Van der Waals equation of state for asymmetric nuclear matter

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Abstract

The application of van der Waals equation of state to the asymmetric nuclear matter is considered in a critical state region. The corrections to the van der Waals pressure and free energy due to the Fermi statistics are obtained starting from the Thomas–Fermi entropy expression which ensures the fulfillment of Nernst theorem. The derived corrections account for the effective nucleon mass and neutron-proton isotopic asymmetry. The parameters of van der Waals equation of state are deduced taking the experimental value of critical temperature for symmetric nuclear matter and testing the model of van der Waals with statistics corrections included against the theory of Skyrme energy density functional. Critical line in pressure-temperature-composition space is considered. Incompressibility coefficient is determined along the critical line as a function of nuclear matter composition. Jump in the value of specific heat upon crossing critical line is discussed.

Keywords: asymmetric nuclear matter, equation of state, critical line

1 Introduction

Significant progress in understanding of the phase transitions and critical phenomena has been made owing to the work of van der Waals [1]. His equation of state (see Eq. (1) below) includes only two parameters $a$ and $b$ that, respectively, account for the effects of particle attraction and size [1–4]. The popularity of van der Waals equation of state comes from its simplicity together with physically meaningful predictions for both vapour and liquid phases for wide area of the phase diagram and, in particular, around the critical point. Caloric measurements in heavy-ion collisions [5–8] have shown signs of a liquid-vapour phase transition in nuclear matter, and the compliance of simple van der Waals-like equations of state [9,10] with the nuclear matter properties became the subject of theoretical study.

The cold (zero temperature) nuclear matter have been studied over many years on the basis of many-body theory. The basic features of nuclear matter follow from the properties of the nucleon-nucleon interaction used. The nuclear forces are, in general, non-local, momentum-dependent and include the exchange interaction terms [11,12]. The use of the effective (momentum and density dependent) nucleon-nucleon interaction [13,14] shows the importance of the three-body interaction for the saturation property of nuclear matter. For Skyrme force [15] the simple expression is obtained for the effective mass of nucleon, $m^*$, which gives an idea on in-medium nucleon-nucleon interaction. The equation of state of symmetric nuclear matter around the saturation point is determined by three quantities: the saturation density, $\rho_{\text{sat}}$, energy per particle, $\epsilon(\rho_{\text{sat}})$, and incompressibility coefficient, $K(\rho_{\text{sat}})$. By the requirement for the nuclear matter to be bound and stable, the energy per particle and incompressibility must be, respectively, negative and positive at the saturation density. Unfortunately, the empirical equation of state of van der Waals does not comply with the properties of cold nuclear matter, since the description of three quantities, e.g. $\rho_{\text{sat}}$, $\epsilon(\rho_{\text{sat}})$ and $K(\rho_{\text{sat}})$, using two adjustable parameters is, strictly speaking, possible by chance only. This equation of state obviously fails when it comes to the description of cold nuclear matter in the vicinity of the saturation point. At zero temperature, $T=0$, the saturation condition for nuclear matter is determined by the mechanical equilibrium of zero pressure. As seen from Eq. (1), the picture at $T=0$ becomes oversimplified and the saturation point is never reached. The mentioned equation violates the Nernst theorem, stating that the entropy should vanish at zero temperature. Van der Waals formula gives for the specific heat per particle at fixed volume $c_V = 3/2$ (the same as for the ideal gas), while the value of $c_V$ vanishes at zero temperature by the Nernst theorem. Due to the constituent nucleons having spin the effect of Fermi statistics and the corresponding corrections of van der Waals equation of state have to be considered in applications to nuclear matter. This has
been done for description of the symmetric [16] as well as asymmetric [17] nuclear matter within the grand canonical ensemble formulation. In the present paper the similar problem is considered by means of non-relativistic theory of energy density functional (canonical ensemble approach) starting from the Thomas–Fermi entropy expression. This allows to highlight the effect of in-medium interaction (effective mass) ignored in Refs. [16][17].

Despite of the above arguments which raise doubts about capabilities of van der Waals equation of state for description of cold nuclear matter, this equation could be still applicable within the pressure-density-temperature space near the critical state. The main goal of this paper is to study the application of van der Waals equation of state for hot (high temperature) nuclear matter in the critical state region. In Sec. 2 the Fermi-statistics corrections to pressure and free energy of van der Waals model are derived. Criterion for application of Fermi statistics is illustrated by the example of specific heat. Section 3 is concerned with effective mass of nucleon. Stability conditions for asymmetric nuclear matter and equations required to obtain the critical line are considered in Sec. 4. Parameters of van der Waals model are determined in Sec. 5. In Sec. 6 the obtained parameters are used to calculate various properties of symmetric and asymmetric nuclear matter. The concluding remarks are summarized in Sec. 7.

2 Van der Waals equation of state and Fermi statistics

The empirical equation of state of van der Waals [1] relates the pressure, \( P = P_{\text{vdW}} \), particle density, \( \rho \), and temperature, \( T \), as

\[
P_{\text{vdW}} = \frac{\rho T}{1 - b\rho} - a\rho^2
\]  

(1)

where \( a \) and \( b \) are positive adjustable parameters. By physical interpretation \( b \) of parameters in Eq. (1), \( b \) is four times the volume of the particle, and \( a \) accounts for the two-body attractive potential between particles. In applications for mixtures of fluids (liquids) one usually substitutes \( a \rightarrow a_{\text{mix}} \) and \( b \rightarrow b_{\text{mix}} \) in Eq. (1), where the new parameters \( a_{\text{mix}} \) and \( b_{\text{mix}} \) are obtained according to certain mixing rules [18,19]. The mixing rules known from the literature are the empirical ones, since there can be no general solution for calculating the properties of a mixture from those of its pure components. The reason is the new forces between particles come into play which are not present in either of the pure components. The nuclear matter is the binary mixture of protons and neutrons. Assuming the neutron and proton to be of equal size, one can adopt \( b_{\text{mix}} = b \), irrespective to the proton and neutron fractions, based on the physical meaning of the parameter \( b \) given above. One might also adopt the empirical mixing rule used for van der Waals equation of state [13], \( a_{\text{mix}} = \sum_{q,q'} x_q x_{q'} a_{qq'} \), where \( x_q = \rho_q/\rho \) stand for the fractions and \( \rho_q \) for the densities of particle species \( q \) (\( q = n \) for neutron and \( q = p \) for proton), \( \rho = \sum_q \rho_q \) is the total density of nucleons. From the charge symmetry of nucleon-nucleon interaction, the following reasonable assumption can be made on the values of \( a_{qq'} \): \( a_{nn} = a_{pp} = a_1 \), \( a_{np} = a_{pn} = a_0 \), where subscripts “\( l \)” and “\( u \)” correspond, respectively, to nucleons with parallel (“like”) and opposite (“unlike”) isospin. Then, for the binary mixture of neutrons and protons one has

\[
a_{\text{mix}} = \sum_{q,q'} x_q x_{q'} a_{qq'} = a_0 + a_1 X^2 .
\]  

(2)

