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VAN DER WAALS EQUATION OF STATE FOR ASYMMETRIC NUCLEAR MATTER

The application of the 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 fulfilment of the Nernst theorem. The derived corrections account for the effective nucleon mass and neutron-proton isotopic asymmetry. The parameters of the van der Waals equation of state are deduced by 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. A critical line in pressure-temperature-composition space is considered. The incompressibility coefficient is determined along the critical line as a function of nuclear matter composition. A jump in the value of specific heat upon crossing a critical line is discussed.

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

1. Introduction

Significant progress in the 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 the van der Waals equation of state comes from its simplicity together with physically meaningful predictions for both vapour and liquid phases for a 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 has been studied over many years on the basis of the 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 - 15] 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 a nucleon, m^*, which gives an idea of 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, ρ_{sat}, energy per particle, $\epsilon(\rho_{sat})$, and incompressibility coefficient, $K(\rho_{sat})$. 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 the state of van der Waals does not comply with the properties of cold nuclear matter, since the description of three quantities, e.g. ρ_{sat}, $\epsilon(\rho_{sat})$ and $K(\rho_{sat})$, 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 the description of the symmetric [16] as well as asymmetric [17] nuclear matter within the grand canonical ensemble formulation. In the present paper, a similar problem is considered by means of the non-relativistic theory of energy density functional (EDF) (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 the above arguments which raise doubts about the capabilities of van der Waals equation of state for the 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 the 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 the van der Waals model are derived. The criterion for application of Fermi statistics is illustrated by the example of specific heat. Sec. 3 is concerned with the 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 the 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 the state of van der Waals [1] relates the pressure, $P = P_{\text{vdW}}$, particle density, ρ, and temperature, T, as

$$P_{\text{vdW}} = \frac{\rho T}{1 - b\rho} - a\rho^2, \qquad (1)$$

where a and b are positive adjustable parameters. By physical interpretation [2] 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 $a \to a_{\text{mix}}$ and $b \to b_{\text{mix}}$ in Eq. (1), where the new parameters a_{mix} and b_{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 of 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 the van der Waals equation of state [18], $a_{\text{mix}} = \sum_{q,q'} x_q x_{q'} a_{qq'}$, where $x_q = \rho_q / \rho$ stand for the fractions and ρ_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 $a_{qq'}$: $a_{nn} = a_{pp} = a_{\text{l}}$, $a_{np} = a_{pn} = a_{\text{u}}$, 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

$$a_{\text{mix}} = \sum_{q,q'} x_q x_{q'} a_{qq'} = a_0 + a_1 X^2 . \qquad (2)$$

Here, $a_0 = (a_{\text{l}} + a_{\text{u}})/2$ and $a_1 = (a_{\text{l}} - a_{\text{u}})/2$ 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:

$$P_{\text{vdW}}(\rho, X) = \frac{\rho T}{1 - b\rho} - \left(a_0 + a_1 X^2\right)\rho^2 . \qquad (3)$$

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

$$\phi_{\text{vdW}}(\rho, X) = T \ln\left(\frac{\rho}{1 - b\rho}\right) -$$

$$-\left(a_0 + a_1 X^2\right)\rho - \frac{3}{2} T \ln(T) - T(1 + \xi(X)) \qquad (4)$$

with $\xi(X) = \xi_{\text{ch}} - \sum_{q=n,p} x_q \ln\left(x_q\right)$. Here $\left[-\sum_{q=n,p} x_q \ln(x_q)\right]$ is the mixing entropy per particle of an ideal gas and $\xi_{\text{ch}} = \ln\left[2\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right]$ 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, $s_{\mathrm{vdW}} = -(\partial \phi_{\mathrm{vdW}} / \partial T)_{\rho,X}$, is written as

$$s_{\mathrm{vdW}} = \frac{5}{2} - \ln\left(\frac{\rho}{1-b\rho}\right) + \frac{3}{2}\ln(T) + \xi(X). \quad (5)$$

