THERMODYNAMICS OF VAN DER WAALS FLUIDS WITH QUANTUM STATISTICS

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We consider thermodynamics of the van der Waals fluid of quantum systems. We derive general relations of thermodynamic functions and parameters of any ideal gas and the corresponding van der Waals fluid. This provides unambiguous generalization of the classical van der Waals theory to quantum statistical systems. As an example, we apply the van der Waals fluid with Fermi statistics to characterize the liquid-gas critical point in nuclear matter. We also introduce the Bose–Einstein condensation in the relativistic van der Waals boson gas, and argue that it exhibits two-phase structure separated in space.

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1. Introduction

The well-known theory of the van der Waals fluid is a very useful extension of the thermodynamics of classical ideal gases. It accounts for the repulsive interactions of particles with extended volume, as well as for the (1943)
inter-particle attractive force. In addition, it makes it possible to study phase transitions. It is a semi-quantitative theory which has many applications to model the observed experimental behaviors of critical phenomena in the liquid-gas phase transition. In particular, under some approximations, it can be used as a phenomenological tool to describe phase structure of nuclear, or thermodynamical properties of hadronic matter [1–16].

In general, the van der Waals equation of state is restricted to describe classical fluids, where the effects of quantum statistics are neglected. Recently, an interesting extension of the theory of quantum ideal gases has been proposed to account for repulsive and attractive interactions in the low density approximation [13, 14]. There, authors argued that a quantum generalization of the van der Waals equation of state is a non-trivial task, and proposed three conditions that such a generalization should satisfy. The first two are rather straightforward, as they require that, (i) in the limit where both repulsive and attractive interactions are negligible, the new equation of state should coincide with that of ideal quantum gases, and (ii) in the limit of Boltzmann statistics, it should reproduce the classical van der Waals equation. The third condition does not concern the equation of state as it requires that the entropy is non-negative and tends to zero for $T \to 0$. Based on the above conditions, the authors in Refs. [13, 14] have proposed an interesting approach to formulate the theory of the van der Waals fluid with quantum statistics.

In the present paper, by a slight extension of the original van der Waals argument we derive, unambiguously, general relations between the thermodynamic functions and parameters of any ideal gas and those of its van der Waals generalization. This allows for a straightforward formulation of thermodynamics and the equation of state of the van der Waals fluids with quantum statistics.

In the above approach, the conditions of Refs. [13, 14] are naturally satisfied. In particular, we show that, in quantum systems with the van der Waals interactions, the entropy does not change. Therefore, the entropy of the van der Waals fluid tends to zero for $T \to 0$ if, and only if, the same is true for the corresponding ideal gas. Since, at constant volume and particle numbers, the entropy is a non-decreasing function of temperature, this also implies that it is non-negative.

As an application, we present thermodynamic functions for the van der Waals fluids with quantum statistics, and show that, for fermions, our results agree with those obtained previously in Ref. [13] by using different approach and methods. For the van der Waals fluid of bosons, we argue that the Bose–Einstein condensation appears and leads to two phases which are separated in space.
2. General analysis

Thermodynamic properties of a system are characterized by an equation of state which relates different state variables associated with the matter. A familiar example is the equation of state of the non-relativistic ideal gas undergoing classical or quantum statistics

\[ p = p_{id}(V, T, N). \]  

For a classical thermodynamic ideal gas, Eq. (1) reduces to a familiar form, \( p_{id}(V, T, N)V = NT \), where \( N \) is the number of particles.

The knowledge of the equation of state, however, is not sufficient to find all relevant thermodynamic functions and parameters, e.g. the equations of state for the ideal gases of monoatomic and of diatomic molecules are identical, but the temperature dependence of the energy of the two gases differs.

The full thermodynamic information is contained in the free energy which is obtained by integrating the thermodynamic identity,

\[ \frac{\partial F(V, T, N)}{\partial V} = -p(V, T, N), \]  

as

\[ F_{id}(V, T, N) = \int_{V_0}^{V} p_{id}(V', T, N) \, dV' + f_{id}(V_0, T, N), \]  

where \( V_0 \) is an arbitrary volume parameter, and \( f_{id} \) is a function which cannot be determined by the equation of state.

