Van der Waals Equation of State with Fermi Statistics for Nuclear Matter

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Abstract

The van der Waals (VDW) equation of state is a simple and popular model to describe the pressure function in equilibrium systems of particles with both repulsive and attractive interactions. This equation predicts an existence of the 1st order liquid-gas phase transition and contains a critical point. Two steps to extend the VDW equation and make it appropriate for new physical applications are done in this paper: 1) the grand canonical ensemble formulation; 2) an inclusion of the quantum statistics. The VDW equation with Fermi statistics is then applied to a description of the system of interacting nucleons. The VDW parameters $a$ and $b$ are fixed to reproduce the properties of nuclear matter at saturation density $n_0 = 0.16 \text{ fm}^{-3}$ and zero temperature. The model predicts a location of the critical point for the symmetric nuclear matter at temperature $T_c \approx 19.7 \text{ MeV}$ and nucleon number density $n_c \approx 0.07 \text{ fm}^{-3}$.

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I. INTRODUCTION

The van der Waals (VDW) equation of state is a simple analytical model of the pressure function $p$ for equilibrium systems of particles with both attractive and repulsive interactions. The VDW model contains the 1st order liquid-gas phase transition which ends at the critical point. In the canonical ensemble (CE), where independent variables are temperature $T$, volume $V$, and number of particles $N$, the VDW equation of state has most simple and transparent form, (see, e.g., Refs. [1, 2]),

$$p(T, n) = \frac{NT}{V - bN} - a\frac{N^2}{V^2} \equiv \frac{nT}{1 - bn} - a n^2,$$

(1)

where $a > 0$ and $b > 0$ are the VDW parameters which describe attractive and repulsive interactions, respectively, and $n \equiv N/V$ is the particle number density. The first term in the right-hand-side of Eq. (1) corresponds to the excluded volume (EV) correction, which manifests itself in a substitution of a total volume $V$ by the available volume, $V_{av} = V - bN$. The second term comes from the mean field which describes attractive interactions between particles. In order to apply the VDW equation of state to systems with variable number of particles it is necessary to switch to the grand canonical ensemble (GCE). This procedure was firstly performed for the EV model, i.e., for $a = 0$ in Eq. (1), in Refs. [3, 4]. In our recent paper [5], the full VDW equation (1), with both attractive and repulsive terms, was transformed from the CE to the GCE for systems with Boltzmann statistics. There are several physical situations when the GCE formulation is desirable (see Ref. [5] for details). Note that the EV and VdW models can also be conveniently treated within the GCE in a framework of the thermodynamic mean-field approach (see Refs. [6–8]).

Equation (1) is valid for classical systems, where the effects of quantum statistics are neglected. In the present paper we suggest a generalization of the VDW equation to include effects of the quantum statistics. Proper treatment of quantum effects appears to be crucially important for a description of statistical equilibrium at small temperatures. The quantum statistics formulation is much easier to introduce in the GCE than in the CE. This is an additional physical example where the GCE formulation is particularly helpful. Thus, we use our recent results of the GCE formulation [5] as a starting point for a quantum generalization of the VDW equation of state. As a next step, the VDW equation of state with Fermi statistics is used to
describe a nuclear matter. The VDW parameters, $a$ and $b$, which correspond respectively to attractive and repulsive interactions between nucleons, are fixed to reproduce the properties of the symmetric nuclear matter at zero temperature: saturation density $n_0 = 0.16 \text{ fm}^{-3}$, binding energy per nucleon $-16 \text{ MeV}$, and zero pressure $p = 0$.

The paper is organized as follows. In Sec. II the VDW equation of state is transformed into the GCE, and the quantum statistical formulation of this equation is elaborated in Sec. III. In Sec. IV the VDW equation of state with Fermi statistics is applied to a description of nuclear matter. A summary in Sec. V closes the article.

II. VDW EQUATION FOR THE BOLTZMANN STATISTICS IN THE GCE

The VDW pressure function (1) corresponds to the Boltzmann approximation, i.e., the effects of quantum statistics (Bose or Fermi) are neglected. In our recent paper [5] the VDW equation of state was formulated in the GCE. The GCE pressure, $p(T, \mu)$, is a function of temperature $T$ and chemical potential $\mu$. It contains a complete information about thermodynamical functions of the system. Particle number density $n(T, \mu)$, entropy density $s(T, \mu)$, and energy density $\varepsilon(T, \mu)$ can be presented in terms of $p$ and its $T$- and $\mu$-derivatives:

$$n(T, \mu) = \left( \frac{\partial p}{\partial \mu} \right)_T, \quad s(T, \mu) = \left( \frac{\partial p}{\partial T} \right)_\mu, \quad \varepsilon(T, \mu) = T \left( \frac{\partial p}{\partial T} \right)_\mu + \mu \left( \frac{\partial p}{\partial \mu} \right)_T - p.$$  \hfill (2)

For $a = b = 0$ the above VDW equations are reduced to the ideal gas expressions for classical particles.