For the purpose to incorporate Fermi statistics into the empirical equation of state (3) let's 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],

$$s = \sum_{q=n,p} x_q \left(\frac{5}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - \eta_q\right), \quad (6)$$

where $J_\nu(\eta_q)$, $\nu = 1/2, 3/2$, is the Fermi integral (see Appendix A), and its argument, η_q, can be found from the condition

$$\rho_q = \frac{1}{2\pi^2}\left(\frac{2mT}{\hbar^2 f_q}\right)^{3/2} J_{1/2}(\eta_q), \quad (7)$$

with $m / f_q = m_q^*$ being the effective nucleon mass. The value of η_q is usually related to the thermodynamic activity and/or fugacity. Eqs. (6) and (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 η_q can be expressed as a function of the ratio $\delta_q = \rho_q^{-1/3} / ƛ_q$, where $\rho_q^{-1/3}$ is about of mean distance between particles of the same isospin, $ƛ_q = \hbar / \sqrt{m_q^* T}$ is of the 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 δ_q gives an idea of whether it is worth accounting for the effects of Fermi statistics. Using the specific heat per particle c_V as an example, it can be shown that the effects of Fermi statistics become negligible within the high-temperature limit, $\delta_q \gg 1$. Using Eqs. (6) and (B.3) one obtains the specific heat per particle at constant volume, c_V, as

$$c_V = T\left(\frac{\partial s}{\partial T}\right)_{\rho,X} =$$

$$= \sum_{q=n,p} x_q \left(\frac{5}{2}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - \frac{9}{2}\frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)}\right) = \sum_{q=n,p} x_q \psi(\eta_q). \quad (8)$$

Here, ψ is the function of η_q only, see also Appendix B. The dependence of the specific heat c_V on the value of $\delta = \rho^{-1/3} / ƛ$ 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 $ƛ_n = ƛ_p = ƛ_{\mathrm{snm}}$ and $\eta_n = \eta_p = \eta_{\mathrm{snm}}$. Thus, Eq. (7) represents two identical relations between η_q and δ_q with $\delta_q^{-3} = \rho ƛ_{\mathrm{snm}}^3 / 2 = \delta_{\mathrm{snm}}^{-3} / 2$, regardless of the isospin index q. From Eq. (8) one obtains $c_V = \psi(\eta_{\mathrm{snm}})$ as a function of $\delta = \delta_{\mathrm{snm}}$, see solid line in Fig. 1. Second special instance is the pure neutron matter ($X = 1$, subscript "pnm" is used). Here, the neutron fraction is present only, $\rho_n = \rho$. The specific heat is determined as $c_V = \psi(\eta_{\mathrm{pnm}})$ with $\eta_{\mathrm{pnm}} = \eta_n$, $\delta_{\mathrm{pnm}} = \delta_n$, see Eqs. (7) and (8). The result of the calculation for c_V versus $\delta = \delta_{\mathrm{pnm}}$ is illustrated by the 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 δ, $\delta_{\mathrm{snm}} < \delta_{\mathrm{pnm}}$. The reason is directly relevant to the isospin degeneracy factor, $\delta_{\mathrm{snm}}^{-3} = 2\delta_{\mathrm{pnm}}^{-3}$. 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 the high-δ region the specific heat is estimated as $c_V \approx \frac{3}{2} - \frac{3\rho}{16}\left(\frac{\pi\hbar^2}{mT}\right)^{3/2} \sum_q x_q^2 f_q^{3/2}$ (see Appendix B). In the opposite case of low temperatures, one has $c_V \approx \left(\frac{\pi}{3\rho}\right)^{2/3} \frac{mT}{\hbar^2} \sum_q x_q^{1/3} / f_q$. The specific heat vanishes as the temperature approaches zero, in accordance with the 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 the intermediate region close to $\delta \approx 1$, as can be concluded from Fig. 1.