Here, \( a_0 = (a_1 + a_u)/2 \) and \( a_1 = (a_1 - a_u)/2 \) are the new parameters for the binary neutron-proton mixture, and \( X = (\rho_n - \rho_p)/\rho = x_n - x_p \) is the isotopic asymmetry parameter. The empirical van der Waals equation of state for asymmetric nuclear matter can be written in the following simple three-parameter form:

\[
P_{\text{vdW}}(\rho, X) = \frac{\rho T}{1 - b\rho} - \left( a_0 + a_1 X^2 \right) \rho^2
\]  

(3)

The corresponding free energy per particle, \( \phi_{\text{vdW}} \), is obtained using [3] with regard to the thermodynamic relation \( P_{\text{vdW}} = \rho^2 (\partial \phi_{\text{vdW}}/\partial \rho)_{T,X} \). Integrating \( P_{\text{vdW}}/\rho^2 \) with respect to total density \( \rho \) at fixed temperature \( T \) and asymmetry parameter \( X \), and assuming the ideal gas asymptote for \( \phi_{\text{vdW}} \) at \( \rho \rightarrow 0 \), one obtains the familiar expression, see [4],

\[
\phi_{\text{vdW}}(\rho, X) = T \ln \left( \frac{\rho}{1 - b\rho} \right) - \left( a_0 + a_1 X^2 \right) \rho - \frac{3}{2} T \ln(T) - T(1 + \xi(X)) ,
\]  

(4)
with \( \xi(X) = \xi_{ch} - \sum_{q=n,p} x_q \ln(x_q) \). Here \(-\sum_{q=n,p} x_q \ln(x_q)\) is the mixing entropy per particle of ideal gas and \( \xi_{ch} = \ln \left[ 2 \left( \frac{m}{2\pi\hbar^2} \right)^{3/2} \right] \) is the chemical constant. The nucleon mass \( m \) is assumed hereafter to be the same for neutron and proton. From Eq. (4), the corresponding entropy per particle, \( s_{vdW} = -(\partial \phi_{vdW}/\partial T)_{\rho,X} \), is written as
\[
s_{vdW} = \frac{5}{2} - \ln \left( \frac{\rho}{1-b\rho} \right) + \frac{3}{2} \ln(T) + \xi(X) .
\] (5)

For the purpose to incorporate Fermi statistics into empirical equation of state (4) let start from the entropy per particle, \( s \), which satisfies the Nernst theorem, e.g. \( s \to 0 \) at the low temperature limit, \( T \to 0 \). Such expression for \( s \) is known from the temperature dependent Thomas–Fermi approximation [20–22],
\[
s = \sum_{q=n,p} x_q \left( \frac{5}{3} J_{1/2}(\eta_q) - \eta_q \right),
\] (6)
where \( J_{\nu}(\eta_q) \), \( \nu = 1/2, 3/2 \), is the Fermi integral (see Appendix A), and its argument, \( \eta_q \), can be found from the condition
\[
\rho_q = \frac{1}{2\pi^2} \left( \frac{2mT}{\hbar^2 f_q} \right)^{3/2} J_{1/2}(\eta_q),
\] (7)
with \( m/f_q = m^* \) being the effective nucleon mass. The value of \( \eta_q \) is usually related to the thermodynamic activity and/or fugacity. Eqs. (6), (7) are obtained using the Thomas–Fermi approximation for the Bloch density matrix [21], and, in that sense, they are generally consistent with the temperature dependent Hartree-Fock calculations. It is seen from Eq. (7) that \( \eta_q \) can be expressed as a function of the ratio \( \delta_q = \rho^{-1/3}_q / x_q \), where \( \rho^{-1/3}_q \) is about of mean distance between particles of the same isospin, \( x_q = \hbar/\sqrt{m^* T} \) is of order of the thermal de Broglie wavelength [3]. This determines some properties of \( \eta_q = \eta_q(\rho, T, X) \), see Appendix B. The value of mentioned ratio \( \delta_q \) gives an idea whether it worth accounting for effects of Fermi statistics. Using the specific heat per particle \( c_V \) as an example, it can be shown that effects of Fermi statistics become negligible within the high temperature limit, \( \delta_q \gg 1 \). Using Eqs. (4) and (B.3) one obtains the specific heat per particle at constant volume, \( c_V \), as
\[
c_V = T \left( \frac{\partial \psi}{\partial T} \right)_{\rho,X} = \sum_{q=n,p} x_q \left( \frac{5}{2} J_{3/2}(\eta_q) - \frac{9}{2} J_{1/2}(\eta_q) \right) = \sum_{q=n,p} x_q \psi(\eta_q).
\] (8)

Here, \( \psi \) is function of \( \eta_q \) only, see also Appendix B. The dependence of the specific heat \( c_V \) on the value of \( \delta = \rho^{-1/3} / x \) is displayed in Fig. 1 by plotting two curves at \( X = 0 \) and 1. Let us consider these two important cases in some detail. First, consider the symmetric nuclear matter (\( X = 0 \), the subscript “snm” is used for the relevant quantities). In this case neutron and proton fractions are equal, \( \rho_n = \rho_p = \rho/2 \). One can also write \( \lambda_n = \lambda_p = \lambda_{snm} \) and \( \eta_n = \eta_p = \eta_{snm} \). Thus, Eq. (7) represents two identical relations between \( \eta_q \) and \( \delta_q \), with \( \delta^{-3}_q = \rho^{-3}_q / x_q^3 / 2 = \delta^{-3}_{\text{snm}} / 2 \), regardless of isospin index \( q \). From Eq. (8) one obtains \( c_V = \psi(\eta_{\text{snm}}) \) as a function of \( \delta = \delta_{\text{snm}} \), see solid line in Fig. 1. Second special instance is the pure neutron matter (\( X = 1 \), subscript “pnn” is used). Here, the neutron fraction is present only, \( \rho_n = \rho \). The specific heat is determined as \( c_V = \psi(\eta_{\text{pnn}}) \) with \( \eta_{\text{pnn}} = \eta_n, \delta_{\text{pnn}} = \delta_n \), see Eqs. (7) and (8). The result of calculation for \( c_V \) versus \( \delta = \delta_{\text{pnn}} \) is illustrated by dashed line in Fig. 1. Referring to the figure, the same value of specific heat \( c_V \) for symmetric nuclear matter and pure nuclear matter is reached at different values of \( \delta, \delta_{\text{snm}} < \delta_{\text{pnn}} \). The reason is directly relevant to isospin degeneracy factor, \( \delta^{-3}_{\text{snm}} = 2\delta^{-3}_{\text{pnn}} \). As can be seen from Fig. 1, \( c_V \) approaches the ideal gas value of 3/2 in the high temperature limit, and the contribution of Fermi statistics is washed out at \( \delta \gg 1 \). Within high-\( \delta \) region the specific heat is estimated as \( c_V \approx \frac{3}{2} - \frac{3}{16} \left( \frac{\pi \hbar^2}{mT} \right)^{3/2} \sum_q x_q^{3/2} / f_q \) (see Appendix B). In the opposite case of low temperatures one has \( c_V \approx \left( \frac{\pi}{3\rho} \right)^{2/3} \left( mT \right)^{2/3} \sum_q x_q^{3/2} / f_q \). The specific heat vanishes
as temperature approaches zero, in accordance with Nernst theorem. This result is consistent with that given in [4] for degenerated Fermi-gas. In addition, the specific heat \( c_V \) is quite sensitive to the neutron-proton asymmetry for intermediate region close to \( \delta \approx 1 \), as can be concluded from Fig. 1.

