Van der Waals equation of state with Fermi statistics for nuclear matter

V. Vovchenko, 1,2,3 D. V. Anchishkin, 4,1,2 and M. I. Gorenstein^{4, 2}

¹*Taras Shevchenko National University of Kiev, 03022 Kiev, Ukraine*

²*Frankfurt Institute for Advanced Studies, Johann Wolfgang Goethe University, D-60438 Frankfurt, Germany*

³GSI Helmholtzzentrum für Schwerionenforschung GmbH, D-64291 Darmstadt, Germany

⁴*Bogolyubov Institute for Theoretical Physics, 03680 Kiev, Ukraine*

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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 the existence of a first-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 carried out in this paper: (i) the grand canonical ensemble formulation and (ii) the 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 $n_0 = 0.16$ 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 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 first-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 the most simple and transparent form (see, e.g., Refs. [\[1,2\]](#page-7-0)),

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

where $a > 0$ and $b > 0$ are the VDW parameters that 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 the 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. To apply the VDW equation of state to systems with variable numbers of particles it is necessary to switch to the grand canonical ensemble (GCE). This procedure was first performed for the EV model, i.e., for $a = 0$ in Eq. (1), in Refs. [\[3,4\]](#page-7-0). In our recent paper [\[5\]](#page-7-0), 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. [\[5\]](#page-7-0) 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 [\[5\]](#page-7-0) 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 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, $n_0 = 0.16$ fm⁻³; binding energy per nucleon, -16 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.](#page-1-0) In Sec. [IV](#page-2-0) the VDW equation of state with Fermi statistics is applied to a description of nuclear matter. A summary in Sec. [V](#page-5-0) 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 [\[5\]](#page-7-0) 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 μ . It contains 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 μ derivatives:

$$
n(T,\mu) = \left(\frac{\partial p}{\partial \mu}\right)_T, \quad s(T,\mu) = \left(\frac{\partial p}{\partial T}\right)_\mu,
$$

$$
\varepsilon(T,\mu) = T\left(\frac{\partial p}{\partial T}\right)_\mu + \mu\left(\frac{\partial p}{\partial \mu}\right)_T - p.
$$
 (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 a transcendental equation for particle number density $n \equiv n(T, \mu)$ as a function of *T* and μ [\[5\]](#page-7-0):

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

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

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

with *d* being the degeneracy factor, *m* the particle mass, and $K_2(x)$ the Bessel function. Note that the relativistic form of a dispersion relation is considered, $\omega(k) = \sqrt{m^2 + k^2}$, where ω and *k* are the free particle energy and momentum, respectively. The GCE VDW pressure $p(T, \mu)$ is then obtained by inserting $n(T, \mu)$ (3) into Eq. [\(1\)](#page-0-0).

The VDW pressure [\(1\)](#page-0-0) is a unique function of variables *T* and *n* for all $T \ge 0$ and $0 \le n \le 1/b$. The VDW equation of state contains a first-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

$$
\left(\frac{\partial p}{\partial n}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial n^2}\right)_T = 0. \tag{5}
$$

The thermodynamical quantities at the critical point are equal to [\[1,2\]](#page-7-0)

$$
T_c = \frac{8a}{27b}, \quad n_c = \frac{1}{3b}, \quad p_c = \frac{a}{27b^2}.
$$
 (6)

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

$$
\left(\frac{\partial p}{\partial n}\right)_T > 0,\t\t(7)
$$

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

$$
\left(\frac{\partial p}{\partial n}\right)_T < 0. \tag{8}
$$

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— $[n_g, n_1]$ 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 equal areas (see, e.g., Refs. [\[1,2\]](#page-7-0)), 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 the 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 the largest pressure survives in accordance with the Gibbs criterion

(see Appendix [A](#page-6-0) for details). The gas-liquid mixed phase in the *T*- μ 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 the zero temperature limit. This is already seen on an ideal gas level. For the ideal Boltzmann gas an entropy density in the nonrelativistic limit $T/m \ll 1$ is equal to

$$
s_{\text{Boltz}}^{\text{id}} \cong \frac{n^{\text{id}}}{T} \left[m + \frac{5}{2}T - \mu \right]. \tag{9}
$$

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

$$
\mu \cong m - \frac{3 T}{2} \ln(T/c_0), \qquad c_0 = \frac{2 \pi n_0^{2/3}}{m}.
$$
 (10)

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

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

$$
s^{\rm id} \cong n_0 \left[\frac{5}{2} + \frac{3}{2} \ln(T/c_0) \right],\tag{11}
$$

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

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.