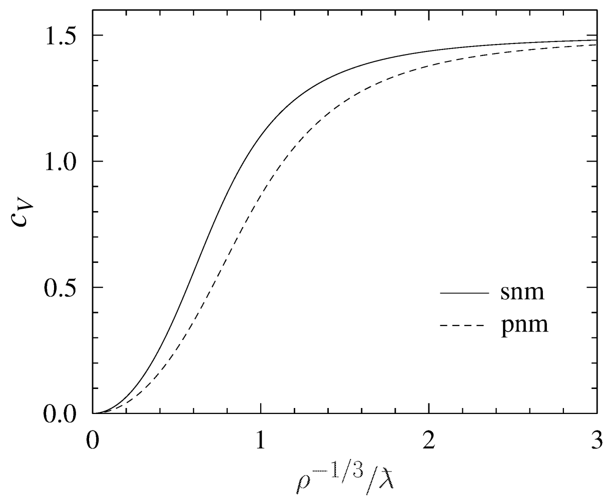

Fig. 1. Specific heat c_V is given by Eqs. (7) and (8) versus the value of $\delta = \rho^{-1/3}/\lambda$. The solid line shows the specific heat as a function of $\delta = \delta_{\text{snm}}$ for the symmetric nuclear matter $(X = 0)$, and the dashed line corresponds to $c_V(\delta = \delta_{\text{pnm}})$ of pure neutron matter $(X = 1)$.

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])

$$T\left(\frac{\partial^2 P}{\partial T^2}\right)_{\rho,X} = -\rho^2\left(\frac{\partial c_V}{\partial \rho}\right)_{T,X}. \qquad (9)$$

Then, let represent the pressure in Eq. (9) as the 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

$$P = P_{\text{vdW}} + P_{\text{stat}}. \qquad (10)$$

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

$$\left(\frac{\partial^2 P_{\text{stat}}}{\partial T^2}\right)_{\rho,X} = -\frac{\rho^2}{T}\frac{\partial}{\partial\rho}\left(\sum_{q=n,p} x_q \psi(\eta_q)\right)_{T,X}, \qquad (11)$$

where the function ψ has been defined by Eq. (8). Now one has the second order differential Eq. (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 the absence of the statistics effects at the high-temperature limit. Taking the high-temperature asymptote (B.7) of ψ, as applied to Eq. (11), one gains that P_{stat} and $\partial P_{\text{stat}}/\partial T$ 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

$$P_{\text{stat}} = \rho T \sum_{q=n,p} x_q \left(1 + \frac{3\rho}{2 f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\left(\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - 1\right), \qquad (12)$$

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

$$P_{\text{stat}} = \frac{2}{5}\left(3\pi^2\right)^{2/3}\sum_{q=n,p}\left(f_q + \frac{3}{2}\rho\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\frac{\hbar^2}{2m}\rho_q^{5/3} -$$

$$-\rho T\sum_{q=n,p} x_q\left(1 + \frac{3\rho}{2 f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right) + O\left(T^2\right), \qquad (13)$$

so P_{stat} is determined by the kinetic energy of Fermi motion within the leading order in temperature. It should be noted that the presence of the term $O(T)$ in Eq. (13) raises the issue as to the fulfilment of the 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_{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 ϕ_{vdW} is determined by Eq. (4), and ϕ_{stat} is obtained from the relationship between ϕ_{stat} and P_{stat}, that is

$$\left(\frac{\partial\phi_{\text{stat}}}{\partial\rho}\right)_{T,X} = \frac{P_{\text{stat}}}{\rho^2}. \qquad (14)$$

It can be seen from Eq. (14) that likewise P_{stat}, the correction ϕ_{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 ρ to the integration with respect to η_q as supported by Eq. (B.9) of Appendix B. This gives

$$\phi_{\text{stat}} = -T\sum_{q=n,p} x_q\left(\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - 1 - \eta_q + \ln\left(2J_{1/2}(\eta_q)/\sqrt{\pi}\right)\right). \quad (15)$$