In order to calculate the correction for Fermi statistics to the van der Waals equation of state, let us take the advantage of thermodynamic relation (see, for example, [4])

\[
T \left( \frac{\partial^2 P}{\partial T^2} \right)_{\rho,X} = -\rho^2 \frac{\partial}{\partial \rho} \left( \sum_{q=n,p} x_q \psi(\eta_q) \right)_{T,X},
\]

(9)

Then, let represent the pressure in Eq. (9) as sum of two terms, the van der Waals pressure \( P_{vdW} \) itself, from the equation of state (3), and the corresponding correction to it for Fermi statistics, \( P_{stat} \), so that

\[
P = P_{vdW} + P_{stat}.
\]

(10)

The van der Waals pressure disappears being inserted to the left-hand side of Eq. (9) since \( P_{vdW} \) is linear in temperature, see Eq. (3). The quantity \(-\rho^2 (\partial c_V / \partial \rho)_{T,X}\) on the right of Eq. (9) can be obtained from known specific heat \( c_V \) of Eq. (8). Therefore, one can rewrite the thermodynamic relation (9) for pressure (10) as

\[
\left( \frac{\partial^2 P_{stat}}{\partial T^2} \right)_{\rho,X} = -\rho^2 \frac{\partial}{\partial \rho} \left( \sum_{q=n,p} x_q \psi(\eta_q) \right)_{T,X},
\]

(11)

where the function \( \psi \) has been defined by Eq. (8). Now one has the second order differential equation (11) which has to be solved to deduce the correction \( P_{stat} \) for Fermi statistics. One should note that the right-hand side of Eq. (11) has no singularity at \( T \to 0 \) since \( \psi(\eta_q) \propto T \) within this limit, see Eq. (B.6).

The necessary boundary conditions for the solution sought are given by the requirement of absence of the statistics effects at high temperature limit. Taking the high temperature asymptote (B.7) of \( \psi \), as applied to Eq. (11), one gains that \( P_{stat} \) and \( \partial P_{stat}/\partial T \) tend to zero as \( T^{-1/2} \) and \( T^{-3/2} \), respectively. In view of just claimed boundary conditions, Eq. (11) is integrated twice over the temperature to yield

\[
P_{stat} = \rho T \sum_{q=n,p} x_q \left( 1 + \frac{3}{2} \rho \left( \frac{\partial f_q}{\partial \rho} \right)_{X} \right) \left( \frac{2}{3} J_{3/2}(\eta_q) - \frac{1}{3} J_{1/2}(\eta_q) \right),
\]

(12)

see Appendix B for more details. As was mentioned, within the high temperature limit the above pressure correction (12) vanishes as \( T^{-1/2} \). This agrees with the results of Refs. [9][10]. For the opposite case of low temperatures one has

\[
P_{stat} = \frac{2}{3} \frac{(3\pi^2)^{2/3}}{2m} \sum_{q=n,p} \left( f_q + \frac{3}{2} \rho \left( \frac{\partial f_q}{\partial \rho} \right)_{X} \right) \frac{\hbar^2}{\rho_q} \rho_q^{5/3} - \rho T \sum_{q=n,p} x_q \left( 1 + \frac{3}{2} \rho \left( \frac{\partial f_q}{\partial \rho} \right)_{X} \right) + O \left( T^2 \right),
\]

(13)
so $P_{\text{stat}}$ is determined by the kinetic energy of Fermi motion within the leading order in temperature. It should be noted that the presence of term $\mathcal{O}(T)$ in Eq. (13) raises the issue as to the fulfilment of Nernst theorem. Generally, the condition $(\partial P/\partial T)_{\rho,X} \to 0$ as $T \to 0$ is not met for the pressure defined by Eq. (10). This issue is addressed more closely in the next section.

Once the correction $P_{\text{stat}}$ to the van der Waals pressure is found, the free energy per particle can be also refined in the same way, $\phi = \phi_{\text{vdW}} + \phi_{\text{stat}}$. The quantity $\phi_{\text{vdW}}$ is determined by Eq. (4), and $\phi_{\text{stat}}$ is obtained from the relationship between $\phi_{\text{stat}}$ and $P_{\text{stat}}$, that is
\[
\left( \frac{\partial \phi_{\text{stat}}}{\partial \rho} \right)_{T,X} = \frac{P_{\text{stat}}}{\rho^2}.
\]  
(14)

It can be seen from Eq. (13) that likewise $P_{\text{stat}}$, the correction $\phi_{\text{stat}}$ should vanish as $T^{-1/2}$ in the high temperature limit. At fixed asymmetry parameter and temperature one may reduce the integration of Eq. (14) over density $\rho$ to the integration with respect to $\eta_q$ as supported by Eq. (15) of Appendix B.

This gives
\[
\phi_{\text{stat}} = -T \sum_{q=n,p} x_q \left( \frac{2J_3/3}{J_1/2} \eta_q - 1 - \eta_q + \ln \left( \frac{2J_1/2}{\sqrt{\pi}} \right) \right).
\]  
(15)

3 Effective mass

The effective mass of nucleon accounts for difference between the free-space and in-medium nucleon-nucleon interaction. The mass renormalization can include the effect of nonlocality of nucleon-nucleon interaction (momentum dependent effective mass [23]) and long-range correlation contribution caused by the vibration of single-particle potential (frequency-dependent effective mass [24,25]). The effective mass enters into the nuclear one-body Hamiltonian and thereby the single-particle level density [26]. Here only the momentum-dependent effective mass is considered, while the contribution due to the frequency dependence is left out. Assuming the interaction between nucleons to be density dependent (in order to simulate many-body forces, see Ref. [14]) and quadratically dependent on the momentum, one has simple form for the effective mass [27,28]. The ratio $f_q = m/m_q^*$, where $m$ is the bare nucleon mass, is given by
\[
f_n = 1 + \frac{k_+}{2} \rho + \frac{k_-}{2} \rho X, \quad f_p = 1 + \frac{k_+}{2} \rho - \frac{k_-}{2} \rho X.
\]  
(16)

Here the coefficients $k_+, k_-$ are density independent and can be associated with the parameters of certain energy density functional (EDF). Density dependence of the effective mass is usually normalized to certain value $m_0^*/m$ at the saturation density $\rho = \rho_{\text{sat}}$ for cold symmetric nuclear matter, $X = 0$. So, by definition, $m_0^*/m$ is related to the coefficient $k_+$ from Eq. (16) as
\[
m_0^*/m = (1 + k_+ \rho_{\text{sat}}/2)^{-1}.
\]  
(17)

The value of $m_0^*$ is one of the crucial characteristics within the EDF theory in determining the saturation properties of nuclear matter. The isotopic asymmetry dependence of nucleon effective mass [16] causes the isovector shift between $m_n^*$ and $m_p^*$ in asymmetric nuclear matter. The mentioned shift taken in the vicinity of saturation point $\rho = \rho_{\text{sat}}$ is written as
\[
\frac{m_n^* - m_p^*}{m} = \frac{m^*}{m} + \mathcal{O}(X^3), \quad \frac{m^*}{m} = -k_- \left( \frac{m_0^*}{m} \right)^2 \rho_{\text{sat}} X.
\]  
(18)

The value of $m_1^*/m$ defined by Eq. (18) is the isovector effective mass splitting (isovector shift) which determines the isotopic asymmetry properties of asymmetric nuclear matter along with the symmetry energy coefficients [27]. Recent analysis [28] of EDF theory in application to the symmetric nuclear matter, pure neutron matter and dipole polarizability of finite nuclei have put the values of $m_0^*$, $m_1^*$ within the reasonable constraints, the reported values are $m_0^*/m = 0.68 \pm 0.04$ and $m_1^*/m = (-0.20 \pm 0.09)X$.