The VDW equation of state in the GCE is obtained in the form of transcendental equation for particle number density $n \equiv n(T, \mu)$ as a function of $T$ and $\mu$ [3]:

$$n(T, \mu) = \frac{n^{id}(T, \mu^*)}{1 + b n^{id}(T, \mu^*)}, \quad \mu^* = \mu - T \frac{bn}{1 - bn} + 2an,$$ \hfill (3)

where $n^{id}$ is a particle number density in the ideal Boltzmann gas

$$n^{id}(T, \mu) = \exp \left( \frac{\mu}{T} \right) \frac{d m^2 T}{2 \pi^2} K_2 \left( \frac{m}{T} \right),$$ \hfill (4)

with $d$ being the degeneracy factor and $m$ the particle mass, $K_2(x)$ is the Bessel function. Note that the relativistic form of a dispersion relation is considered, $\omega(k) = \sqrt{m^2 + k^2}$, where $\omega$ and
$k$ are the free particle energy and momentum, respectively. The GCE VDW pressure $p(T, \mu)$ is then obtained by inserting $n(T, \mu)$ into Eq. (1).

The VDW pressure (1) is a unique function of variables $T$ and $n$ for all $T \geq 0$ and $0 \leq n \leq 1/b$. The VDW equation of state contains a 1st order liquid-gas phase transition and has a critical point. The critical point $(T_c, n_c)$ corresponds to the temperature and particle number density, where

$$
(\frac{\partial p}{\partial n})_T = (\frac{\partial^2 p}{\partial n^2})_T = 0.
$$

(5)

The thermodynamical quantities at the critical point are equal to $[1, 2]$:

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

(6)

At $T > T_c$ the following equation is always valid,

$$
(\frac{\partial p}{\partial n})_T > 0,
$$

(7)

while at $T < T_c$ the unstable region appears with

$$
(\frac{\partial p}{\partial n})_T < 0.
$$

(8)

Therefore, the VDW isotherm $p(n, T)$ at $T < T_c$ has a local maximum at $n = n_1$ and a local minimum at $n = n_2 > n_1$. The unstable part (8) of the VDW isotherm at the interval $[n_1, n_2]$, together with two additional parts – $[n_1, n_g]$ and $[n_2, n_l]$ (they are called metastable) – are transformed to a mixture of two phases: a gas with density $n_g < n_1$ and a liquid with density $n_l > n_2$. This is done according to the Maxwell rule of the equal areas (see, e.g., Refs. [1, 2]) which leads to a constant pressure $p(T, n_g) = p(T, n_l)$ inside the density interval $[n_g, n_l]$.

In the GCE the mixed phase region appears in a different way. At $T > T_c$ there is a unique solution of Eq. (3), while at $T < T_c$ it may have either one solution or three different solutions for particle number density $n(T, \mu)$. Therefore, either one or three different solutions may also appear for the VDW pressure $p(T, \mu)$. In a case when three different values of $p(T, \mu)$ are possible, the solution with a largest pressure survives in accordance to the Gibbs criterion (see Appendix A for details). The gas-liquid mixed phase on the $T$-$\mu$ plane belongs to the line $\mu = \mu(T)$, where the solutions $n_g(T, \mu)$ and $n_l(T, \mu)$ correspond to equal pressures, $p_g(T, \mu) = p_l(T, \mu)$.
The classical Boltzmann statistics leads to nonphysical behavior in zero temperature limit. This is already seen on an ideal gas level. For the ideal Boltzmann gas an entropy density in non-relativistic limit $T/m \ll 1$ is equal to

$$s_{\text{Boltz}}^{\text{id}} \approx \frac{n^{\text{id}}}{T} \left[ m + \frac{5}{2} T - \mu \right].$$  \hspace{1cm} (9)

In Eq. (9) we use expressions $p^{\text{id}} = n^{\text{id}}T$ and $\varepsilon^{\text{id}} \approx n^{\text{id}}(m + 3T/2)$ for the ideal gas pressure and (non-relativistic) energy density, respectively. Using an asymptotic expansion for $K_2$ Bessel function at large arguments, $K_2(x) \approx \sqrt{\frac{\pi}{2x}} \exp(-x)$, one finds from Eq. (4) that to have a finite (nonzero) value $n_0$ of particle number density at $T \to 0$ the chemical potential should be equal to

$$\mu \approx m - \frac{3T}{2} \ln(T/c_0), \hspace{1cm} c_0 = \frac{2\pi n_0^{2/3}}{m}. $$ \hspace{1cm} (10)

Thus, only one limiting value $\mu = m$ is admitted in the Boltzmann gas at $T = 0$ (this corresponds to zero value of chemical potential, $\mu_{\text{non-rel}} \equiv \mu - m$, used in non-relativistic statistical physics). For $\mu > m$ or $\mu < m$ at $T = 0$ one finds for the particle number density $n = 0$ or $n = \infty$, respectively.