3. Effective mass

The effective mass of nucleon accounts for the difference between the free-space and in-medium nucleon-nucleon interaction. 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 a 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

$$f_n = 1 + \frac{k_+}{2}\rho + \frac{k_-}{2}\rho X, \quad f_p = 1 + \frac{k_+}{2}\rho - \frac{k_-}{2}\rho X. \quad (16)$$

Here the coefficients k_+, k_- are density-independent and can be associated with the parameters of EDF. Density dependence of the effective mass is usually normalized to a certain value of 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

$$m_0^*/m = (1 + k_+\rho_{\text{sat}}/2)^{-1}. \quad (17)$$

The value of m_0^* is one of the crucial characteristics of 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 the saturation point $\rho = \rho_{\text{sat}}$ is written as

$$\frac{m_n^* - m_p^*}{m} = \frac{m_1^*}{m} + O(X^3), \quad \frac{m_1^*}{m} = -k_-\left(\frac{m_0^*}{m}\right)^2 \rho_{\text{sat}} X. \quad (18)$$

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]. A 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_{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 $(\partial P/\partial T)_{\rho,X} = -\rho^2(\partial s/\partial\rho)_{T,X} = O(T)$ for the case of Skyrme EDF. However, on the assumption of Eq. (10) one obtains for low temperatures

$$\left(\frac{\partial P}{\partial T}\right)_{\rho,X} = \frac{\rho}{1-b\rho} - \sum_{q=n,p}\rho_q\left(1 + \frac{3\rho}{2f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right) + O(T) \quad (19)$$

as evident from Eqs. (3) and (13). On the one hand, the presence of $O(T^0)$ 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 P_{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

$$f_n = f_p = (1-b\rho)^{-2/3}. \quad (20)$$

This choice makes the contribution of $O(T^0)$ 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 η_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 $\rho_q \to \rho_q/(1-b\rho)$. In the high-temperature limit,

$\delta_q \gg 1$, the series (A.3) of Appendix A can be applied to obtaining 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. (6), (7) and taking the effective mass given by (20), one obtains the expression for van der Waals entropy per particle s_{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 $f_q \approx 1 + 2b\rho/3$ 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_+, $b \sim 3k_+/4$, by comparison of Eqs. (20) and (16). It is notable that Eq. (20) describes only the isoscalar effective mass in contrast to Eq. (16) which includes the isovector effective mass splitting, see Eq. (18).

4. Stability conditions and critical line

The 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]:

$$\left(\frac{\partial \mu_q}{\partial x_q}\right)_{P,T} \geq 0. \tag{21}$$

Here μ_q 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 $x_n\left(\partial\mu_n/\partial x_n\right)_{P,T} = = x_p\left(\partial\mu_p/\partial x_p\right)_{P,T}$. 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 that 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 coexistent phases (liquid and saturated vapour) are represented by a binodal surface in three-dimensional (P, T, X)-space, and a 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 the 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]

$$\left(\frac{\partial \mu_q}{\partial x_q}\right)_{P,T} = \left(\frac{\partial^2 \mu_q}{\partial x_q^2}\right)_{P,T} = 0. \tag{22}$$

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's consider the special case of symmetric nuclear matter states on a binodal surface. One should note that symmetric nuclear matter ($X = 0$ or $x_n = x_p = 1/2$) is known to be an azeotrope[1] [22]. To be more specific, the binary mixture of neutrons and protons forms a *negative* azeotrope (according to the convention based on Gibbs-Konovalov laws, see Ref. [29]) located at a maximum of (T, X)-diagram. The nuclear matter azeotropy at $X = 0$ is caused by the 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

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,X=0} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T,X=0} = 0. \tag{23}$$