Let now turn back to the starting point, Eqs. (6) and (7), from which the correction $P_{\text{stat}}$ of Eq. (12) is derived. Fermi statistics is an inherent feature of Skyrme EDF, and Eqs. (6), (7) are compatible with the requirements of the Nernst theorem. In particular, within the low-temperature limit one has
\( (\partial P / \partial T)_{\rho,X} = -\rho^2 (\partial s / \partial \rho)_{T,X} = \mathcal{O}(T) \) for the case of Skyrme EDF. However, on the assumption of Eq. (10) one obtains for low temperatures
\[
\left( \frac{\partial P}{\partial T} \right)_{\rho,X} = \frac{\rho}{1 - b \rho} - \sum_{q=n,p} \rho_q \left( 1 + \frac{3 \rho}{2 f_q} \left( \frac{\partial f_q}{\partial \rho} \right)_{X} \right) + \mathcal{O}(T) \tag{19}
\]
as evident from Eqs. (3), (13). On the one hand, the presence of \( \mathcal{O}(T^0) \) terms in the above Eq. (19) means that the Nernst theorem does not hold. On the other hand, the explicit density dependence of the effective mass is not used for the derivation of \( P_{\text{stat}} \) given in the previous section, so the conditions of the Nernst theorem can still be satisfied for the specific choice of the ratio \( f_q = m/m_q^* \) as
\[
f_n = f_p = (1 - b \rho)^{-2/3} . \tag{20}
\]
This choice makes the contribution of \( \mathcal{O}(T^0) \) terms in Eq. (19) to be the exact zero. Formally, Eq. (20) establishes a link of effective mass to the van der Waals excluded volume. The argument of Fermi integral \( \eta_q \) is in fact a function of the ratio \( \delta_q = \rho_q^{-1/3} / \lambda_q \) as supported by Eq. (7). This ratio is left unchanged if one takes \( \lambda_q = \hbar / \sqrt{mT} \) for the bare nucleon mass and applies the concept of van der Waals excluded volume by the substitution \( \rho_q \rightarrow \rho_q / (1 - b \rho) \). In the high temperature limit, \( \delta_q \gg 1 \), the series \( \{A,3\} \) of Appendix A can be applied in obtaining of Fermi integrals. Within this limit the main contribution to the value of Fermi integrals is given by the first leading term, \( J_\nu(\eta_q) = \Gamma(\nu + 1) \exp(\eta_q) \), which corresponds to the classical Boltzmann statistics. Using only the main term of series \( \{A,3\} \) to calculate Fermi integrals involved in Eqs. (3), (7) and taking the effective mass given by (20), one obtains the expression for van der Waals entropy per particle \( s_{\text{vdW}} \), see Eq. (5). In other words, the Thomas–Fermi entropy coincides with that of van der Waals provided the Boltzmann statistics is assumed. One can make the estimation \( f_q \approx 1 + 2 b \rho / 3 \) assuming the small value of \( b \rho \ll 1 \) near the critical state. In this case a correlation can be made between \( b \) and \( k_+ \), \( b \sim 3 k_+ / 4 \), by comparison of Eqs. (20) and (14). It is notable that Eq. (20) describes only the isoscalar effective mass in contrast to Eq. (10) which includes the isovector effective mass splitting, see Eq. (18).

### 4 Stability conditions and critical line

Asymmetric nuclear matter is a mixture of neutrons and protons. The existence of such a binary mixture is subject to the condition of chemical stability (stability with respect to variation of mixture composition) [4]:
\[
\left( \frac{\partial \mu_n}{\partial x_n} \right)_{P,T} \geq 0 . \tag{21}
\]
Here \( \mu_n \) is the chemical potential for the component \( q \) of the mixture. It makes no difference whether \( q = n \) or \( p \) is taken in Eq. (21) due to thermodynamic relation \( x_n (\partial \mu_n / \partial x_n)_{P,T} = x_p (\partial \mu_p / \partial x_p)_{P,T} \). The thermal, \( c_V \geq 0 \), and mechanical, \( K \geq 0 \), stability conditions must also be fulfilled to ensure that asymmetric nuclear matter exists in thermodynamic equilibrium. Here \( K = 9 (\partial P / \partial \rho)_{T,X} \) is the isothermal incompressibility coefficient.

The number of thermodynamic degrees of freedom (the number of variables which can be freely varied without violation of thermodynamic equilibrium) is calculated from the phase rule of Gibbs [4]. A single phase of asymmetric nuclear matter has three degrees of freedom. That is, three intensive variables, \( P, T, \) and \( X, \) may all be changed (within some limits) without causing any new phase to appear. Two coexisting phases (liquid and saturated vapour) are represented by binodal surface in three-dimensional \( (P,T,X) \)-space, and set of critical states forms the critical line which lies on the binodal surface [22]. The critical state of asymmetric nuclear matter corresponds to a point of binodal surface at which all the intensive properties of the coexisting phases become identical. The critical line of asymmetric nuclear matter is determined by [4, 22]
\[
\left( \frac{\partial \mu_n}{\partial x_n} \right)_{P,T} = \left( \frac{\partial^2 \mu_n}{\partial x_n^2} \right)_{P,T} = 0 . \tag{22}
\]
This critical line is univariant in a three-dimensional space, and any intensive critical quantity can be calculated by specifying a single value of mixture composition.
Let consider the special case of symmetric nuclear matter states on a binodal surface. One should note that symmetric nuclear matter \((X = 0\text{, }\alpha_n = x_n = x_p = 1/2)\) is known to be an azeotrope \([22]\). To be more specific, the binary mixture of neutrons and protons forms a negative azeotrope (according to convention based on Gibbs-Konovalov laws, see Ref. \([29]\)) located at a maximum of \((P, T, X)\)-diagram. The nuclear matter azeotropy at \(X = 0\) is caused by charge symmetry of nuclear forces. Symmetric nuclear matter can be considered as a pure substance along the azeotrope \((P, T)\)-line \([22, 29]\). In particular, the critical point of symmetric nuclear matter is determined as

\[
\left(\frac{\partial P}{\partial \rho}\right)_{T,X=0} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T,X=0} = 0 .
\]

This point is located on the critical line at \(X = 0\) being the high-temperature endpoint of azeotrope line, see Ref \([22]\).