Therefore, the entropy of the ideal Boltzmann gas (9) at $T \to 0$ is

$$s^{\text{id}} \approx n_0 \left[ \frac{5}{2} + \frac{3}{2} \ln(T/c_0) \right],$$ \hspace{1cm} (11)

and it becomes negative in zero temperature limit, in a contradiction with the 3rd law of thermodynamics. The quantum statistics is needed to describe a physical system at $T \to 0$.

### III. VDW EQUATION OF STATE WITH QUANTUM STATISTICS

Quantum generalization of the VDW equation of state is not a trivial task. Let us outline some general requirements for the quantum version of this equation of state:

1. It should be transformed to the ideal quantum gas at $a = b = 0$.

2. It should be equivalent to the classical VdW equation of state (1) in a region of thermodynamical parameters where quantum statistics can be neglected.
3. The entropy should be a non-negative quantity and go to zero at $T \to 0$.

Pressure of the ideal quantum gas in the GCE reads

$$p_{\text{id}}(T, \mu) = \frac{d}{3} \int \frac{d^3k}{(2\pi)^3} \sqrt{\frac{k^4}{\sqrt{m^2 + k^2}}} \left[ \exp \left( \frac{\sqrt{m^2 + k^2} - \mu}{T} \right) + \eta \right]^{-1}.$$  \hspace{1cm} (12)

In Eq. (12), $\eta$ equals +1 for Fermi statistics, -1 for Bose statistics, and 0 for the Boltzmann approximation. All other thermodynamical functions can be calculated from Eqs. (2). Ideal quantum gas expressions for thermodynamical functions satisfy the 3rd law of thermodynamics, i.e., $s \geq 0$ and $s \to 0$ at $T \to 0$.

Let us now formulate a generalization of the VDW equation of state which includes effects of the quantum statistics. Note that $p(T, \mu)$ for the Boltzmann case can be rewritten using Eq. (3) as

$$p(T, \mu) = p_{\text{id}}(T, \mu^*) - an^2,$$  \hspace{1cm} (13)

where

$$\mu^* = \mu - b p(T, \mu) - abn^2 + 2an.$$  \hspace{1cm} (14)

The function $p_{\text{id}}$ in Eq. (13) corresponds to the ideal gas pressure in the Boltzmann approximation, i.e. $\eta = 0$ in Eq. (12). We suggest the quantum VDW equation of state in the same form as Eq. (13) but with ideal quantum gas pressure $p_{\text{id}}$, i.e., for quantum case we propose to take $\eta = \pm 1$ in Eq. (12) which corresponds to the Fermi or Bose statistics.

In accordance with (2), one has for the particle number density

$$n(T, \mu) \equiv \left( \frac{\partial p}{\partial \mu} \right)_T = n_{\text{id}}(T, \mu^*) \left( 1 - bn \right) \left( 1 + 2a \frac{\partial n}{\partial \mu} \right) - 2an \frac{\partial n}{\partial \mu}.$$  \hspace{1cm} (15)

This equation can be transformed to

$$\left[ n_{\text{id}}(T, \mu^*) \left( 1 - bn \right) - n \right] \left( 1 + 2a \frac{\partial n}{\partial \mu} \right) = 0.$$  \hspace{1cm} (16)

Solution of this equation which has a physical meaning reads

$$n(T, \mu) = \frac{n_{\text{id}}(T, \mu^*)}{1 + bn_{\text{id}}(T, \mu^*)}, \quad n_{\text{id}}(T, \mu) = \frac{d}{2\pi^2} \int_0^\infty dk k^2 \left[ \exp \left( \frac{\sqrt{m^2 + k^2} - \mu}{T} \right) + \eta \right]^{-1},$$  \hspace{1cm} (17)

and it has the same form as Eq. (3). However, a principal difference is that $n_{\text{id}}$ in Eq. (17) is a particle number density of the ideal quantum gas, whereas $n_{\text{id}}$ in Eq. (3) corresponds to the
ideal classical gas, i.e., $\eta = 0$, and is given by Eq. (11). We also note that, in the quantum case, expression (11) for the shifted chemical potential $\mu^*$ should be used instead of (3).

Equations (13) and (17) correspond to the system of two equations for two unknown functions: $p(T, \mu)$ and $n(T, \mu)$. The VDW model defined by these equations possesses all the required properties. Firstly, at $a = b = 0$ Eqs. (13) and (17) are reduced to the ideal quantum gas expressions. Secondly, for those $T$ and $\mu^*$ values, where quantum expressions for $p^{id}$ and $n^{id}$ can be approximated by the Boltzmann statistics, i.e., by Eq. (4) for $n^{id}$ and $p^{id} = T n^{id}$ for the ideal gas pressure, Eqs. (13) and (17) become automatically equivalent to the classical VdW equation of state (1). Thirdly, the entropy density has the following form

$$s(T, \mu) \equiv \frac{\partial p}{\partial T} \mu = \frac{s^{id}(T, \mu^*)}{1 + b n^{id}(T, \mu^*)},$$

thus, it is always positive for the quantum ideal gas expressions of $s^{id}$, and $s \to 0$ at $T \to 0$.