- (i) It should be transformed to the ideal *quantum* gas at $a = b = 0.$
- (ii) It should be equivalent to the classical VDW equation of state [\(1\)](#page-0-0) in a region of thermodynamical parameters where quantum statistics can be neglected.
- (iii) The entropy should be a non-negative quantity and go to zero at $T \to 0$.

The pressure of the ideal quantum gas in the GCE reads

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

In Eq. [\(12\)](#page-1-0), η equals +1 for Fermi statistics, -1 for Bose statistics, and 0 for the Boltzmann approximation. All other thermodynamical functions can be calculated from Eqs. [\(2\)](#page-0-0). Ideal quantum gas expressions for thermodynamical functions satisfy the third law of thermodynamics, i.e., $s \ge 0$ and $s \to 0$ at $T \rightarrow 0$.

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

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

where

$$
\mu^* = \mu - bp(T, \mu) - abn^2 + 2an. \tag{14}
$$

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

In accordance with Eq. (2) , one has the following for the particle number density:

$$
n(T,\mu) \equiv \left(\frac{\partial p}{\partial \mu}\right)_T
$$

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

This equation can be transformed to

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

The solution of this equation, which has a physical meaning, reads

$$
n(T,\mu) = \frac{n^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)},
$$
\n(17)

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

and it has the same form as Eq. (3) . However, a principal difference is that n^{id} in Eq. (17) is the particle number density of the ideal *quantum* gas, whereas *n*id in Eq. [\(3\)](#page-1-0) corresponds to the ideal *classical* gas, i.e., $\eta = 0$, and is given by Eq. [\(4\)](#page-1-0). We also note that, in the quantum case, expression (14) for the shifted chemical potential μ^* should be used instead of Eq. [\(3\)](#page-1-0).

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. First, at $a = b = 0$ Eqs. (13) and (17) are reduced to the ideal *quantum* gas expressions. Second, for those *T* and μ^* values, where *quantum* expressions for p^{id} and *n*id can be approximated by the Boltzmann statistics, i.e., by Eq. [\(4\)](#page-1-0) 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 [\(1\)](#page-0-0). Third, the entropy density has the following form:

$$
s(T,\mu) \equiv \left(\frac{\partial p}{\partial T}\right)_{\mu} = \frac{s^{\text{id}}(T,\mu^*)}{1 + b n^{\text{id}}(T,\mu^*)};\tag{18}
$$

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. [\(2\)](#page-0-0) as

$$
\varepsilon(T,\mu) = [\overline{\epsilon}_{\text{id}}(T,\mu^*) - an]n,\tag{19}
$$

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

$$
\overline{\epsilon}_{\text{id}}(T,\mu) = \frac{\varepsilon^{\text{id}}(T,\mu)}{n^{\text{id}}(T,\mu)}.
$$
\n(20)

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

$$
\mu^*(n,T) = \mu^{\text{id}}\left(\frac{n}{1-bn},T\right),\tag{21}
$$

where μ ^{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* :

$$
n = \frac{d}{2\pi^2} \int_0^\infty dk k^2 \Bigg[\exp\left(\frac{\sqrt{m^2 + k^2} - \mu^{\text{id}}}{T}\right) + \eta \Bigg]^{-1}.
$$
 (22)

Equation (13) can be then rewritten as

$$
p = p^{\text{id}} \Big[T, \mu^{\text{id}} \Big(\frac{n}{1 - bn}, T \Big) \Big] - an^2. \tag{23}
$$