In order to emphasize the isotopic asymmetry effects, the isoscalar, \(\mu_0 = (\mu_n + \mu_p)/2\), and isovector, \(\mu_1 = (\mu_n - \mu_p)/2\), chemical potentials are conveniently introduced, see Appendix C. Having the chemical potentials \(\mu_0\) and \(\mu_1\), the equivalent to Eq. \([22]\) definition of critical line is written as

\[
\left(\frac{\partial \mu_\tau}{\partial X}\right)_{P,T} = \left(\frac{\partial^2 \mu_\tau}{\partial X^2}\right)_{P,T} = 0 ,
\]

where \(\tau = 0\) or 1. Due to charge symmetry of nuclear forces, the density \(\rho_{\text{cr}}\), temperature, \(T_{\text{cr}}\), and pressure, \(P_{\text{cr}}\), at the critical line are even functions of \(X\). One may write for small displacements from the critical point of symmetric nuclear matter (within the order of \(\mathcal{O}(X^2)\)):

\[
\frac{\rho_{\text{cr}}(X) - \rho_{\text{cr}}(0)}{\rho_{\text{cr}}(0)} = \alpha_\rho X^2 , \quad \frac{T_{\text{cr}}(X) - T_{\text{cr}}(0)}{T_{\text{cr}}(0)} = \alpha_T X^2 , \quad \frac{P_{\text{cr}}(X) - P_{\text{cr}}(0)}{P_{\text{cr}}(0)} = \alpha_P X^2 ,
\]

where the critical curvatures \(\alpha_\rho\), \(\alpha_T\) and \(\alpha_P\) are introduced for description of small displacements along the critical line in variables of \(\rho\), \(T\) and \(P\), respectively. By the use of Eq. \([24]\) the curvature \(\alpha_z\) for the critical compression factor \(z_{\text{cr}} = \left(\frac{P}{\rho T}\right)_{\text{cr}}\) is obtained as

\[
\alpha_z = \frac{1}{2z_{\text{cr}}(0)} \left(\frac{d^2 z_{\text{cr}}(X)}{dX^2}\right)_{X=0} = \alpha_P - \alpha_\rho - \alpha_T .
\]

One should note that the above-described critical curvatures are the properties of asymmetric nuclear matter, even though they are calculated at \(X = 0\). In support of this claim, in the next section the curvature \(\alpha_z\) will be used to determine the model parameter \(a_1\) of Eq. \([3]\).

5 Model parameters

The empirical van der Waals equation of state \([3]\), with the correction for the Fermi statistics \([12]\) included, has three parameters \(a_0\), \(a_1\) and \(b\) which need to be determined from the properties of nuclear matter. One should stress here that the application of such a simple model to the saturation point of cold nuclear matter \((T = 0)\) should be avoided if at all possible. This model seems to be oversimplified when it comes to the description of the saturation point observables. In particular, such model gives unacceptably high estimate for the value of incompressibility coefficient, see \([30]\) for instance, which is several times larger than the value of about \(K = 230\) MeV determined from the experimental strength distributions of giant resonances \([31, 32]\). As a consequence, one may also see the overestimation of the critical density \(\rho_{\text{cr}}\) as compared to the value of about \(\rho_{\text{sat}}/3\) which is obtained within the Skyrme EDF approach (see Table \([1]\) below) or the relativistic mean field theory \([33]\) parameterized to be consistent with the experimental value of \(K\). So, simultaneous description of density, energy per particle and incompressibility coefficient at the saturation point cannot be achieved within the van der Waals model corrected for Fermi statistics. In this respect it seems methodologically incorrect to determine parameters

\footnote{Azeotropy is the liquid mixture property of distilling without change in composition.}
of the model from the saturation point area where this model is not supposed to agree with experiment. Instead, more attention will be focused on the description of critical state region, the field of success of van der Waals theory \[1\]. Out of critical state observables, only the critical temperature of symmetric nuclear matter is well established experimentally for the moment \[6,8\]. The rest of information for determination of parameters \(a_0\), \(a_1\) and \(b\) will be taken from testing the present model against more realistic Skyrme EDF theory.

The values of densities and effective nucleon masses relevant to the saturation and critical points of symmetric nuclear matter are collected in Table \(1\) for different Skyrme parametrizations. The choice of particular Skyrme EDFs is made in accord with recommendations of Ref. \[33\] where 240 Skyrme parametrizations known from literature were examined as to their ability to predict nuclear matter properties in a wide range of applications of nuclear physics and astrophysics. As seen from Table \(1\) the ratio of critical to saturation density is almost the same for all presented Skyrme forces, \(\rho_{ct}/\rho_{sat} \approx 1/3\). This allows to fix the values of parameters \(a_0\) and \(b\) for the equation of state given by Eqs. \(9\), \(10\) and \(12\). Taking the ratio \(\rho_{ct}/\rho_{sat} = 1/3\) at \(\rho_{sat} = 0.165\ \text{fm}^{-3}\) together with the experimentally determined value of critical temperature \(T_{cr} = 16.6\ \text{MeV} \[6\], one obtains the values of parameters \(a_0 = 365.4\ \text{MeVfm}^3\), \(b = 4.418\ \text{fm}^3\). It has to be noted that the given estimate uses the isoscalar effective mass of Eq. \(20\) in correcting van der Waals equation of state for Fermi statistics. The last row of Table \(1\) shows the values of curvature \(\alpha_z\) for the critical compression factor \(z_{ct} = \left(\frac{P}{\rho T}\right)_{ct}\), see Eq. \(20\), calculated for different Skyrme EDFs. One can see from the table that value of \(\alpha_z\) is close to 1. Also, there is some scatter in the value depending on the choice of Skyrme force. Fixing the curvature of the critical compression factor at the level of \(\alpha_z = 1\) for the presented model of van der Waals with Fermi-statistics correction, one obtains \(a_1 = -191.3\ \text{MeVfm}^3\). The value of the parameter \(a_1\) is negative. This corresponds to the extra repulsion between particles. So, in line with properties of cold nuclear matter, the asymmetric nuclear matter at critical state region is less bound as compared to the symmetric one. In addition, it can be learned from Table \(1\) that the isovector effective mass shift \(m_i^*/m\) at saturation density \(\rho_{sat}\) becomes of about twice smaller at the critical density \(\rho_{ct}\). As for the isoscalar effective mass, its value becomes closer to bare nucleon mass as density decreases from saturation to critical value.

Table 1: Saturation and critical properties of symmetric and asymmetric nuclear matter for different Skyrme EDFs. In order of rows: saturation density \(\rho_{sat}\); isoscalar, \(m_0^*/m\), and isovector, \(m_1^*/m\), effective nucleon masses at saturation point, see Eqs. \(17\), \(18\); ratio of critical to saturation density \(\rho_{ct}/\rho_{sat}\); isoscalar, \(m_0^*/m\), and isovector, \(m_1^*/m\), effective nucleon masses at critical point; curvature \(\alpha_z\) of critical compression factor, see Eqs. \(25\), \(26\). Calculations were carried out for Skyrme parametrizations KDE0v1 \[35\], LNS \[36\], NRAPR \[37\], SKRA \[38\] and SQMC700 \[39\].

| Quantity | KDE0v1 | LNS | NRAPR | SKRA | SQMC700 |
|----------|--------|-----|-------|------|---------|
| \(\rho_{sat}\), \text{fm}^{-3}\ | 0.165  | 0.175 | 0.161 | 0.159 | 0.170 |
| \(m_0^*/m\) at \(\rho_{sat}\) | 0.74   | 0.83  | 0.69  | 0.75  | 0.76   |
| \(m_1^*/m\) at \(\rho_{sat}\) | \(-0.13X\) | 0.22X | 0.21X | 0.29X | 0.27X |
| \(\rho_{ct}/\rho_{sat}\) | 0.330  | 0.328 | 0.337 | 0.329 | 0.333 |
| \(m_0^*/m\) at \(\rho_{ct}\) | 0.90   | 0.94  | 0.87  | 0.90  | 0.90   |
| \(m_1^*/m\) at \(\rho_{ct}\) | \(-0.06X\) | 0.09X | 0.11X | 0.14X | 0.13X |
| \(\alpha_z\) | 1.09   | 0.77  | 0.81  | 0.73  | 0.80   |