The energy density can be calculated from Eq. (2) as

$$\varepsilon(T, \mu) = \left[ \overline{\varepsilon}_{id}(T, \mu^*) - a n \right] n,$$

where $\overline{\varepsilon}_{id}(T, \mu)$ is the average energy per particle in the ideal gas

$$\overline{\varepsilon}_{id}(T, \mu) = \frac{\varepsilon^{id}(T, \mu)}{n^{id}(T, \mu)}.$$

One can rewrite the VDW pressure as a function of temperature $T$ and particle density $n$. It follows from Eq. (17) that $\mu^*$ can be written as a function of $T$ and $n$,

$$\mu^*(n, T) = \mu^{id}\left(\frac{n}{1 - bn}, T\right),$$

where $\mu^{id}(n, T)$ is the chemical potential of the ideal quantum gas which is a solution of the following transcendental equation for the given $n$ and $T$:

$$n = \frac{d^2}{2\pi^2} \int_0^{\infty} dk \, k^2 \left[ \exp\left(\frac{\sqrt{m^2 + k^2} - \mu^{id}}{T}\right) + \eta \right]^{-1}.$$  

Equation (13) can be then rewritten as

$$p = p^{id}\left[T, \mu^{id}\left(\frac{n}{1 - bn}, T\right)\right] - a n^2.$$
One can easily check that this equation coincides with Eq. (1) in a case of the Boltzmann statistics and, thus, can be indeed regarded as a quantum generalization of the classical VDW equation in the CE. It can be also instructive to consider a formulation of the VDW equation with quantum statistics within the thermodynamic mean-field approach developed in Refs. [6–8]. This is presented in Appendix B.

IV. NUCLEAR MATTER

The properties of nuclear matter have been described in many different models, particularly those which employ a self-consistent mean field approach [9–13]. Excluded-volume corrections in the mean-field models have been considered in Refs. [4, 7, 14]. We now use the VDW equation of state with quantum statistics to describe the properties of symmetric nuclear matter. Namely, a Fermi gas of nucleons ($m \approx 938$ MeV and $d = 4$) will be considered with attractive and repulsive interactions described by the $a$ and $b$ VDW parameters, respectively. Our consideration will be restricted to small temperatures, $T \leq 30$ MeV, thus, a pion production will be neglected. We also neglect a possible formation of nucleon clusters (i.e., ordinary nuclei) and baryonic resonances (like $N^*$ and $\Delta$) which may be important at low and high baryonic density, respectively. Within these approximations, the number of nucleons $N$ becomes a conserved number and an independent variable in the CE. The chemical potential $\mu$ of the GCE regulates the number density of nucleons.

A. Properties at $T = 0$

For calculations of the thermodynamic functions in the GCE, Eqs. (13), (17), (18), and (19) will be used. In terms of variable $\mu^*$ (13) thermodynamical functions of the quantum VDW gas can be presented in terms of the corresponding functions of the ideal quantum gas as the following

$$
\begin{align*}
n(T, \mu) &= \frac{n^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)}, \\
p(T, \mu) &= p^{\text{id}}(T, \mu^*) - a \left[ \frac{n^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)} \right]^2, \\
\varepsilon(T, \mu) &= \frac{\varepsilon^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)} - a \left[ \frac{n^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)} \right]^2, \\
s(T, \mu) &= \frac{s^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)}.
\end{align*}
$$
At zero temperature the ideal gas quantities in Eqs. (24) and (25) can be written as

\[ n_{id}(T=0, \mu^*) = \frac{d}{2\pi^2} \frac{\sqrt{\mu^*^2 - m^2}}{\int_0^\infty dk k^2} = \frac{d}{6\pi^2} (\mu^*^2 - m^2)^{3/2}, \]  

\[ p_{id}(T=0, \mu^*) = \frac{d}{6\pi^2} \frac{\sqrt{\mu^*^2 - m^2}}{\int_0^\infty dk \frac{k^4}{\sqrt{k^2 + m^2}}} = \frac{d}{48\pi^2} \mu^* \sqrt{\mu^*^2 - m^2 (2\mu^*^2 - 5m^2)} 
- \frac{d}{16\pi^2} m^4 \ln \frac{m}{\mu^* + \sqrt{\mu^*^2 - m^2}}, \]  

\[ \epsilon_{id}(T=0, \mu^*) = \frac{d}{2\pi^2} \frac{\sqrt{\mu^*^2 - m^2}}{\int_0^\infty dk k^2 \sqrt{k^2 + m^2}} = \frac{d}{16\pi^2} \mu^* \sqrt{\mu^*^2 - m^2 (2\mu^*^2 - m^2)} 
+ \frac{d}{16\pi^2} m^4 \ln \frac{m}{\mu^* + \sqrt{\mu^*^2 - m^2}}, \]  

\[ s_{id}(T=0, \mu^*) = \lim_{T\to0} \frac{\epsilon_{id}(T, \mu^*) + p_{id}(T, \mu^*) - \mu^* n_{id}(T, \mu^*)}{T} = 0. \]  