One can easily check that this equation coincides with Eq. [\(1\)](#page-0-0) in the 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. [\[6–8\]](#page-7-0). This is presented in Appendix [B.](#page-7-0)

IV. NUCLEAR MATTER

In this section the VDW equation of state with quantum statistics is used to describe the properties of symmetric nuclear matter. Namely, a Fermi gas of nucleons ($m \approx$ 938 MeV and $d = 4$) is considered with attractive and repulsive interactions described by the *a* and *b* VDW parameters, respectively. A study of nuclear matter has a long history. The thermodynamics of nuclear matter and its applications to the production of nuclear fragments in heavy ion collisions were considered in Refs. $[9-13]$ $[9-13]$ in the 1980s. A review of these early developments can be found in Ref. [\[14\]](#page-8-0). Nowadays, the properties of nuclear matter are described by many different models, particularly by those that employ a selfconsistent mean-field approach [\[15–19\]](#page-8-0). Excluded-volume corrections in the mean-field models have been considered in Refs. [\[4,7,](#page-7-0)[20\]](#page-8-0). Experimentally, a presence of the liquidgas phase transition in nuclear matter was first reported in Refs. [\[21–23\]](#page-8-0) by indirect observations. The first direct measurements of the nuclear caloric curve were done by the ALADIN Collaboration [\[24\]](#page-8-0) and later followed by other experiments [\[25,26\]](#page-8-0).

Our consideration is restricted to small temperatures, $T \leqslant$ 30 MeV; thus, pion production is neglected. In the present work, we also neglect the possible formation of nucleon clusters (i.e., ordinary nuclei) and baryonic resonances (like N^* and Δ), 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 μ of the GCE regulates the number density of nucleons.

A. Properties at $T = 0$

For calculations of the thermodynamic functions in the GCE, Eqs. [\(13\)](#page-2-0), [\(17\)](#page-2-0), [\(18\)](#page-2-0), and [\(19\)](#page-2-0) are used. In terms of variable μ^* [\(13\)](#page-2-0), thermodynamical functions of the quantum VDW gas can be presented in terms of the corresponding functions of the ideal quantum gas as the following:

$$
n(T,\mu) = \frac{n^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)}, \quad p(T,\mu) = p^{id}(T,\mu^*) - a \left[\frac{n^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)} \right]^2,
$$
\n(24)

$$
\varepsilon(T,\mu) = \frac{\varepsilon^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)} - a \left[\frac{n^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)} \right]^2, \quad s(T,\mu) = \frac{s^{id}(T,\mu^*)}{1 + b n^{id}(T,\mu^*)}.
$$
 (25)

At zero temperature the ideal gas quantities in Eqs. (24) and (25) can be written as

$$
n^{\text{id}}(T=0,\mu^*) = \frac{d}{2\pi^2} \int_0^{\sqrt{\mu^{*2}-m^2}} dk k^2 = \frac{d}{6\pi^2} (\mu^{*2} - m^2)^{3/2},\tag{26}
$$

$$
p^{\rm id}(T=0,\mu^*) = \frac{d}{6\pi^2} \int_0^{\sqrt{\mu^{*2}-m^2}} dk \frac{k^4}{\sqrt{k^2+m^2}} = \frac{d}{48\pi^2} \mu^* \sqrt{\mu^{*2}-m^2} (2\mu^{*2}-5m^2) - \frac{d}{16\pi^2} m^4 \ln \frac{m}{\mu^* + \sqrt{\mu^{*2}-m^2}},\tag{27}
$$

$$
\varepsilon^{\rm id}(T=0,\mu^*) = \frac{d}{2\pi^2} \int_0^{\sqrt{\mu^{*2}-m^2}} dk k^2 \sqrt{k^2+m^2} = \frac{d}{16\pi^2} \mu^* \sqrt{\mu^{*2}-m^2} (2\mu^{*2}-m^2) + \frac{d}{16\pi^2} m^4 \ln \frac{m}{\mu^* + \sqrt{\mu^{*2}-m^2}},\tag{28}
$$

$$
s^{\rm id}(T=0,\mu^*) = \lim_{T \to 0} \frac{\varepsilon^{\rm id}(T,\mu^*) + p^{\rm id}(T,\mu^*) - \mu^* n^{\rm id}(T,\mu^*)}{T} = 0.
$$
\n(29)

