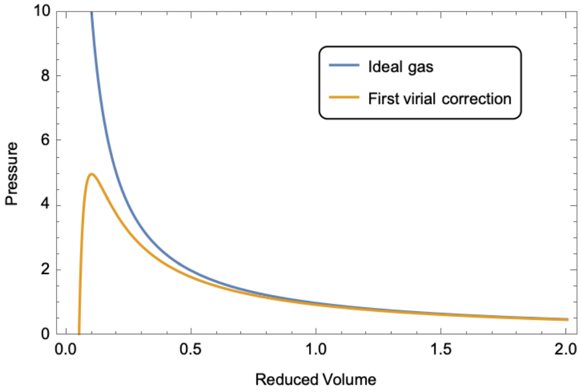

FIG. 1: Comparison of the pressure P and reduced volume V/N along isotherms (here, $k_BT = 1$) under the ideal gas law (1) and the first virial correction (2).

In the following sections, we introduce the formalism necessary to describe quantum states of N identical particles and the different dynamics observed under parity operations. Then, we review the results from statistical mechanics for quantum systems including the quantum forms of the partition function and the free energy. Finally, we derive the first-order virial correction to the ideal gas law for quantum gases and compare the first order results to the exact theoretical solutions for ideal quantum gases in various density regimes.

II. QUANTUM STATISTICAL MECHANICS

In this section, we derive much of the formalism and background necessary for the computation of the quantum gas equation of state. We begin with the statistics of Bose and Fermi gases.

A. Bose and Fermi Statistics

The treatment of identical particles differs slightly between classical and quantum mechanics [5, 6]. Suppose we have N identical classical particles labeled $i = 1 \dots N$.

Then, there are $N!$ ways of observing a configuration of particle positions at a particular set $x_1, x_2, \ldots x_N$; thus in the space of possible configurations of N indistinguishable classical particles, each state has to be divided by the overcounting factor $N!$.

However, for a quantum gas, the probability of finding a system of N particles is given by the magnitude of the wavefunction $|\psi(\vec{x}_1, \ldots \vec{x}_N)|^2$, where each argument of the wavefunction corresponds to the position of that particle. Then, we note in particular, upon the switching of two particles this probability density must remain unchanged:

$$|\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)|^2 = |\psi(\vec{x}_2, \vec{x}_1 \ldots \vec{x}_N)|^2 . \tag{3}$$

The wavefunctions must then obey

$$|\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N\rangle = e^{i\phi} |\psi(\vec{x}_2, \vec{x}_1 \ldots \vec{x}_N\rangle \tag{4}$$

for some real ϕ. However, applying this particle exchange operation twice must yield the identity, so ϕ is restricted to 0 or π. Thus, one of two constrains must be true for the wavefunction of this system of N particles under exchange:

$$|\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N\rangle = |\psi(\vec{x}_2, \vec{x}_1 \ldots \vec{x}_N\rangle , \text{ or} \tag{5}$$
$$|\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N\rangle = - |\psi(\vec{x}_2, \vec{x}_1 \ldots \vec{x}_N\rangle . \tag{6}$$

To generalize this idea of symmetric and antisymmetric wavefunctions to $N > 2$ particles, we introduce the permutation operator $\hat{P}$. $\hat{P}$ maps a sequence $\{1, 2, \ldots, N\}$ to a permutation of that sequence; the *parity* of this permutation is

$$(-1)^{\hat{P}} \equiv \begin{cases} +1 & \text{if } \hat{P} \text{ has an even number of exchanges} \\ -1 & \text{if } \hat{P} \text{ has an odd number of exchanges} \end{cases} \tag{7}$$

Thus, upon action by the permutation operator, we can define the states where

$$\hat{P} |\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)\rangle = + |\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)\rangle \tag{8}$$

to be *bosons* and the states

$$\hat{P} |\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)\rangle = (-1)^{\hat{P}} |\psi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)\rangle \tag{9}$$

to be *fermions*. Now that we have established how the wavefunctions must behave under a permutation operation, we can explicitly construct the form of the wavefunctions ψ. Given the free Hamiltonian

$$\hat{H}^{(N)} = \sum_i \hat{H}_i = \sum_i -\frac{p_i^2}{2m} \tag{10}$$

where the total N-body Hamiltonian is simply the sum of single-particle Hamiltonians. Then, we can write the fermion and boson wavefunctions as a function of the energy eigenstates parameterized by the wavenumber $k_i = p_i/\hbar$. Thus, the wavefunction corresponding to the N particles having a set of wavenumbers $\{k_i\}$ is for bosons

$$|k_1, k_2 \ldots, k_N\rangle_+ = \frac{1}{\sqrt{N! \prod_k n_k!}} \sum_P \hat{P} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_N\rangle \tag{11}$$

where n_k is the number of particles in state k, and the square root is present to ensure the inner product is normalized. For fermions, this relation is simpler since there is at most 1 particle in a given state:

$$|k_1, k_2 \ldots, k_N\rangle_- = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\hat{P}} \hat{P} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_N\rangle \tag{12}$$