This point is located on the critical line at $X = 0$ being the high-temperature endpoint of the 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 μ_0 and μ_1, the equivalent to Eq. (22) definition of a critical line is written as

$$\left(\frac{\partial \mu_\tau}{\partial X}\right)_{P,T} = \left(\frac{\partial^2 \mu_\tau}{\partial X^2}\right)_{P,T} = 0, \tag{24}$$

where $\tau = 0$ or 1. Due to the charge symmetry of nuclear forces, the density, ρ_{cr}, temperature, T_{cr},

[1]Azeotropy is the liquid mixture property of distilling without change in composition.

and pressure, P_{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 $O(X^2)$):

$$\frac{\rho_{\text{cr}}(X)-\rho_{\text{cr}}(0)}{\rho_{\text{cr}}(0)}=\alpha_{\rho}X^2,$$

$$\frac{T_{\text{cr}}(X)-T_{\text{cr}}(0)}{T_{\text{cr}}(0)}=\alpha_{T}X^2,$$

$$\frac{P_{\text{cr}}(X)-P_{\text{cr}}(0)}{P_{\text{cr}}(0)}=\alpha_{P}X^2, \qquad (25)$$

where the critical curvatures α_ρ, α_T and α_P are introduced for the description of small displacements along the critical line in variables of ρ, T and P, respectively. By the use of Eq. (25) the curvature α_z for the critical compression factor $z_{\text{cr}}=\left(\frac{P}{\rho T}\right)_{\text{cr}}$ is obtained as

$$\alpha_z=\frac{1}{2z(0)}\left(\frac{d^2z(X)}{dX^2}\right)_{X=0}=\alpha_P-\alpha_\rho-\alpha_T. \qquad (26)$$

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 α_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 a model gives an 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 ρ_{cr} as compared to the value of about $\rho_{\text{sat}}/3$ which is obtained within the Skyrme EDF approach (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 the parameters of the model from the saturation point area where this model is not supposed to agree with the experiment. Instead, more attention will be focused on the description of the critical state region, the field of success of the 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 the information for the determination of parameters a_0, a_1 and b will be taken from testing the present model against a more realistic Skyrme EDF theory.

Table 1. **Saturation and critical properties of symmetric and asymmetric nuclear matter for different Skyrme EDFs**

Quantity	KDE0v1	LNS	NRAPR	SKRA	SQMC700
ρ_{sat}, fm^{-3}	0.165	0.175	0.161	0.15	0.170
m_0^*/m at ρ_{sat}	0.74	0.83	0.69	0.75	0.76
m_1^*/m at ρ_{sat}	$-0.13X$	$0.22X$	$0.21X$	$0.29X$	$0.27X$
$\rho_{\text{cr}}/\rho_{\text{sat}}$	0.330	0.328	0.337	0.329	0.333
m_0^*/m at ρ_{cr}	0.90	0.94	0.87	0.90	0.90
m_1^*/m at ρ_{cr}	$-0.06X$	$0.09X$	$0.11X$	$0.14X$	$0.13X$
α_z	1.09	0.77	0.81	0.73	0.80

N o t e. In order of rows: saturation density ρ_{sat}; isoscalar, m_0^*/m, and isovector, m_1^*/m, effective nucleon masses at saturation point, see Eqs. (17) and (18); the ratio of critical to saturation density $\rho_{\text{cr}}/\rho_{\text{sat}}$; isoscalar, m_0^*/m, and isovector, m_1^*/m, effective nucleon masses at a critical point; curvature α_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].