We fix parameters *a* and *b* in such a way to reproduce the properties of nuclear matter in its ground state (see, e.g., Ref. [\[27\]](#page-8-0)), i.e., it should be $p = 0$ and $\varepsilon/n = m + E_B \cong 922$ MeV at $T = 0$ and $n = n_0 \approx 0.16$ fm⁻³. Here $E_B \approx -16$ MeV is the binding energy per nucleon. One then finds $a \approx$ 329 MeV fm³ and $b \approx 3.42$ fm³. Note that parameter *b* of the proper particle volume can be expressed in terms of the hard-core radius *r* as $b = 16\pi r^3/3$. This gives $r \approx 0.59$ fm for the hard-core nucleon radius.

The pressure p and binding energy E_B as functions of nucleon density *n* at $T = 0$ are shown in Figs. [1\(a\)](#page-4-0) and [1\(b\),](#page-4-0) respectively. The stable VDW isotherms are depicted in Fig. [1](#page-4-0) by solid lines, while the metastable and unstable parts are depicted by dash-dotted and dotted lines, respectively. 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,](#page-4-0) can, however, exist as a metastable state only.

Note that at any $T > 0$ the chemical potential has a welldefined limiting behavior $\mu \to -\infty$ at $n \to 0$. At $T = 0$ the situation is different: at $n = 0$ the chemical potential may have any value smaller than the particle mass. The mixed gas-liquid phase at $T = 0$ is depicted by the horizontal lines in Figs. $1(a)$ and $1(b)$. The two coexisting phases at $T = 0$ are the liquid phase, with $n = 0.16$ fm⁻³, $p = 0$, and $\mu = 922$ MeV, and the gaseous phase, with $n = 0$, $p = 0$ and $\mu = 922$ MeV.

This corresponds to the Gibbs conditions of phase equilibrium, i.e., equal temperatures, pressures, and chemical potentials for coexisting phases. The stable gaseous phase at $T = 0$ is, in fact, a vacuum with $n = 0$.

B. Phase diagram

The VDW pressure isotherms are depicted in (T, v) and (T, n) coordinates $(v = 1/n)$ in Figs. [3\(a\)](#page-4-0) and [3\(b\),](#page-4-0) respectively. They are calculated within the quantum VDW equation of state using Eq. [\(23\)](#page-2-0) with $a \approx 329$ MeV fm³ and $b \approx 3.42$ fm³. The critical temperature is found to be $T_c \approx 19.7$ MeV. The value of the critical temperature in our model is close to the experimental estimates in Refs. [\[25,26\]](#page-8-0). At $T < T_c$ two phases appear: the gas and the liquid phases separated by a first-order phase transition. The mixed phase region is obtained from the Maxwell construction of equal areas for $p(v)$ isotherms (see Appendix [A\)](#page-6-0), and it is depicted by horizontal lines in Fig. $3(a)$ and by the shaded gray area in Fig. $3(b)$. The nucleon number density at the critical point is found to be $n_c \approx 0.07$ fm⁻³ $\approx 0.4 n_0$. Normal nuclear matter with $n = n_0 \approx 0.16$ fm⁻³ and $T = 0$ corresponds to a point placed exactly on the boundary between the mixed and the liquid phases. Note also that the maximal value of the nucleon

FIG. 1. Dependence of the pressure p (a) and the binding energy E_B (b) on the nucleon density n at $T = 0$. The VDW parameters are *a* ≃ 329 MeV fm³ and *b* ≅ 3.42 fm³ (*r* ≅ 0.59 fm). The open circle corresponds to the ground state of nuclear matter. The dash-dotted line corresponds to the metastable part of the VDW isotherm, whereas the dotted line corresponds to the unstable part.