We fix parameters \( a \) and \( b \) in a way to reproduce the properties of nuclear matter in its ground state (see, e.g., Ref. \[15\]), i.e., it should be \( p = 0 \) and \( \epsilon/n = m + E_B \approx 922 \text{ MeV} \) at \( T = 0 \) and \( n = n_0 \approx 0.16 \text{ fm}^{-3} \). Here \( E_B \approx -16 \text{ MeV} \) is the binding energy per nucleon. One then finds, \( a \approx 329 \text{ MeV fm}^{-3} \) and \( b \approx 3.42 \text{ fm}^{-3} \). Note that parameter \( b \) of the proper particle volume can be expressed in terms of hard-core radius \( r \) as \( b = 16\pi r^3/3 \). This gives \( r \approx 0.59 \text{ fm} \) for the hard-core nucleon radius.

The pressure \( p \) and binding energy \( E_B \) as functions on nucleon density \( n \) at \( T = 0 \) are shown in Fig. 1(a) and (b), respectively. The stable part of the VDW isotherm is depicted by solid lines, while metastable and unstable parts are depicted by dash-dotted and dotted lines, respectively. We note that horizontal part of the isotherm corresponds to the mixed phase and results from the Maxwell construction (see more details below). At very small densities a gaseous phase with almost ideal gas behavior is always present. At \( T = 0 \) this phase, seen more clearly in Fig. 2, can, however, exist as a metastable state only.
Figure 1: Dependence of pressure $p$ (a) and binding energy $E_B$ (b) on the nucleon density $n$ at $T = 0$. The VDW parameters are $a \approx 329$ MeV·fm$^3$ and $b \approx 3.42$ fm$^3$ ($r \approx 0.59$ fm). The open circle corresponds to the ground state of nuclear matter. The dash-dotted line corresponds to the metastable part of VDW isotherm, whereas the dotted line corresponds to the unstable part.

Figure 2: The same as in Fig. 1 but for small values of $n$.

B. Phase diagram

The VDW pressure isotherms are depicted in $(T, v)$ and $(T, n)$ coordinates ($v \equiv 1/n$) in Fig. 3 (a) and (b), respectively. They are calculated within the quantum VDW equation of state using Eq. (23) with $a \approx 329$ MeV·fm$^3$ and $b \approx 3.42$ fm$^3$. The critical temperature is found to be $T_c \approx 19.7$ MeV. This value is close to experimental estimates in Refs. [16, 17]. At $T < T_c$ two phases appear: the gas and liquid phases separated by a first-order phase
Figure 3: Pressure isotherms in (a) \((p, v)\) and (b) \((p, n)\) coordinates, calculated in the quantum Van der Waals equation of state with parameters \(a \approx 329 \text{ MeV} \cdot \text{fm}^3\) and \(b \approx 3.42 \text{ fm}^3\) \((r \approx 0.59 \text{ fm})\). The dashed-dotted lines present the metastable parts of the VDW isotherms at \(T < T_c\), whereas the dotted lines correspond to unstable parts. The full circle on the \(T = T_c\) isotherm corresponds to the critical point, while the open circle at \(T = 0\) in (b) shows the ground state of nuclear matter. Shaded grey area in (b) depicts the mixed phase region.

transition. The horizontal lines correspond to the Maxwell construction of equal areas and the shaded grey area in Fig. 3 (b) depicts the resulting mixed phase region. The nucleon number density at the critical point is found to be \(n_c \approx 0.07 \text{ fm}^{-3} \approx 0.4 n_0\). Normal nuclear matter with \(n = n_0 \approx 0.16 \text{ fm}^{-3}\) and \(T = 0\) corresponds to a point placed exactly on the boundary between the mixed and liquid phases. Note also that the maximal value of the nucleon number density in the VDW model is \(n_{\text{max}} = 1/b\), which equals to \(n_{\text{max}} \approx 0.29 \text{ fm}^{-3}\) for the chosen value of parameter \(b\).

In the mixed phase region, the particle number density is given by

\[
    n = \xi n_g + (1 - \xi) n_l, \tag{30}
\]

where \(\xi\) and \(1 - \xi\) are the volume fractions of the gaseous and liquid components, respectively. The values of \(n_g\) and \(n_l\) in Eq. (30) are the particle densities of, respectively, the gaseous and liquid phases at the corresponding boundaries with the mixed phase. A behavior of the mixed phase at \(T = 0\) is rather special. The gaseous phase is absent at \(T = 0\), i.e., \(n_g = 0\) at the mixed phase boundary as this boundary starts from the point \(T = 0\) and \(n = 0\). The gaseous
phase exists however at any $T > 0$ for small enough values of the particle number density.