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. [34] where 240 Skyrme parametrizations known from the 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 in Table 1, the ratio of critical to saturation density is almost the same for all presented Skyrme forces, $\rho_{\rm cr}/\rho_{\rm sat} \approx 1/3$. This allows to fix the values of parameters a_0 and b for the equation of state given by Eqs. (3), (10) and (12). Taking the ratio $\rho_{\rm cr}/\rho_{\rm sat} = 1/3$ at $\rho_{\rm sat} = 0.165\,{\rm fm}^{-3}$ together with the experimentally determined value of critical temperature $T_{\rm cr} = 16.6\,{\rm MeV}$ [6], one obtains the values of parameters $a_0 = 365.4\,{\rm MeV\,fm}^3$, $b = 4.418\,{\rm fm}^3$. It has to be noted that the given estimate uses the isoscalar effective mass of Eq. (20) in correcting the van der Waals equation of state for Fermi statistics. The last row of Table 1 shows the values of curvature α_z for the critical compression factor $z_{\rm cr} = \left(\frac{P}{\rho T}\right)_{\rm cr}$, see Eq. (26), calculated for different Skyrme EDFs. One can see from the table that the value of α_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 $a_1 = -191.3\,{\rm MeV\,fm}^3$. The value of the parameter a_1 is negative. This corresponds to the extra repulsion between particles. So, in line with the properties of cold nuclear matter, the asymmetric nuclear matter at the 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_1^*/m at saturation density $\rho_{\rm sat}$ becomes about twice smaller at the critical density $\rho_{\rm cr}$. As for the isoscalar effective mass, its value becomes closer to bare nucleon mass as density decreases from saturation to critical value.

6. Results and discussion

Calculations for a 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 $a_0 = 365.4\,{\rm MeV\,fm}^3$, $a_1 = -191.3\,{\rm MeV\,fm}^3$ and $b = 4.418\,{\rm fm}^3$ obtained in the previous section. The chemical potentials required to determine the critical line by means of Eq. (24) were obtained utilizing Eq. (C.2) with $\phi = \phi_{\rm vdW}$ (vdW) and $\phi = \phi_{\rm vdW} + \phi_{\rm stat}$ (vdW + stat), see Eqs. (4) and (15). For the last case, the explicit expressions for isoscalar and isovector chemical potentials are given by Eq. (C.4) of Appendix C.

In Table 2 the results of calculations for various properties of nuclear matter at a 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.

Table 2. **Properties of the critical state of symmetric and asymmetric nuclear matter**

Model	$T_{\rm cr}$, MeV	$P_{\rm cr}$, ${\rm MeV\cdot fm}^{-3}$	$\rho_{\rm cr}$, ${\rm fm}^{-3}$	$(m_0^*/m)_{\rm cr}$	Δc_V	α_T	α_P	α_ρ	α_z
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

N o t e. Critical values of temperature $T_{\rm cr}$, pressure $P_{\rm cr}$, density $\rho_{\rm cr}$, isoscalar effective mass $(m_0^*/m)_{\rm cr}$, and jump in specific heat Δc_V (see text) upon crossing the critical line are presented in the second to sixth columns. Columns from seventh to tenth contain critical curvatures α_T, α_P, α_ρ and α_z, see Eqs. (25) and (26). Calculations were carried out for three cases. The first row (vdW) corresponds to the equation of the state (3) of van der Waals. The second row (vdW + stat) shows the results of the vdW case corrected for Fermi statistics. In the third row, the results of calculations for KDE0v1 Skyrme EDF [35] are presented. All results in the table were calculated for the critical line at $X = 0$.

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 $T_{\rm cr}$, $P_{\rm cr}$ and $\rho_{\rm cr}$ for symmetric nuclear matter obtained in the vdW + stat model differ noticeably from the corresponding results of the vdW model. The consideration of Fermi-statistics contribution lowers the values of critical temperature, pressure, and density. The reverse situation, with $(m_0^*/m)_{\rm cr}$ value of the vdW + stat model above the vdW value, is seen in the fifth column of Table 2. The results placed in the fifth column do also demonstrate that the isoscalar effective mass at the critical point is a bit underestimated for both vdW and vdW + stat cases as compared to the result shown for Skyrme EDF