A very well-known, and phenomenologically relevant, extension of an ideal gas equation of state is the van der Waals generalization, which accounts for the repulsive and attractive interactions in a fluid. Denoting by \( a \) and \( b \), the parameters which control the strength of the attractive and repulsive interactions, respectively, the equation of state of the van der Waals fluid reads [17]

\[ p(V, T, N) = \frac{NT}{V - bN} - an^2, \]  

where \( n = N/V \) is the particle density.

The van der Waals equation of state (4) can be obtained from the ideal gas equation of state (1) by the following replacements

\[ \begin{align*}
   p_{id}(V - bN, T, N) &= p(V, T, N) + an^2, \\
   V_{id} &= V - bN,
\end{align*} \]  

\(^{1}\) It is assumed that there is no Bose–Einstein condensate.
where $V$ is the volume of the van der Waals fluid, and $n(V, T, N)$, the corresponding particle density. According to substitution (6), the density in an ideal gas, $n_{id}(V_{id}, T, N)$ is related to $n(V, T, N)$, as

$$\frac{1}{n_{id}(V - bN, T, N)} = \frac{1}{n(V, T, N)} - b.$$  

The replacements in Eqs. (5) and (6), applied in the ideal gas equation of state, $p_{id}(V_{id}, T, N)V_{id} = NT$, yield indeed the standard van der Waals equation of state (4).

In the statistical systems, knowing the equation of state is already sufficient to characterize the phase transition. Indeed, supplementing it by the conditions

$$\frac{\partial p}{\partial n} = 0, \quad \frac{\partial^2 p}{\partial n^2} = 0,$$

it is possible to identify the critical point (CP), if any. In the classical van der Waals fluid e.g., one can express the parameters, $n_c$, $T_c$, $p_c$, at the CP by the interaction constants, $a$ and $b$, as

$$n_c = \frac{1}{3b}, \quad T_c = \frac{8a}{27b}, \quad p_c = \frac{a}{27b^2}.$$  

From the equation of state, one can also calculate fluctuations of the particle number, which are important characteristics of the phase transition [15, 18–25]. These are quantified by the corresponding cumulants $\chi_k$ of the order of $k > 0$, as

$$\frac{\chi_k}{VT^{k-1}} = \frac{\partial^k p}{\partial \mu^k} \bigg|_T = \left( n \frac{\partial}{\partial p} \right)^k p \bigg|_T,$$

where to get the second equality, we have used the Gibbs–Duhem equation.

In order to find, however, all thermodynamic functions of the van der Waals gas, one needs the free energy. Integrating the equation of state of the van der Waals fluid as in Eq. (2), one finds

$$F(V, T, N) = \int_{V_0}^{V} \left( p_{id} \left( V' - bN, T, N \right) - a \frac{N^2}{V'^2} \right) dV' + f(V_0, T, N),$$

where $f$ is an integration “constant”. 

\footnote{In general, the coefficients can depend on the dimensionless parameter $\frac{a}{mb}$, where $m$ is the particle mass.}
On the other hand, Eq. (3) for the ideal gas can be rewritten as

\[ F_{id}(V - bN, T, N) = \int_{V_0 + bN}^{V_0} p_{id}(V' - bN, T, N) \, dV' + f_{id}(V_0, T, N). \]  

(12)

In the following, we assume that for sufficiently large \( V_0 \), the upper limit of the integration in Eq. (12) can be replaced by \( V_0 \). A sufficient condition is that, in the low density limit, \( p_{id}(V, T, N) \) is proportional to \( \frac{1}{V} \). The two preceding equations can be combined to give

\[
F(V, T, N) - F_{id}(V - N b, T, N) = \int_{V}^{\infty} [p(V', T, N) - p_{id}(V' - bN, T, N)] \, dV' + f(\infty, T, N) - f_{id}(\infty, T, N) = -a \frac{N^2}{V} + [f(\infty, T, N) - f_{id}(\infty, T, N)].
\]

(13)

In the spirit of the van der Waals approach, we make the assumption

\[ f(\infty, T, N) = f_{id}(\infty, T, N). \]  

(14)

Consequently,

\[ F(V, T, N) = F_{id}(V - bN, T, N) - aNn. \]  

(15)

The above equation relates the free energy of the ideal and van der Waals gas, and thus allows to extract all relevant thermodynamic quantities in a transparent way. In particular, differentiating relation (15) with respect to the temperature, one gets the relation between entropies

\[ S(V, T, N) = S_{id}(V - bN, T, N). \]  

(16)

It is rather transparent that conditions (14) and (16) are equivalent. Indeed, in the van der Waals picture, the effect of the excluded volumes around the particles is assumed to be compensated by a suitable increase of the total volume. If so, the number of states accessible to the gas, and consequently its entropy, should remain unchanged. Another argument is that, since the replacements (5) and (6) leave the temperature and the number of particles unchanged, there is no reason to expect that \( f(T, \infty) \neq f_{id}(T, \infty) \).