Parameters of the critical point found in the VDW case with Fermi statistics for nucleons differ significantly from those values for the classical VDW gas. With the same VDW parameters $a$ and $b$ as in the Fermi statistics, the classical VDW equation (1), i.e., with Boltzmann statistics, would give $T_c = 8a/27b \approx 28.5$ MeV and $n_c = 1/3b \approx 0.10$ fm$^{-3}$. This further indicates an importance of the effects of quantum statistics: these effects are not only crucial in the limit $T \to 0$, but also remain quantitatively important even near the critical point.

In Fig. 4 the phase diagram of the symmetric nuclear matter in ($T, \mu$) coordinates is depicted. The nucleon density at different temperature $T$ and chemical potential $\mu$ is presented. At $T < T_c$ there is the $T-\mu$ region with three different solutions for $p(T, \mu)$ at given $T$ and $\mu$. According to the Gibbs criterion, a solution with a largest pressure survives (see Appendix A), and only this solution for $n(T, \mu)$ is depicted in Fig. 4. A location of the critical point is shown in Fig. 4 by the full circle, while the normal nuclear matter state corresponds to the open circle. Note that $\mu_0 \approx 922$ MeV corresponds to the chemical potential of the normal nuclear matter which is placed on a boundary with the liquid phase. The values $\mu < \mu_0$ are forbidden at $T = 0$ (these values of $\mu$ lead formally to $n = 0$). The values $\mu > \mu_0$ at $T = 0$ are possible and correspond to the nuclear liquid.

The phase transition line, $\mu = \mu_{\text{mix}}(T)$, shown in Fig. 4 starts from the normal nuclear matter state with $T = 0$, $\mu \approx 922$ MeV and ends at the critical point with $T_c \approx 19.7$ MeV, $\mu_{\text{mix}}(T_c) \approx 908$ MeV. This line presents the whole mixed phase region shown by the grey area in Fig. 3. At each $T < T_c$ two solutions, $n_g(T, \mu)$ and $n_l(T, \mu)$, with different particle densities, $n_g(T, \mu) < n_l(T, \mu)$ and equal pressures, $p_g(T, \mu) = p_l(T, \mu)$, exist at the phase transition line $\mu = \mu_c(T)$. On this line, the discontinuities of thermodynamical quantities $n$, $\varepsilon$, and $s$ take place.

At $T > T_c$ there is only one solution $n(T, \mu)$ for any $T$ and $\mu$ values, i.e., there are no distinct gaseous or liquid phases. Nevertheless, as seen from Fig. 3 very rapid, although continuous, changes of particle number density take place in a narrow $T-\mu$ region even at $T > T_c$. This is a manifestation of the so called smooth crossover phenomenon.

At any $T > 0$, there are no restrictions on possible values of the chemical potential, i.e., any values of $\mu$ between $-\infty$ and $+\infty$ are possible. When $\mu$ decreases the particle number density
Figure 4: Density of the symmetric nuclear matter in $(T, \mu)$ coordinates, calculated in the quantum van der Waals equation of state with parameters $a \approx 329$ MeV fm$^3$ and $b \approx 3.42$ fm$^3$ ($r \approx 0.59$ fm). The open circle denotes the ground state of nuclear matter, the full circle corresponds to the critical endpoint, and the phase transition curve is depicted by the solid black line.

decreases too and goes to zero at $\mu \to -\infty$. At very small $n$, both the particle interactions and Fermi statistics effects become negligible. The system of nucleons behaves then as the ideal Boltzmann gas. In an opposite limit, $\mu \to \infty$, nucleon density $n(T, \mu)$ goes to its upper limiting value $1/b$. The VDW pressure behaves then approximately as $p \approx nT/(1 - bn)$ and goes to infinity. Different theoretical models and their comparison with experimental estimates of the nuclear matter properties have been widely discussed in the literature, see, e.g., Refs. [18–20]. In the present paper we do not attempt to make any detail comparison of the developed VDW quantum model with existing data for nuclear matter. Some extensions of the model will probably be needed. These questions are, however, beyond the scope of the present paper.
V. SUMMARY

In the present paper we have formulated a generalization of the van der Waals (VDW) equation of state to include effects of quantum statistics. In the grand canonical ensemble a system of two transcendental equations for the pressure and particle density is obtained. These equations can be solved for all possible values of temperature, $T \geq 0$, and chemical potential, $-\infty < \mu < \infty$. Our quantum generalization of the VDW equation satisfies all basic requirements: it reduces to the ideal Fermi or Bose gas for $a = b = 0$, to the classical VDW equation in the Boltzmann limit, and it satisfies the 3rd law of thermodynamics, i.e. $s \to 0$ as $T \to 0$.