FIG. 2. The same as in Fig. 1, but for small values of *n*.

FIG. 3. (Color online) Pressure isotherms in (a) (*p,v*) and (b) (*p,n*) coordinates, calculated in the quantum VDW equation of state with parameters *a* ≃ 329 MeV fm³ and *b* ≅ 3.42 fm³ (*r* ≅ 0.59 fm). The dashed-dotted lines present the metastable parts of the VDW isotherms at $T < T_c$, whereas the dotted lines correspond to the unstable parts. The full circle on the $T = T_c$ isotherm corresponds to the critical point, while the open circle at *T* = 0 in panel (b) shows the ground state of the nuclear matter. The shaded gray area in panel (b) depicts the mixed phase region obtained from the Maxwell construction of equal areas for $p(v)$ isotherms in panel (a).

FIG. 4. (Color online) Density of the symmetric nuclear matter in (T, μ) coordinates, calculated in the quantum VDW equation of state with parameters $a \approx 329$ MeV fm³ and $b \approx 3.42$ fm³ ($r \approx 0.59$ fm). The open circle denotes the ground state of the nuclear matter, the solid circle corresponds to the critical endpoint, and the phase transition curve is depicted by the solid black line.

number density in the VDW model is $n_{\text{max}} = 1/b$, which is equal to $n_{\text{max}} \cong 0.29 \text{ fm}^{-3}$ for the chosen value of parameter *b*.

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

$$
n = \xi n_g + (1 - \xi)n_l,
$$
 (30)

where ξ 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 the liquid phases at the corresponding boundaries with the mixed phase. A behavior of the mixed phase at $T = 0$ is rather special. The stable gaseous phase is absent at $T = 0$, i.e., $n_g =$ 0 at the mixed phase boundary because this boundary starts from the point $T = 0$ and $n = 0$. Therefore, only a metastable gaseous phase at small densities can exist at $T = 0$ as depicted in Fig. [2.](#page-4-0) The stable gaseous phase exists however at any *T >* 0 for small enough values of the particle number density, smaller than the n_e density of the gaseous phase in the mixed phase region resulting from the Maxwell construction.

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 [\(1\)](#page-0-0), i.e., with Boltzmann statistics, would give $T_c = 8a/27b$ ≅ 28.5 MeV and $n_c = 1/3b \approx 0.10 \text{ fm}^{-3}$. This further indicates an importance of the effects of quantum statistics: these effects are not only crucial in the limit $T \rightarrow 0$ but also remain quantitatively important even near the critical point.

In Fig. 4 the phase diagram of the symmetric nuclear matter in (T, μ) coordinates is depicted. The nucleon density at different temperature T and chemical potential μ is presented. At $T < T_c$ there is the $T - \mu$ region with three different solutions for $p(T, \mu)$ at given *T* and μ . According to the Gibbs criterion, the solution with the largest pressure survives (see Appendix [A\)](#page-6-0), and only this solution for $n(T, \mu)$ is depicted in Fig. 4. The location of the critical point is shown in Fig. 4 by the solid circle, while the normal nuclear matter state corresponds

to the open circle. Note that $\mu_0 \cong 922$ MeV corresponds to the chemical potential of the normal nuclear matter that is placed on a boundary with the liquid phase. The values $\mu < \mu_0$ are forbidden at $T = 0$ (these values of μ 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, $\mu = \mu_{mix}(T)$, shown in Fig. 4, starts from the normal nuclear matter state with $T = 0$ and $\mu \cong$ 922 MeV and ends at the critical point with $T_c \approx 19.7$ MeV and $\mu_{\text{mix}}(T_c) \cong 908$ MeV. This line presents the whole mixed phase region shown by the gray area in Fig. [3.](#page-4-0) 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 the thermodynamical quantities *n*, *ε*, and *s* take place.