(KDE0v1). Within the classical theory of critical point [4], when moving along the critical isochore of symmetric nuclear matter at $\rho = \rho_{\rm cr}$ the specific heat exhibits a finite jump $\Delta c_V = c_V(T_{\rm cr} - 0) - c_V(T_{\rm cr} + 0)$ upon crossing the critical temperature. The value of Δc_V is provided in the sixth column of Table 2. For the two-phase part of the critical isochore $(T < T_{\rm cr})$, the entropy density $s\rho$ and particle density ρ are determined as sums of contributions from each phase,

$$s\rho = \lambda^{\rm liq} s^{\rm liq} \rho^{\rm liq} + \lambda^{\rm vap} s^{\rm vap} \rho^{\rm vap},$$

$$\rho = \lambda^{\rm liq} \rho^{\rm liq} + \lambda^{\rm vap} \rho^{\rm vap} = \rho_{\rm cr}, \ \lambda^{\rm liq} + \lambda^{\rm vap} = 1. \quad (27)$$

Here superscripts “liq” and “vap” are used to denote liquid and vapour phases, $\lambda^{\rm liq} = V^{\rm liq}/V$ and $\lambda^{\rm vap} = V^{\rm vap}/V$ 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 $\rho^{\rm liq}$ and $\rho^{\rm vap}$ are determined from the conditions of liquid-vapour equilibrium which requires the equality of P and μ_0 for liquid and vapour ($\mu_1 = 0$ for both phases at $X = 0$). Taking $c_V = T(\partial s/\partial T)_{\rho=\rho_{\rm cr},\, T<T_{\rm cr}}$ built on Eq. (27) together with its counterpart of a single phase $(T > T_{\rm cr})$ one obtains $\Delta c_V = \lim_{T\to T_{\rm cr}} \left[c_V(T < T_{\rm cr}) - c_V(T > T_{\rm cr})\right] > 0.$ The value of Δc_V on the critical isochore for the van der Waals model is known to be equal to $9/2$, see, for example, Ref. [40]. With Fermi statistics taken into consideration, this value is substantially reduced, as can be seen from the 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 the 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) and (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 from zero. It is notable that the value of α_ρ is almost unaffected by the Fermi statistics treatment as compared to the rest of the critical curvatures given in Table 2.

The calculation results for the critical values of isoscalar, $\mu_{0,\rm cr}$, and isovector, $\mu_{1,\rm cr}$, chemical potentials, and incompressibility coefficient $K_{\rm cr}$ are displayed in Fig. 2. Calculations performed for KDE0v1 Skyrme force [35] are shown in the figure by dashed lines. Solid lines represent the results obtained using the van der Waals model corrected for Fermi statistics. One can see from Fig. 2 that $K_{\rm cr}$ is a monotonically increasing function of the asymmetry parameter in the presented interval $X > 0$. The critical incompressibility $K_{\rm cr}$ has a positive value throughout the plot except for the critical point of symmetric nuclear matter $(X = 0)$ where $K_{\rm cr}$ vanishes. The dependence $K_{\rm cr} \propto X^2$ (for small X) due to charge symmetry of nuclear forces is also seen in Fig. 2. Results of $\mu_{0,\rm cr}$ calculations displayed in Fig. 2 demonstrate a fairly weak dependence on asymmetry parameter, $\mu_{0,\rm cr}(X) \approx \mu_{0,\rm cr}(0)(1 + \alpha_{\mu_0} X^2)$, with a small value of the critical curvature α_{μ_0}. Isovector chemical potential is an odd function of X (see Appendix C), so $\mu_{1,\rm cr}$ is expected to be linear in asymmetry parameter at least for small values of X. This linearity is clearly seen in Fig. 2. Comparing results of two models, vdW + stat and Skyrme force KDE0v1, for various quantities shown in Fig. 2 one can conclude that there is an agreement between these models at least in a qualitative sense.