We use the shorthand $|\{k_i\}\rangle_\eta$ to refer to these states, where $\eta = 1$ corresponds to the bosonic subspace and $\eta = -1$ corresponds to the fermionic subspace. While these are useful definitions for the states, it is often simpler to work with them in a basis that is parameterized by the state of the particles.

B. Second quantization

We can define creation and annihilation operators $a_k^\dagger$ and a_k and a ground state $|\Omega\rangle$ such that

$$\hat{a}_k |\Omega\rangle = 0 \tag{13}$$

and

$$|\{k_i\}\rangle_\eta = \frac{1}{\sqrt{\prod_k n_k!}} \hat{a}_{k_1}^\dagger \ldots \hat{a}_{k_N}^\dagger |\Omega\rangle \tag{14}$$

where the creation operator $\hat{a}_k^\dagger$ creates a particle with wavenumber k and the corresponding annihilation operator destroys one [7]. In particular, for states $|k, n_k\rangle$ with wavenumber k and n_k particles, and states $|k\rangle$ with arbitrary number of particles, we note the following familiar identities:

$$\begin{aligned} \hat{a}_k |k, n_k\rangle &= \sqrt{n_k} |k, n_k - 1\rangle \\ \hat{a}_k^\dagger |k, n_k\rangle &= \sqrt{n_k + 1} |k, n_k + 1\rangle \\ \hat{a}_k |\ell\rangle = \hat{a}_k^\dagger |\ell\rangle &= 0, \quad k \neq \ell \end{aligned} \tag{15}$$

These ladder operators obey the usual commutation relations for bosons, and anticommutation relations for fermions. We can then define the Fock space as the space spanned by the sum of states containing any number of particles; specifically, instead of defining an N-particle state by the states of each unique particle, we define it as a superposition of occupied states. Specifically,

$$|\{k_i\}\rangle_\eta = \sum_k \left(\hat{a}_k^\dagger\right)^{n_k} |\Omega\rangle \tag{16}$$

Using this formalism, we can also use the resolution of the identity to convert a N-body operator $\hat{O}^{(N)} = \sum_{i=1}^N \hat{O}$ in the N-particle basis to the Fock space basis using

$$\hat{O}^{(N)} = \sum_{k,\ell} \langle \ell| \hat{O} |k\rangle \hat{a}_\ell^\dagger \hat{a}_k. \tag{17}$$

Now that we know how to work with fermionic and bosonic states, we can introduce the canonical ensemble for these particles.

C. Grand Canonical Partition Function

The grand canonical ensemble is the ensemble of states at a given temperature and chemical potential. The general form of the grand canonical partition function is

$$Q = \mathrm{tr}\left(e^{-\hat{H}^{(N)}/k_BT + \mu\hat{N}^{(N)}/k_BT}\right) \tag{18}$$

for chemical potential μ in the usual N-particle basis. The trace is most conveniently performed in a basis of orthonormal states, so we can write (18) as a sum over the Fock space and use (17) to calculate the values of these operators:

$$\begin{aligned} Q = \sum_k \langle k| \exp\Bigg(\frac{1}{k_BT}\sum_{k',\ell'}\Big[-\langle k'|\hat{H}|\ell'\rangle \hat{a}_{\ell'}^\dagger \hat{a}_{k'} \\ +\mu \langle k'|\hat{N}|\ell'\rangle \hat{a}_{\ell'}^\dagger \hat{a}_{k'}\Big]\Bigg)|k\rangle \end{aligned} \tag{19}$$

Using the conventional ladder operator identities (15) and enforcing orthonormality of Fock states we get

$$\begin{aligned} Q = \sum_k \exp\Bigg(\frac{1}{k_BT}\Big[-\langle k|\hat{H}|k\rangle n_k \\ +\mu\langle k|\hat{N}|k\rangle n_k\Big]\Bigg) \end{aligned} \tag{20}$$