Following Eq. (16) and applying the thermodynamic identity, \( E = F + TS \), one gets the energy of the van der Waals fluid

\[ E(V, T, N) = E_{id}(V - bN, T, N) - a \frac{N^2}{V}. \]  

(17)
Finally, differentiating both sides of Eq. (15) with respect to $N$, we obtain the following relation between chemical potentials of the ideal and the van der Waals gases

$$\mu(V, T, N) = \mu_{id}(V - bN, T, N) + bp_{id}(V - bN, T, N) - 2an(V, T, N). \quad (18)$$

Let us notice that the van der Waals equation of state can be justified from statistical physics only in the low density limit. It is an intuitive extrapolation, though a very useful one.

### 3. van der Waals fluids with quantum statistics

In the previous section, we have established the relation between the free energy, and some other state variables, of the ideal and the van der Waals gas. Following previous discussions in Refs. [13] and [14], we focus now, on the quantum statistics generalization of the van der Waals fluid. We assume first, that for bosons, there is no Bose–Einstein condensate contribution.

Let us consider the ideal gases with quantum statistics. In general, the equation of state for quantum ideal gases is given in a parametric form

$$\frac{N}{V} = \frac{d}{2\pi^2} \int_0^\infty \frac{k^2dk}{e^{\beta[\epsilon(k)-\mu_{id}]} + \eta}, \quad (19)$$

$$p(V, T, N) = \frac{d}{6\pi^2} \int_0^\infty \frac{k^4dk}{e^{\beta[\epsilon(k)-\mu_{id}]} + \eta \epsilon(k)}, \quad (20)$$

where $\beta = 1/T$, $\epsilon(k) = \sqrt{k^2 + m^2}$ is the particle energy, and $d$ its degeneracy factor, while $\eta = 1$ for fermions and $\eta = -1$ for bosons.

For a study of this equation of state, the chemical potential is a derived variable. For given values of $V, T, N$, the parameter $\mu_{id}$ can be calculated from equation (19), and substituting it into Eq. (20), the corresponding value of $p(T, V, N)$ can be found.

For the van der Waals fluids with quantum statistics, we derive the equations of state by making the substitutions (5) and (6) in Eqs. (19) and (20). Consequently, we obtain the following parametric equation of state:

$$\frac{N}{V - bN} = \frac{d}{2\pi^2} \int_0^\infty \frac{k^2dk}{e^{\beta[\epsilon(k)-\mu_{id}]} + \eta}, \quad (21)$$

and

$$p(V, T, N) = \frac{d}{6\pi^2} \int_0^\infty \frac{k^4dk}{e^{\beta[\epsilon(k)-\mu_{id}]} + \eta \epsilon(k)} - an\frac{N^2}{V^2}, \quad (22)$$
The parameter $\mu_{id}$ in Eq. (19) is the chemical potential of the ideal gas. Therefore, comparing with equation (21), one finds that

$$\bar{\mu} = \mu_{id}(V - bN, T, N)$$

(23)

is not the chemical potential (18) of the quantum van der Waals fluid.

Equations (17) and (18) can be used to calculate the energy and the chemical potential of the quantum van der Waals fluids in terms of the thermodynamic functions and parameters of the corresponding ideal gases. Furthermore, according to Eq. (16), the entropy of the quantum van der Waals fluids vanishes at $T = 0$.

To illustrate the importance of the effects of quantum statistics on the van der Waals equation of state and its critical properties, we consider its application to the description of the liquid-gas phase transition in nuclear matter [1, 2, 26–28]. Following Ref. [13], we model the nuclear matter as a gas of nucleons. Thus, in Eqs. (21) and (22), the parameters are chosen as: $\eta = +1, d = 4$ and $m = 0.939$ GeV. In addition, to fix the interaction strength parameters, we take as inputs, at $T = 0$ and $p = 0$, the experimental values of the particle density $n_0 = 0.16$ fm$^{-3}$, and the energy per nucleon $\epsilon_0 = \frac{E}{N} = 0.922$ GeV.