At $T > T_c$ there is only one solution $n(T, \mu)$ for any *T* and *μ* values; i.e., there are no distinct *gaseous* or *liquid* phases. Nevertheless, as seen from Fig. [3,](#page-4-0) very rapid, although continuous, changes of the 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 μ between $-\infty$ and $+\infty$ are possible. When μ decreases the particle number density decreases too and goes to zero at $\mu \to -\infty$. At very small *n*, both the particle interactions and the 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 $p \cong n/\frac{1}{1 - bn}$ 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. [\[28–30\]](#page-8-0)). In the present paper we do not attempt to make any detailed 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 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, $T \ge 0$, 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 $a = b = 0$ and to the classical VDW equation in the Boltzmann limit, and it satisfies the third law of thermodynamics, i.e., $s \to 0$ as $T \to 0$. Note that at $T > 0$ the chemical potential has the well-defined limiting behavior $\mu \rightarrow -\infty$ at $n \rightarrow 0$. This is implicitly used to derive the Maxwell rule of equal areas from Gibbs conditions of phase equilibrium for VDW isotherms (see Appendix [A\)](#page-6-0). For a Fermi gas at $T = 0$ the situation is different: at $n = 0$ the

FIG. 5. The 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 panel (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 the metastable and unstable phases, while point 1'(2') corresponds to the same value of the chemical potential reached in the pure liquid (gaseous) phase. In panel (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.

chemical potential may have any value smaller than particle mass, $\mu < m$.

The VDW equation with Fermi statistics has then been 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: $T = 0, p = 0, n = n_0$ 0.16 fm⁻³, and $E_B = -16$ MeV. We find $a \approx 329$ MeV fm³ and $b \approx 3.42 \text{ fm}^3$. With these parameters the VDW model predicts a first-order liquid-gas phase transition with a critical endpoint located at $T_c \cong 19.7$ MeV and $n_c \cong 0.07$ fm⁻³. Extensions of the presented formulation as well as new physical applications will be the subject of 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 *μ*. Two distinct phases, *gas* and *liquid*, coexist if their pressures are equal, $p_g(T,\mu) = p_l(T,\mu)$. In the 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 the first-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 the horizontal line $p = p_{\text{mix}}$,

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

$$
\int_{v_l}^{v_0} dv \, [p_{\text{mix}} - p(v, T)] = \int_{v_0}^{v_g} dv \, [p(v, T) - p_{\text{mix}}], \quad (A1)
$$

where $v_l < v_0 < v_g$ and $p(v_0, T) = p_{\text{mix}}$. The replaced parts of the isotherm are interpreted as metastable (*∂p/∂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 the thermodynamical identity

$$
\left(\frac{\partial \mu}{\partial p}\right)_T = v,\tag{A2}
$$

one can present the chemical potential μ_A at any point *A* on the isotherm as

$$
\mu_A = \mu_B + \int_{p_B}^{p_A} dp' v(p', T), \tag{A3}
$$

where *B* is an arbitrary point on the isotherm, and integration in Eq. $(A3)$ is performed along the path from point *B* to point *A* on the isotherm.

With Eqs. $(A1)$ and $(A3)$ one can easily prove that

$$
\mu(v_l, T) = \mu(v_g, T) \equiv \mu_{\text{mix}};
$$
 (A4)

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

According to Eq. $(A3)$ the chemical potential decreases with *v* if $(\partial p/\partial v)_T < 0$, and it 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 $\mu = \mu_2 < \mu_{\text{mix}}$ at $v = v_2$ and its maximal value $\mu = \mu_1 > \mu_{\text{mix}}$ 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 $v \rightarrow b$ and $\mu \rightarrow -\infty$ at $v \rightarrow \infty$. 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 $\mu > \mu_1$ 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\(b\):](#page-6-0) point a_1 in the gaseous phase with $v_g < v_1^a < v_2^b$, point a_2 in the metastable liquid phase with $v_1 < v_2^a < v_2$, and point a_3 in the unstable phase with $v_2 < v_3^a < v_1$. Using Eq. [\(A3\)](#page-6-0) one finds that

$$
\int_{p_1^{a}}^{p_{\text{mix}}} dp' v(p', T) = \int_{p_2^{a}}^{p_{\text{mix}}} dp' v(p', T)
$$