If each energy eigenstate had energy E_k, we can write the partition function (20) as the sum of states with wavenumber k to get

$$\begin{aligned} Q &= \sum_{\{n_k\}} \exp\left[\sum_k (-E_k n_k + \mu n_k)/k_BT\right] \\ &= \sum_{\{n_k\}} \prod_k \exp\left[(-E_k n_k + \mu n_k)/k_BT\right] \end{aligned} \tag{21}$$

where we note that $\sum_k n_k = N$, and that the outer sum is performed over all valid states $\{n_k\}$. This sum over valid states (e.g. only 0 or 1 occupancy for fermions) simplifies calculations significantly: we get, for fermions, that the grand partition function simplifies to

$$Q_- = \prod_k \left(1 + \exp\left[(-E_k + \mu)/k_BT\right]\right) \tag{22}$$

and for bosons

$$\begin{aligned} Q_+ &= \prod_k \left(\sum_{n=0}^\infty \exp\left[n(-E_k + \mu)/k_BT\right]\right) \\ &= \prod_k \left(1 - \exp\left[(-E_k + \mu)/k_BT\right]\right)^{-1} \end{aligned} \tag{23}$$

Thus, to write both cases succinctly, we have

$$\log Q_\eta = -\eta \sum_k \log\left(1 - \eta \exp\left[(-E_k + \mu)/k_BT\right]\right) \tag{24}$$

Now that we have established the form of the grand partition function for a general quantum gas, we can derive the macroscopic state variables in the following sections [5].

III. DERIVATION OF THE EQUATION OF STATE

We can now make some substitution that will simplify our calculations for the ideal gas equation of state, taking advantage of the fact that we know the form of the (free) Hamiltonian and that we are in 3 dimensions. From the Hamiltonian we get that the energy of the states is

$$E_k = \frac{\hbar^2 k^2}{2m}$$

for a particle of mass m. Now, we want to somehow convert the sum over all 3D wavefunctions k to an integral this space that we can more feasibly perform. To do so, we have to determine the density of these momentum states; let us assume we are in a 3D box with sides of length $\sqrt[3]{V}$, where V is the volume of the box we are considering. Imposing periodic boundary conditions, assuming the k_i basis is orthogonal, yields

$$\Delta k_i = \frac{2\pi}{V^{1/3}} \Rightarrow \Delta k^3 = \frac{(2\pi)^3}{V}. \tag{25}$$

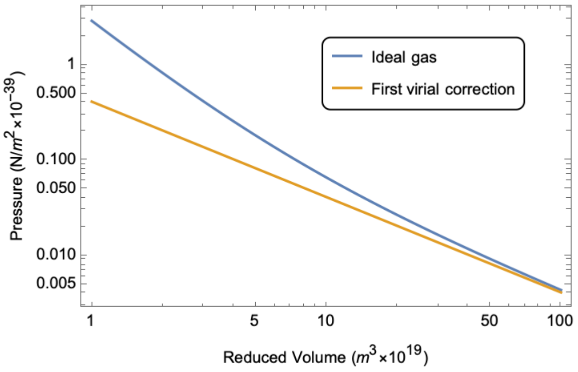

FIG. 2: Comparison of the pressure P and reduced volume V/N along isotherms at $T = 300$K for an electron-mass fermi gas treated classically and quantum mechanically, in the high temperature limit at which these corrections are valid [8].

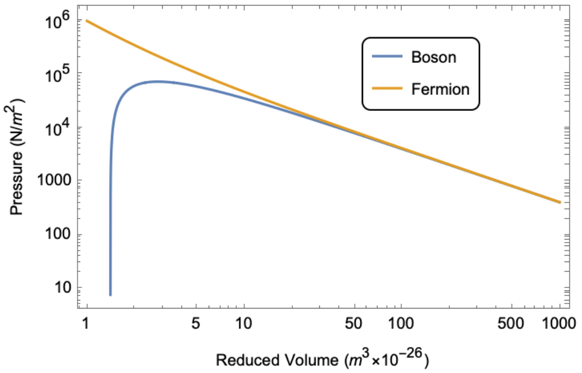

FIG. 3: The divergence of the pressures of the Fermi and Bose gases (34), highlighted here in the high density limit with two isotherms at $T = 300K$.