The issue is to find in the van der Waals fluid the density $n_c$, temperature $T_c$ and pressure $p_c$ at the critical point with quantum statistics.

We first determine the parameters $a$ and $b$ from the input data. To proceed, it is convenient to define the following functions:

$$f_n = \frac{d(-1)^n n!}{6\pi^2} \int_0^\infty \frac{dk k^4}{\epsilon(k)} \frac{e^{\beta n(\epsilon(k)-\bar{\mu})}}{(e^{\beta(\epsilon(k)-\bar{\mu})} + \eta)^{n+1}},$$

(24)

$$g_n = \frac{d(-1)^n n!}{2\pi^2} \int_0^\infty \frac{dk k^2 e^{\beta n(\epsilon(k)-\bar{\mu})}}{(e^{\beta(\epsilon(k)-\bar{\mu})} + \eta)^{n+1}},$$

(25)

$$\epsilon_{id} = \frac{d}{2\pi^2} \int_0^\infty \frac{\epsilon(k)k^2dk}{e^{\beta(\epsilon(k)-\bar{\mu})} + \eta}.$$  

(26)

Then, Eqs. (21), (22) and (17), applied at $T = 0$ and $p = 0$, yield:

$$\frac{n_0}{1 - bn_0} = g_0(0, \bar{\mu}),$$

(27)

$$p = f_0(0, \bar{\mu}) - an_0^2 = 0,$$

(28)

$$\epsilon_0 = \epsilon_{id}(0, \bar{\mu})(n_0^{-1} - b) - an_0.$$  

(29)
Thus, the value of $\mu$ is obtained from

$$n_0(\epsilon_{id}(0, \mu) - g_0(0, \mu)\epsilon_0) = f_0(0, \mu)g_0(0, \mu).$$

(30)

Its solution, $\mu = 0.9994$ GeV, substituted into the first two equations, yields

$$a = 0.3291 \text{ GeV fm}^3, \quad b = 3.416 \text{ fm}^3,$$

(31)

in agreement with the results of Ref. [13].

In order to find the parameters at the CP, we need, in addition to the equation of state (21) and (22), also relations (8). For the present case, they can be written in the following form

$$f_1(T, \mu)(1 + bg_0(T, \mu))^3 - 2ag_0(T, \mu)g_1(T, \mu) = 0,$$

(32)

$$f_2(T, \mu) - \frac{g_2(T, \mu)}{f_1(T, \mu)} + \frac{g_1(T, \mu)}{g_0(T, \mu)} \frac{2bg_0(T, \mu) - 1}{1 + bg_0(T, \mu)} = 0.\quad(33)$$

Solving this pair of equations for $T$ and $\mu$, yields

$$T_c = 19.72 \text{ MeV}, \quad \mu_c = 0.9484 \text{ GeV}.$$

(34)

Substituting these values of the critical temperature and the parameter $\mu_c$ into the equation of state, we get

$$n_c = 0.072 \text{ fm}^{-3}, \quad p_c = 0.526 \text{ MeV fm}^{-3},$$

(35)

as the critical density and pressure at the CP of the nuclear matter modeled as the van der Waals fluid with quantum statistic.

The results in Eqs. (34) and (35) agree with those obtained in Ref. [13], showing that our formulation of the van der Waals model with quantum statistics is quantitatively consistent with previous findings.

It is worth noting that in the van der Waals model with Boltzmann statistics, and at the same values of $a$ and $b$, the critical temperature at the CP is by almost ten degrees higher. Thus, in the application of this model to the liquid-gas phase transition in nuclear physics, the quantum statistic effects are important, and make the location of the CP closer to that extracted in the experiments.

4. Bose–Einstein condensation in the van der Waals quantum fluids

The van der Waals model is not sufficiently detailed to describe quantitatively the Bose–Einstein condensation, a qualitative description, however, can be given.
Let us consider first the ideal gas of bosons. As it is seen from Eq. (19), the particle density, at any given temperature, increases with the chemical potential up to $\mu_{id}^c = m$, and beyond that value the integral becomes divergent. Consequently, when more particles are introduced into the system, they form a condensate, i.e. a fluid of particles distributed uniformly over the volume $V$, where each particle is in its ground state, i.e. has momentum zero.