=
$$
\int_{p_2}^{p_{\text{mix}}} dp' v(p', T) - \int_{p_2}^{p_3^{a}} dp' v(p', T).
$$
 (A5)

Applying the mean value theorem to integrals in Eq. $(A5)$ one obtains

$$
(p_{\text{mix}} - p_1^a) \overline{v}_1 = (p_{\text{mix}} - p_2^a) \overline{v}_2
$$

= $(p_{\text{mix}} - p_2) \overline{v}_{31} - (p_2 - p_3^a) \overline{v}_{32}$, (A6)

where $v_l < \overline{v}_2 < v_2^a$, $v_g < \overline{v}_1 < v_1^a$, $v_l < \overline{v}_{31} < v_2 < \overline{v}_{32}$ v_3^a , and $p_2 = p(v_2, T)$. It follows from Eq. (A6) that $p_1^a > p_2^a$ and $p_1^a > p_3^a$; i.e., at $\mu_2 < \mu < \mu_{\text{mix}}$ the gaseous phase should be realized according to the Gibbs criteria as its pressure is larger than the 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 the pressures of both metastable and unstable states. Therefore, for the VDW equation of state the Maxwell construction of the equal areas and the 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 isotherms depicted in Fig. [3.](#page-4-0)

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

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presented as

$$
p(T, \mu) = p^{\text{id}}[T, \mu_{\text{id}}(n, T)] + P^{\text{ex}}(n, T), \quad (B1)
$$

$$
n(T, \mu) = n^{id}[T, \mu - U(n, T)],
$$
 (B2)

where $P^{ex}(n,T)$ and $U(n,T)$ are, respectively, the excess pressure and the thermodynamic mean field. The presence of nonzero quantities $P^{ex}(n,T)$ and $U(n,T)$ in Eqs. (B1) and (B2) corresponds to interaction between particles, and the condition of thermodynamic consistency reads [8]

$$
n\frac{\partial U}{\partial n} = \frac{\partial P^{\text{ex}}}{\partial n}.
$$
 (B3)

For a specific choice of $P^{\text{ex}}(n,T)$ and $U(n,T)$ functions, one proceeds by solving Eq. (B2) for $n = n(T, \mu)$, and then the pressure $p(T, \mu)$ can be obtained from Eq. (B1) (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 $(B1)$ and (B2). In order to determine $P^{ex}(n,T)$ and $U(n,T)$ we rewrite Eq. [\(23\)](#page-2-0) for the VDW pressure as

$$
p = p^{\text{id}}[T, \mu^{\text{id}}(n, T)] + p^{\text{id}} \left[T, \mu^{\text{id}} \left(\frac{n}{1 - bn}, T \right) \right]
$$

$$
- p^{\text{id}} [T, \mu^{\text{id}}(n, T)] - an^2. \tag{B4}
$$

Comparing Eqs. $(B1)$ and $(B4)$ one finds

$$
P_{\text{VdW}}^{\text{ex}}(n,T) = p^{\text{id}} \bigg[T, \mu^{\text{id}} \bigg(\frac{n}{1 - bn}, T \bigg) \bigg] - p^{\text{id}} [T, \mu^{\text{id}}(n,T)] - an^2. \tag{B5}
$$

The mean field $U_{\text{VdW}}(n,T)$ can be then calculated from Eq. $(B3)$ as

$$
U_{\text{VdW}}(n,T) = \int_0^n \frac{1}{n'} \frac{\partial P_{\text{VdW}}^{\text{ex}}(n',T)}{\partial n'} \, dn'. \tag{B6}
$$

For the Boltzmann statistics, Eqs. $(B5)$ and $(B6)$ are simplified to the following analytical expressions:

$$
P_{\text{VdW}}^{\text{ex}}(n,T) = Tn \frac{bn}{1 - bn} - an^2,\tag{B7}
$$

$$
U_{\text{VdW}}(n,T) = T \frac{bn}{1 - bn} - T \ln(1 - bn) - 2an. \quad (B8)
$$

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