The VDW equation with Fermi statistics has been then applied to a system of interacting nucleons to describe the properties of symmetric nuclear matter. The VDW parameters $a$ and $b$ of interacting nucleons are fixed by the properties of the nuclear matter ground state: $T = p = 0$, $n = n_0 = 0.16 \text{ fm}^{-3}$, $E_B = -16 \text{ MeV}$. We find $a \approx 329 \text{ MeV fm}^3$ and $b \approx 3.42 \text{ fm}^3$. With these parameters the VDW model predicts a 1st order liquid-gas phase transition with a critical endpoint located at $T_c \approx 19.7 \text{ MeV}$ and $n_c \approx 0.07 \text{ fm}^{-3}$. Extensions of the presented formulation as well as new physical applications will be a subject of the further studies.

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Appendix A: Gibbs criteria and Maxwell construction

A statistical system in the GCE is defined by two independent variables, $T$ and $\mu$. Two distinct phases, gas and liquid, co-exist if their pressures are equal, $p_g(T, \mu) = p_l(T, \mu)$. In a case of $p_g(T, \mu) \neq p_l(T, \mu)$, only a phase with a larger pressure survives. These statements are known as the Gibbs criteria for the 1st order phase transition (see, e.g., Refs. [1, 2]). We
now prove that the Gibbs criteria are equivalent to the Maxwell construction of equal areas for the VDW equation of state.

At $T < T_c$, the Maxwell construction replaces a part of the VDW isotherm $p = p(v, T)$ by a horizontal line $p = p_{mix}$ which corresponds to the mixed phase region for all $v$ in the interval $[v_l, v_g]$. This is shown in Fig. 5. The Maxwell equal areas are:

$$
\int_{v_l}^{v_0} dv \left[ p_{mix} - p(v, T) \right] = \int_{v_0}^{v_g} dv \left[ p(v, T) - p_{mix} \right], \quad (A.1)
$$

where $v_l < v_0 < v_g$ and $p(v_0, T) = p_{mix}$. The replaced parts of the isotherm are interpreted as metastable ($\partial p / \partial v < 0$) and unstable ($\partial p / \partial v > 0$) states. They are shown in Fig. 5 by the dashed-dotted and dotted lines, respectively.

Using thermodynamical identity

$$
\left( \frac{\partial \mu}{\partial p} \right)_T = v, \quad (A.2)
$$

one can present the chemical potential $\mu_A$ at any point $A$ on the isotherm as

$$
\mu_A = \mu_B + \int_{p_B}^{p_A} dp' v(p', T), \quad (A.3)
$$

where $B$ is an arbitrary point on the isotherm, and integration in (A.3) is performed along the path from point $B$ to point $A$ on the isotherm. With Eqs. (A.1) and (A.3) one can easily prove that

$$
\mu(v_l, T) = \mu(v_g, T) \equiv \mu_{mix}, \quad (A.4)
$$

thus, the Maxwell and Gibbs constructions for the mixed phase are equivalent.

According to Eq. (A.3) the chemical potential decreases with $v$ if $(\partial p / \partial v)_T < 0$, and increases if $(\partial p / \partial v)_T > 0$. Therefore, inside the mixed phase region $[v_l, v_g]$ the chemical potential reaches its minimal value $\mu = \mu_2 < \mu_{mix}$ at $v = v_2$ and its maximal value $\mu = \mu_1 > \mu_{mix}$ at $v = v_1$. The points $v_1$ and $v_2$, where $(\partial p / \partial v)_T = 0$, correspond to the boundaries between the metastable and unstable parts of the VDW isotherm. At $v < v_l$ and $v > v_g$ the chemical potential is a monotonously decreasing function of $v$, with $\mu \to -\infty$ at $v \to b$ and $\mu \to -\infty$ at $v \to \infty$. Therefore, there is a point $v'_2 > v_g$ in the gaseous phase where $\mu = \mu_2$, and a point $v'_1 < v_l$ in the liquid phase where $\mu = \mu_1$. These two points are depicted in Fig. 5(a). At both $\mu > \mu_1$
Figure 5: A generic VDW isotherm $p(v, T)$ for $T < T_c$. Points $l$ and $g$ on the isotherm correspond to the boundaries of the mixed phase. In (a) point 1 (2) on the isotherm corresponds to the maximum (minimum) value of the chemical potential inside the mixed phase, which is reached at the boundary between metastable and unstable phases, while point $l'$ ($2'$) corresponds to the same value of the chemical potential reached in the pure liquid (gaseous) phase. In (b) points $a_1$ (gaseous phase), $a_2$ (metastable liquid phase) and $a_3$ (unstable phase) which all correspond to the same value of the chemical potential are depicted on the VDW isotherm.

and $\mu < \mu_2$ the GCE VDW pressure $p(T, \mu)$ is a unique function. On the other hand, there are three different solutions for the VDW pressure at $\mu_2 < \mu < \mu_1$.