6 Results and discussion

Calculations for simple model of van der Waals (vdW), Eq. \(3\), as well as for vdW with Fermi statistics correction (vdW+stat), Eq. \(10\), were carried out using parameters \(a_0 = 365.4\ \text{MeVfm}^3\), \(a_1 = -191.3\ \text{MeVfm}^3\) and \(b = 4.418\ \text{fm}^3\) obtained in previous section. The chemical potentials required to
determine the critical line by means of Eq. (24) were obtained utilizing Eq. (22) with $\phi = \phi_{\text{vdW}}$ (vdW) and $\phi = \phi_{\text{vdW}} + \phi_{\text{stat}}$ (vdW+stat), see Eqs. (1), (12). For last case the explicit expressions for isoscalar and isovector chemical potentials are given by Eq. (44) of Appendix C.

In Table 2 the results of calculations for various properties of nuclear matter at critical state are shown. Calculation results obtained in the context of vdW and vdW+stat models are presented, respectively, in the first and second rows of Table 2. For the purpose of comparison the same quantities obtained for the case of Skyrme force KDE0v1 [35] are collected in the third row of the table. It is seen from Table 2 that the values of $T_{\text{cr}}$, $P_{\text{cr}}$ and $\rho_{\text{cr}}$ for symmetric nuclear matter obtained in vdW+stat model differ noticeably from the corresponding results of vdW model. The consideration of Fermi-statistics contribution lowers the values of critical temperature, pressure and density. The reverse situation, with $(m_0^*/m)_{\text{cr}}$ value of vdW+stat model above the vdW value, is seen from the fifth column of Table 2. The results placed in the fifth column do also demonstrate that the isoscalar effective mass at critical point is a bit underestimated for both vdW and vdW+stat cases as compared to the result shown for Skyrme EDF (KDE0v1). Within classical theory of critical point [4], when moving along the critical isochore of symmetric nuclear matter at $\rho = \rho_{\text{cr}}$ the specific heat exhibits a finite jump $\Delta c_V = c_V(T_{\text{cr}} - 0) - c_V(T_{\text{cr}} + 0)$ upon crossing the critical temperature. The value of $\Delta c_V$ is provided by sixth column of Table 2. For two-phase part of the critical isochore $(T < T_{\text{cr}})$ the entropy density $s_p$ and particle density $\rho$ are determined as sums of contributions from each phase,

$$s_p = \lambda_{\text{liq}} s_{\text{liq}} \rho_{\text{liq}} + \lambda_{\text{vap}} s_{\text{vap}} \rho_{\text{vap}}, \quad \rho = \lambda_{\text{liq}} \rho_{\text{liq}} + \lambda_{\text{vap}} \rho_{\text{vap}} = \rho_{\text{cr}}, \quad \lambda_{\text{liq}} + \lambda_{\text{vap}} = 1. \tag{27}$$

Here superscripts “liq” and “vap” are used to denote liquid and vapour phases, $\lambda_{\text{liq}} = V_{\text{liq}}/V$ and $\lambda_{\text{vap}} = V_{\text{vap}}/V$ stand for the liquid and vapour volume fractions of the total volume $V$, respectively. In Eq. (27) the first equality determines the entropy density for the region of phase coexistence, the second equality ensures that the particle density corresponds to critical isochore, and the last one provides the volume conservation (isochore). The densities $\rho_{\text{liq}}$ and $\rho_{\text{vap}}$ are determined from the conditions of liquid-vapour equilibrium which requires the equality of $P$ and $\mu_0$ for liquid and vapour ($\mu_1 = 0$ for both phases at $X = 0$). Taking $c_V = T(\partial s/\partial T)_{\rho = \mu, T < T_{\text{cr}}}$ built on Eq. (27) together with its counterpart of a single phase $(T > T_{\text{cr}})$ one obtains $\Delta c_V = \lim_{T \to T_{\text{cr}}^-} [c_V(T < T_{\text{cr}}) - c_V(T > T_{\text{cr}})] > 0$. The value of $\Delta c_V$ on the critical isochore for van der Waals model is known to be equal to 9/2, see, for example, Ref. [10]. With Fermi statistics taken into consideration this value is substantially reduced, as can be seen from comparison of vdW and vdW+stat results from Table 2 (sixth column).

The values of curvatures of the critical line with respect to the temperature, pressure, density and compression factor variables at $X = 0$ are shown in seventh to tenth columns of Table 2. These curvatures are the properties of asymmetric nuclear matter, each of them determines the behavior of the appropriate quantity with the variation in nuclear matter composition along the critical line, see Eqs. (25), (26). As seen from signs of the curvatures presented in Table 2 on the critical line the temperature goes lower while the pressure, density and compression factor raise with deviation in the asymmetry parameter.

| $T_{\text{cr}}$, MeV | $P_{\text{cr}}$, MeVfm$^{-3}$ | $\rho_{\text{cr}}$, fm$^{-3}$ | $(m_0^*/m)_{\text{cr}}$ | $\Delta c_V$ | $\alpha_T$ | $\alpha_P$ | $\alpha_{\rho}$ | $\alpha_\lambda$ |
|------------------|------------------------|------------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| vdW              | 24.5                   | 0.693            | 0.0754          | 0.76           | 4.50           | -0.24          | 0.61           | 0.26           | 0.59           |
| vdW+stat         | 16.6                   | 0.337            | 0.0550          | 0.83           | 2.00           | -0.51          | 0.73           | 0.24           | 1.00           |
| KDE0v1           | 14.9                   | 0.225            | 0.0545          | 0.90           | 2.57           | -0.40          | 0.94           | 0.25           | 1.09           |
Van der Waals equation of state was considered from the viewpoint of applying to the asymmetric nuclear matter. With the aim of describing the nuclear matter as a binary mixture of neutrons and protons, the dependence on isotopic asymmetry has been introduced in the equation of state, particularly in the part that responsible for the two-body attraction between nucleons. As a result, the two-parametric equation of state (1) for pure substance has been modified into the three-parametric form of Eq. (3) for binary mixture. Fermi-statistics corrections have been derived to bring into the equation of state the properties of Fermi motion, which has ensured the fulfilment of Nernst theorem. For this purpose the widely-used expression (6) for entropy from Thomas-Fermi theory was applied. The level of significance for statistics effect is determined by the ratio $\delta_q = \rho_q^{-1/3}/\lambda_q$ of mean distance between particles $\rho_q^{-1/3}$ to the thermal de Broglie wavelength $\lambda_q$. This well-known statement has been confirmed once again by the example of specific heat calculation, see Fig. 1 and Eqs. (B.6), (B.7). Specific heat $c_V$ vanishes in the low-temperature limit $\delta_q \ll 1$ (the consequence of Nernst theorem) and approaches its ideal gas limit of 3/2 for high temperatures, e.g. $\delta_q \gg 1$.