Let us denote by $n_c$ the density of particles from the condensate, and by $n_a$ the density of active particles with the momentum distribution given by the integrand in Eq. (19). Thus,

$$n = n_a + n_c$$  \hspace{1cm} (36)

is the total density of particles in the system.

The particles from the condensate do not strike the walls and, therefore, do not contribute to the pressure. Consequently, after $n_a$ reaches its maximum value, the pressure does not depend on the particle density $n$. Therefore, the gas satisfies the thermodynamic stability condition

$$\left( \frac{\partial p}{\partial n} \right)_T \geq 0.$$  \hspace{1cm} (37)

For the van der Waals gas with a condensate, the substitution in Eq. (6) remains valid, whereas Eq. (5) becomes

$$p_{id}(V - bN, T, N) = p(V, T, N) + ann_a.$$  \hspace{1cm} (38)

This is because only the active particles hit the walls, while all the particles contribute to the force pulling back a particle about to hit the wall. In the region considered, the pressure $p_{id}$ does not depend on the total particle density. Consequently, the pressure $p$, decreases with increasing $n$. This contradicts the stability condition (37).

In order to see how the system collapses, let us consider a vessel, containing the fluid with the condensate, divided into two parts $A$ and $B$ by a mobile wall impermeable to particles. We start with the fluid with both $n_a$ and $n_c$ being constant. Suppose now, that the wall has moved by fluctuations, so that volume $A$ increases a little at the expense of volume $B$. Consequently, in $A$, the number of places for active particles has increased and the amount of condensate has decreased. The density of active particles does not change, but the density $n$ gets reduced because the volume has increased. As a result, the pressure of the fluid on the walls in $A$ increases. A similar argument shows that the pressure in $B$ decreases. Thus, $A$ goes on growing and $B$ shrinking. The particles of the van der Waals
fluid, however, have finite volumes. Therefore, when the particle density in $B$ becomes of the order of $1/b$, an additional contribution to the pressure in $B$ appears, and the process gets stopped. Another wall can be introduced into the increased volume $A$, and the process may be repeated. Let us keep the notation $A$ for the expanding part of the volume. After enough repetition, the region $A$ will contain only active particles. This is an implication of the fact that for the van der Waals fluid, as opposed to the ideal gas, a homogenous phase consisting of both active and condensate particles is unstable. Thus, in the van der Waals fluid with Bose–Einstein’s condensate, one expects the appearance of the two separated phases.

The above discussion is not enough to conclude whether the two, well-separated phases will be formed in the system, or one of the phases will be dispersed in the form of small droplets, in the other. The need for the separation, however, follows directly from the relation between the pressure and the total particle density.

5. Conclusions

The objective of these studies was to establish the generalization of the van der Waals fluid to account for the quantum statistics. The main result is the transparent and unambiguous derivation of the relation between the free energy of any ideal gas and the corresponding van der Waals fluid.

In order to establish such generalization, it is not enough to use the equations of state, but some additional assumptions are needed. The reason is rather straightforward, since the free energy, expressed as a function of thermal variables, defines all relevant thermodynamic functions of the system, but the equation of state does not. The additional assumption needed was that in the large volume limit the free energy of the ideal and van der Waals gas coincide.

The theory based on the relation between the free energy of the ideal gas and van der Waals fluid provides complete description of the equation of state and thermodynamics of quantum systems. For practical applications, it also implies transparent relations between entropies, energies and chemical potentials of quantum ideal gases and the van der Waals fluids.

The simplicity of our approach is illustrated by discussing the van der Waals gas with Fermi statistics and its application to a phenomenological description of liquid-gas critical point in the nuclear matter. The Bose–Einstein condensation in the van der Waals gas was argued to imply the structure of two phases separated in space. This is because, in the presence of the condensate, the stability condition, which requires non-decreasing pressure with density at constant temperature, and which is fulfilled in the ideal Bose gas, is not satisfied by the van der Waals quantum system.
The quantum effective theory of fluids proposed here was shown to satisfy all necessary conditions introduced in Ref. [13] to generalize the van der Waals thermodynamic system to quantum statistics. However, these conditions are not enough to formulate it.

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REFERENCES