Thus, each term in the summation has to be weighted by its volume in phase space (25) – or equivalently, the integral has to weighted by the density of the k-states. The resulting substitution is then

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k \tag{26}$$

Performing this substitution, the log partition function becomes

$$\begin{aligned} \log Q_\eta = -\eta \frac{V}{(2\pi)^3} \int d^3k \log \big(1- \\ \eta \exp\left[\left(-\frac{\hbar^2 k^2}{2m} + \mu\right)/k_B T\right]\big) \end{aligned} \tag{27}$$

To motivate the connection with macroscopic state variables, recall the definition of the Landau free energy

$$\begin{aligned} \mathcal{F} &\equiv E - TS - \mu N = -PV \\ &= -k_B T \log Q \end{aligned} \tag{28}$$

where S is the entropy of the system. Defining $z \equiv e^{\mu/k_B T}$, we can write the pressure using (28) to get

$$\begin{aligned} P_\eta &= k_B T \frac{\log Q_\eta}{V} \\ &= -\eta \int \frac{d^3k}{(2\pi)^3} \log\left(1 - z\eta \exp\left[-\frac{\hbar^2 k^2}{2mk_B T}\right]\right) \end{aligned} \tag{29}$$

Since the only argument in the integral is the magnitude of the wavenumber k, we make the substitution $x = \frac{\hbar^2 k^2}{2mk_B T}$ and define for convenience

$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}.$$

Then, we can perform integration by parts on P_η from (29) to get

$$P_\eta = \frac{4}{3\lambda^3\sqrt{\pi}} \int_0^\infty dx \frac{x^{3/2}}{z^{-1}e^x - \eta} \tag{30}$$

This integral is not analytically solvable, so we look for another approach. Remembering the form of the equation of state (2), we must specify the number of particles in the system. However, in the grand canonical ensemble, this value is not fixed and it is really the expectation of the number of particles that is macroscopically relevant. Thus, inspired by the form of (21), we can write the expected particle density as:

$$\begin{aligned} n_\eta &= \frac{1}{V}\langle n \rangle = -\frac{1}{V}\frac{\partial \log Q}{\partial(E_k/k_B T)} \\ &= \frac{1}{(2\pi)^3} \int d^3k \left(z^{-1} \exp\left[-\frac{\hbar^2 k^2}{2mk_B T}\right] - \eta\right)^{-1} \\ &= \frac{2}{\lambda^3\sqrt{\pi}} \int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^{-x} - \eta} \end{aligned} \tag{31}$$

In the limit of small z (high temperature), we can expand (30) and (31) to get:

$$P_\eta = \frac{k_B T}{\lambda^3}\left(z + \eta \frac{z^2}{2^{5/2}} + \dots\right) \tag{32}$$

$$n_\eta = \frac{1}{\lambda^3}\left(z + \eta \frac{z^2}{2^{3/2}} + \dots\right) \tag{33}$$

Finally, we can write P_η in terms of n_η to second-lowest order to get

$$P_\eta = n_\eta k_B T \left[1 - \frac{\eta}{2^{5/2}} n_\eta \lambda^3\right] \tag{34}$$

where we can identify the virial coefficient $-\frac{\eta}{2^{5/2}} n_\eta \lambda^3$ which is negative (attractive) for bosons and positive (repulsive) for fermions.

Figure 2 shows compares the isotherms of a gas treated classically and quantum-mechanically in the dilute limit, where we note the presence of the λ term in (34) significantly suppresses the higher order contributions of the number density. As a result, in this limit, the difference between Bose and Fermi statistics for a quantum gas is negligible compared to the first-order classical correction.

The difference between the two types of quantum gases is much more apparent in the high density. Although our result (34) is only valid in the high-temperature limit, at small enough volumes the quantum interactions become significant and alter the dynamics of these gases (Figure 3). The sharp divergence to negative pressure exhibited by the Bose gas hints at the existence of a physical phenomenon not accounted for here; indeed, above a critical density on the order of λ^{-3}, a Bose gas forms a Bose-Einstein condensate which has a finite density-independent pressure [9].

IV. CONCLUSION

In this paper, we derived from fundamental statistical mechanics principles the the first virial correction to the ideal gas law for a quantum gas. The behavior of a quantum and classical gas diverges as we leave the low-density limit, and the different statistics of bosons and fermions becomes macroscopically evident in the high-density limit. These results motivate the existence of Bose-Einstein condensates, and set up a potential analysis of these systems in the low-temperature limit as well.

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