Let us first consider $\mu_2 < \mu_a < \mu_{\text{mix}}$. There are three points on the VDW isotherm with $\mu = \mu_a$ shown in Fig. 5 (b): point $a_1$ in the gaseous phase with $v_g < v_{a_1} < v_{a_2}$, point $a_2$ in the metastable liquid phase with $v_l < v_{a_2} < v_2$, and point $a_3$ in the unstable phase with $v_2 < v_{a_3} < v_1$. Using Eq. (A.3) one finds that

$$\int_{p_{a_1}^l}^{p_{\text{mix}}} d\nu' v'(p', T) = \int_{p_{a_2}^g}^{p_{\text{mix}}} d\nu' v'(p', T) = \int_{p_{a_3}^2}^{p_{\text{mix}}} d\nu' v'(p', T) - \int_{p_{a_3}^3}^{p_{\text{mix}}} d\nu' v'(p', T). \quad (A.5)$$

Applying the mean value theorem to integrals in Eq. (A.5) one obtains

$$(p_{\text{mix}} - p_{a_1}^l) \overline{v}_1 = (p_{\text{mix}} - p_{a_2}^g) \overline{v}_2 = (p_{\text{mix}} - p_2) \overline{v}_{31} - (p_2 - p_{a_3}^3) \overline{v}_{32}, \quad (A.6)$$

where $v_l < \overline{v}_2 < v_{a_2}^g$, $v_g < \overline{v}_1 < v_{a_1}^g$, $v_l < \overline{v}_{31} < v_2 < \overline{v}_{32} < v_{a_3}^3$, and $p_2 = p(v_2, T)$. It follows from Eq. (A.6) that $p_{a_1}^l > p_{a_2}^g$ and $p_{a_1}^l > p_{a_3}^3$, i.e., at $\mu_2 < \mu < \mu_{\text{mix}}$ the gaseous phase should be realized.
according to the Gibbs criterium as its pressure is larger than pressures of both metastable and unstable states.

The same arguments are applied to $\mu_{\text{mix}} < \mu < \mu_1$ and show that the liquid pressure is then larger than pressures of both metastable and unstable states. Therefore, for the VDW equation of state the Maxwell construction of the equal areas and Gibbs criteria are fully equivalent. The Maxwell construction is applied in the CE, whereas the Gibbs criteria are used in the GCE. We emphasize that this statement is valid not only for the classical VDW equation of state, but also for the VDW equation with Fermi statistics with the isotherms depicted in Fig. 8.

Appendix B: Thermodynamic mean-field approach

In the framework of the thermodynamic mean-field (TMF) approach [6–8] the pressure and particle number density are presented as

$$p(T, \mu) = p^{\text{id}}[T, \mu_{\text{id}}(n, T)] + P^{\text{ex}}(n, T), \quad (B.1)$$

$$n(T, \mu) = n^{\text{id}}[T, \mu - U(n, T)], \quad (B.2)$$

where $P^{\text{ex}}(n, T)$ and $U(n, T)$ are, respectively, the excess pressure and the thermodynamic mean field. A presence of non-zero quantities $P^{\text{ex}}(n, T)$ and $U(n, T)$ in Eqs. (B.1) and (B.2) correspond to interaction between particles, and the condition of thermodynamic consistency reads [8]:

$$n \frac{\partial U}{\partial n} = \frac{\partial P^{\text{ex}}}{\partial n}. \quad (B.3)$$

For a specific choice of $P^{\text{ex}}(n, T)$ and $U(n, T)$ functions, one proceeds by solving of Eq. (B.2) for $n = n(T, \mu)$, and then the pressure $p(T, \mu)$ can be obtained from Eq. (B.1) (see some examples in Ref. [8]).

The VDW equation of state with quantum statistics defined by Eqs. (13) and (17) can be rewritten in the TMF form (B.1) and (B.2). In order to determine $P^{\text{ex}}(n, T)$ and $U(n, T)$ we rewrite Eq. (23) for the VDW pressure as

$$p = p^{\text{id}}[T, \mu_{\text{id}}(n, T)] + p^{\text{id}}\left[T, \mu_{\text{id}}\left(\frac{n}{1 - bn}, T\right)\right] - p^{\text{id}}[T, \mu_{\text{id}}(n, T)] - an^2. \quad (B.4)$$
Comparing (B.1) and (B.4) one finds

$$P_{\text{ex}}^{\text{VdW}}(n, T) = \rho^{\text{id}}[T, \mu^{\text{id}}(\frac{n}{1-bn}, T)] - \rho^{\text{id}}[T, \mu^{\text{id}}(n, T)] - an^2. \quad (B.5)$$

The mean field $U_{\text{VdW}}(n, T)$ can be then calculated from Eq. (B.3) as

$$U_{\text{VdW}}(n, T) = \int_0^n \frac{1}{n'} \frac{\partial P_{\text{ex}}^{\text{VdW}}(n', T)}{\partial n'} dn'. \quad (B.6)$$

For the Boltzmann statistics, Eqs. (B.5) and (B.6) are simplified to the following analytical expressions:

$$P_{\text{ex}}^{\text{VdW}}(n, T) = Tn \frac{bn}{1-bn} - an^2, \quad (B.7)$$

$$U_{\text{VdW}}(n, T) = T \frac{bn}{1-bn} - T\ln(1-bn) - 2an. \quad (B.8)$$

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