The emphasis has been put on determination of model parameters from the properties of critical

![Figure 2: Critical values of isoscalar chemical potential ($\mu_{0,cr}$), isovector chemical potential ($\mu_{1,cr}$), and incompressibility coefficient ($K_{cr}$) versus asymmetry parameter $X$. The corresponding notations are placed near the curves. Solid lines show results for vdW+stat model, dashed lines represent the calculations for KDE0v1 Skyrme energy density functional [35].](image-url)
state. Towards this end, the values of critical density \( \rho_{cr} \) and curvature of critical line \( \alpha_z \) have been taken from the analysis of Skyrme EDFs (Table 1) in conjunction with the experimental value of critical temperature \( T_{cr} \) \[6\]. The values of obtained parameters for the equation of state (3) have been found to be \( a_0 = 365.4 \text{MeVfm}^3 \), \( a_1 = -191.3 \text{MeVfm}^3 \) and \( b = 4.418 \text{fm}^3 \). Using the parameters listed the calculations have been carried out to obtain various properties of symmetric and asymmetric nuclear matter for the critical state region (Table 2 and Fig. 2). Some of the calculated quantities, like critical pressure \( P_{cr} \) and jump in heat capacity \( \Delta c_V \), were shown to be affected considerably by the account of Fermi statistics, see Table 2. The comparison of presented van der Waals model corrected for particles statistics with Skyrme EDF approach has been made for the high-temperature region of critical line. Within the overall picture of the comparison one might conclude that these two models agree in a qualitative sense.

In closing, it has to be stressed that the account for particles statistics, the way it has been incorporated into the equation of state, still have disadvantage of ignoring the exchange interaction between nucleons. Nevertheless, this disadvantage is presumably of less importance for the critical state of hot nuclear matter than for description of the saturation point of cold nuclear matter.

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**Appendix A  Fermi integrals \( J_\nu(\eta) \)**

For applications of the Thomas–Fermi theory at finite temperature the well-known Fermi integrals are used

\[
J_\nu(\eta) = \int_0^\infty \frac{y^\nu dy}{1 + \exp(y - \eta)} . \tag{A.1}
\]

The integral (A.1) is defined for \( \nu > -1 \). It obeys the recurrence relation

\[
\frac{d}{d\eta} J_\nu(\eta) = \nu J_{\nu-1}(\eta) . \tag{A.2}
\]

This relation can be used for analytic continuation of Fermi integrals \[41\] to obtain \( J_\nu(\eta) \) at \( \nu \leq -1 \) needed for some applications like, for instance, the study of finite Fermi-systems. To calculate \( J_\nu(\eta) \) for negative values of \( \eta \), such that \( \exp(\eta) \ll 1 \), the following expansion is used \[42\]:

\[
J_\nu(\eta) = \Gamma(\nu + 1) \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\exp(k\eta)}{k^{\nu+1}} . \tag{A.3}
\]

Here \( \Gamma(\nu + 1) \) denotes the Euler gamma function. In the opposite case of large positive values of \( \eta \gg 1 \), the Sommerfeld’s asymptotic series \[43\] is usually applied,

\[
J_\nu(\eta) = \frac{\eta^{\nu+1}}{\nu + 1} \left( 1 + \sum_{k=1}^{\infty} \left( 1 - 2^{1-2k} \right) \frac{2\Gamma(\nu + 2)\zeta(2k)}{\Gamma(\nu + 2 - 2k)} \frac{1}{\eta^{2k}} \right) = \frac{\eta^{\nu+1}}{\nu + 1} \left( 1 + \frac{\pi^2}{6}(\nu + 1)\nu \frac{1}{\eta^2} + \frac{7\pi^4}{720}(\nu + 1)(\nu - 1)(\nu - 2) \frac{1}{\eta^4} + \ldots \right) , \tag{A.4}
\]

where \( \zeta(2k) \) is the Riemann zeta function.
Appendix B  Properties of $\eta_q(\rho, T, X)$ and related functions

In this Appendix some properties of quantity $\eta_q$ ($q = n$ for neutrons and $q = p$ for protons) are considered. This quantity is usually associated with thermodynamic activity and/or fugacity and appears as an argument of Fermi integrals in the expression (3) for the entropy per particle. The properties of $\eta_q$ as a function of the total nucleon density $\rho$, temperature $T$, and asymmetry parameter $X$ (or $x_q$, the fraction of nucleon species $q$) are determined by the condition

$$\rho_q = \frac{1}{2\pi^2} \left( \frac{2m_q^* T}{\hbar^2} \right)^{3/2} J_{1/2}(\eta_q) \; ,$$  

(B.1)

where $\rho_q = x_q \rho$, and $m_q^*$ is the effective nucleon mass determined by the ratio $f_q(\rho, X) = m/m_q^*$, see Eqs. (10), (20). The effective mass is density dependent and usually normalized to certain value of density. One have to put $f_q = 1$ to leave out the effective mass contribution. Differentiating Eq. (B.1) at fixed $X$ ($dX = 0$) and using (A.2), one writes

$$d\eta_q = \frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)} \left[ 1 + \frac{3 \rho}{2 f_q} \left( \frac{\partial f_q}{\partial \rho} \right)_X \right] \frac{2d\rho}{\rho} - \frac{3dT}{T} \; .$$  

(B.2)

From Eq. (B.2) one obtains partial derivatives of $\eta_q$ with respect to the density and temperature,

$$\left( \frac{\partial \eta_q}{\partial \rho} \right)_{T,X} = \frac{2}{\rho} \left( 1 + \frac{3 \rho}{2 f_q} \left( \frac{\partial f_q}{\partial \rho} \right)_X \right) \frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)} \; , \quad \left( \frac{\partial \eta_q}{\partial T} \right)_{\rho,X} = -\frac{3}{T} \frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)} \; ,$$  

(B.3)

and also the relation between them,

$$\left( \frac{\partial \eta_q}{\partial \rho} \right)_{T,X} = -\frac{2T}{3\rho} \left( 1 + \frac{3 \rho}{2 f_q} \left( \frac{\partial f_q}{\partial \rho} \right)_X \right) \left( \frac{\partial \eta_q}{\partial T} \right)_{\rho,X} \; .$$  

(B.4)

The above relation (B.4) results from the fact that after inverting Eq. (B.1), $\eta_q$ is derived as a function of the ratio $\rho_q/(m_q^* T)^{3/2}$. One can conveniently use $\eta_q = \eta_q(\delta_q)$, the dependence on the dimensionless quantity $\delta_q = \rho_q^{-1/3}/\lambda_q$. Here $\lambda_q = \hbar/\sqrt{m_q^* T}$ denotes the thermal de Broglie wavelength.

Let consider the function $\psi = \psi(\eta_q)$, which appears in the expression for the specific heat (5), namely,

$$\psi(\eta_q) = \frac{5}{2} \frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - \frac{9}{2} \frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)} = T \frac{\partial}{\partial T} \left( \frac{5}{3} \frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - \eta_q \right)_{\rho,X} - \frac{\partial}{\partial T} \left( T \frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} \right)_{\rho,X} \; .$$  

(B.5)

It is readily apparent from Eq. (B.1) that the behavior of $\psi$ at $\eta_q \to \infty$ and $\eta_q \to -\infty$ will correspond, respectively, to the asymptote within the low temperature limit $\delta_q \ll 1$ ($T \to 0$ at fixed $\rho$, $X$) and high temperature limit $\delta_q \gg 1$ ($T^{-1} \to 0$ at fixed $\rho$, $X$). Using Eq. (B.1) together with series (A.4) one derives $\psi$ at low temperature limit,

$$\psi(\eta_q) = \left( \frac{\pi}{3\rho_q} \right)^{2/3} \frac{m_q^* T}{\hbar^2} + O \left( \frac{1}{\rho_q^2 \delta_q^6} \right) = \left( \frac{\pi}{3} \right)^{2/3} \delta_q^2 + O \left( \delta_q^6 \right) \; .$$  

(B.6)

Applying expansion (A.3) to Eq. (B.1), the corresponding high temperature asymptote is given by

$$\psi(\eta_q) = \frac{3}{2} - \frac{3}{16} \rho_q \left( \frac{\pi h^2}{m_q^* T} \right)^{3/2} + O \left( \rho_q^2 \delta_q^6 \right) = \frac{3}{2} - \frac{3\pi^{3/2}}{16} \delta_q^{-3} + O \left( \delta_q^{-6} \right) \; .$$  

(B.7)

In Sec. 2 the differential equation (11) is written for $P_{\text{stat}}$, the correction of pressure for Fermi statistics. In order to solve Eq. (11) one have to integrate twice the expression $-\rho^2 (\partial \psi/\partial \rho)_{T,X} / T$ over the temperature at fixed particle density $\rho$ and asymmetry parameter $X$. The first integration with respect to $T$ can be performed after transforming this expression as

$$-\frac{\rho^2}{T} \left( \frac{\partial \psi(\eta_q)}{\partial \rho} \right)_{T,X} = 2\rho \left( 1 + \frac{3 \rho}{2 f_q} \left( \frac{\partial f_q}{\partial \rho} \right)_X \right) \left( \frac{\partial \psi(\eta_q)}{\partial T} \right)_{\rho,X} \; ,$$  

(B.8)
based on the relation (3.4). The second integration is confined to integrating \( \psi \) over \( T \) and can be easily carried out by using the very right-hand side equality of Eq. (3.5).

The correction \( \phi_{\text{stat}} \) to free energy per particle is also calculated in Sec. 2 starting from the corresponding correction to pressure (12). For this purpose one has to perform the integration over density of the integrand \( \left( 1 + \frac{3 \rho}{2 f_q} \frac{\partial f_q}{\partial \rho} \right) \left( \frac{2}{3} J_{3/2}(\eta_q) - 1 \right) \frac{d \rho}{\rho} \) as it follows from Eqs. (12), (14). Taking Eq. (3.2) at fixed temperature (\( dT = 0 \)) and using definition for the derivative of Fermi integral (A.2) one obtains

\[
\left( 1 + \frac{3 \rho}{2 f_q} \frac{\partial f_q}{\partial \rho} \right) \left( \frac{2}{3} J_{3/2}(\eta_q) - 1 \right) \frac{d \rho}{\rho} = \frac{1}{2} \frac{J_{-1/2}(\eta_q)}{J_{1/2}(\eta_q)} \left( \frac{2}{3} J_{3/2}(\eta_q) - 1 \right) d \eta_q =  \\
d \left( \eta_q - \frac{2}{3} J_{3/2}(\eta_q) \right) - \ln \left( J_{1/2}(\eta_q) \right) .
\]

### Appendix C Chemical potentials

The neutron, \( \mu_n \), and proton, \( \mu_p \), chemical potentials are defined as derivatives of free energy \( F \) of a system with respect to the neutron number, \( N \), and proton number, \( Z \), respectively. That is, \( \mu_n = (\partial F/\partial N)_{V,T,Z} \) and \( \mu_n = (\partial F/\partial Z)_{V,T,N} \), where \( V \) is the system volume, and \( T \) is the temperature. To consider the isospin asymmetry effects, it is useful to take the total number of particles \( A = N + Z \) and the neutron excess \( N - Z \) for arguments of free energy. This defines the isoscalar, \( \mu_0 \), and isovector, \( \mu_1 \), chemical potentials as

\[
\mu_0 = \left( \frac{\partial F}{\partial A} \right)_{V,T,N-Z} = \frac{\mu_n + \mu_p}{2} , \quad \mu_1 = \left( \frac{\partial F}{\partial (N-Z)} \right)_{V,T,N} = \frac{\mu_n - \mu_p}{2} .
\]

Turning now to the intensive properties, namely, to the free energy per particle \( \phi = F/A \), total density \( \rho = A/V = \rho_n + \rho_p \) and asymmetry parameter \( X = (N - Z)/A = (\rho_n - \rho_p)/\rho \), the definitions (C.1) are rewritten as

\[
\mu_0(\rho, T, X) = \left( \frac{\partial \phi}{\partial \rho} \right)_{T,X} - X \left( \frac{\partial \phi}{\partial X} \right)_{\rho,T} , \quad \mu_1(\rho, T, X) = \left( \frac{\partial \phi}{\partial X} \right)_{\rho,T} .
\]

Charge symmetry of nuclear forces governs the properties of \( \mu_\tau \) (\( \tau = 0 \) for the isoscalar and \( \tau = 1 \) for the isovector chemical potential) with regard to the sign of the asymmetry parameter, \( \mu_\tau(\rho, T, X) = (-1)^\tau \mu_\tau(\rho, T, X) \). In view of thermodynamic relation \( \partial \mu_0/\partial X \rho,P,T + X \partial \mu_1/\partial X \rho,P,T = 0 \), the condition of chemical stability, Eq. (21), is rewritten as \( (-1)^\tau (\partial \mu_\tau/\partial X)_{\rho,P,T} \leq 0 \) with \( \tau = 0 \) or 1. For calculation of derivatives with respect to \( X \) at fixed pressure, needed to determine the critical line defined in Eq. (24), the transformation is made by the use of corresponding Jacobians [4]

\[
\left( \frac{\partial \mu_\tau}{\partial X} \right)_{\rho,T} = \left( \frac{\partial \mu_\tau}{\partial X} \right)_{\rho,T} - \left( \frac{\partial \mu_\tau}{\partial \rho} \right)_{X,T} \left( \frac{\partial P}{\partial X} \right)_{\rho,T} \left( \frac{\partial P}{\partial \rho} \right)^{-1} .
\]

The second derivative \( (\partial^2 \mu_\tau/\partial X^2)_{\rho,P,T} \) is obtained from (C.3) straightforwardly.

In Secs. [4, 10] various properties of nuclear matter are calculated using Skyrme density functional and simple model of van der Waals with correction for Fermi statistics. For last case, the free energy per particle is defined as \( \phi = \phi_{vdW} + \phi_{\text{stat}} \), see Eqs. (11), (10). This suggests the following expressions for \( \mu_0 \) and \( \mu_1 \) determined from (C.2) taking into consideration the effective mass (21):

\[
\mu_0 = -2a_0 \rho + T \frac{\eta_n + \eta_p}{2} + \frac{2bT}{3\pi^2} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \frac{J_{3/2}(\eta_q)}{2} + \frac{J_{5/2}(\eta_p)}{2} , \quad \mu_1 = -2a_1 \rho X + T \frac{\eta_n - \eta_p}{2} .
\]

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