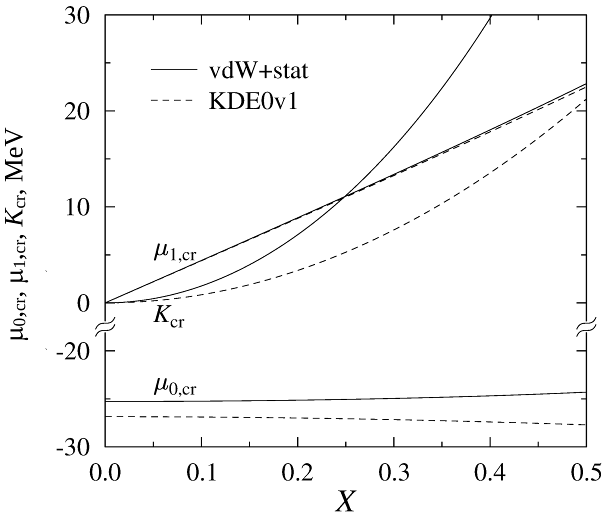

Fig. 2. Critical values of isoscalar chemical potential $(\mu_{0,\rm cr})$, isovector chemical potential $(\mu_{1,\rm cr})$, and incomepressibility coefficient $(K_{\rm cr})$ versus asymmetry parameter X. The corresponding notations are placed near the curves. Solid lines show results for vdW + stat model, and dashed lines represent the calculations for KDE0v1 Skyrme EDF [35].

7. Summary

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 is 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 the binary mixture. Fermi-statistics corrections have been derived to bring into the equation of state (3) the properties of Fermi motion, which has ensured the fulfilment of the Nernst theorem. For this purpose, the widely-used expression (6) for entropy from the Thomas-Fermi theory was applied. The level of significance for the statistics effect is determined by the ratio $\delta_q = \rho_q^{-1/3} / \lambdabar_q$ of the mean distance between particles $\rho_q^{-1/3}$ to the thermal de Broglie wavelength $\lambdabar_q$. 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 the 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 the determination of model parameters from the properties of the critical state. Towards this end, the values of critical density ρ_{cr} and curvature of the critical line α_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 $a_0 = 365.4\,\mathrm{MeV\,fm}^3$, $a_1 = -191.3\,\mathrm{MeV\,fm}^3$ and $b = 4.418\,\mathrm{fm}^3$. 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 (see Table 2 and Fig. 2). Some of the calculated quantities, like critical pressure P_{cr} and jump in heat capacity Δc_V, were shown to be affected considerably by the account of Fermi statistics, see Table 2. The comparison of the presented van der Waals model corrected for particle statistics with the Skyrme EDF approach has been made for the high-temperature region of the 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 particle statistics, the way it has been incorporated into the equation of state, still has the 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 the 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

$$J_\nu(\eta) = \int_0^\infty \frac{y^\nu dy}{1+\exp(y-\eta)}. \qquad \text{(A.1)}$$

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

$$\frac{d}{d\eta} J_\nu(\eta) = \nu J_{\nu-1}(\eta). \qquad \text{(A.2)}$$

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

$$J_\nu(\eta) = \Gamma(\nu+1) \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\exp(k\eta)}{k^{\nu+1}}. \qquad \text{(A.3)}$$

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

$$J_\nu(\eta) = \frac{\eta^{\nu+1}}{\nu+1}\left(1 + \sum_{k=1}^{\infty}\left(1-2^{1-2k}\right)\frac{2\Gamma(\nu+2)\zeta(2k)}{\Gamma(\nu+2-2k)}\frac{1}{\eta^{2k}}\right) = \frac{\eta^{\nu+1}}{\nu+1}\left(1 + \frac{\pi^2}{6}(\nu+1)\nu\frac{1}{\eta^2} + \frac{7\pi^4}{760}(\nu+1)\nu(\nu-1)(\nu-2)\frac{1}{\eta^4} + \dots\right), \qquad \text{(A.4)}$$

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 η_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 (6) for the entropy per particle. The properties of η_q as a function of the total nucleon density ρ, temperature T, and asymmetry parameter X (or x_q, the fraction of nucleon species q) are determined by the condition

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

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. (16) and (20). The effective mass is density-dependent and usually normalized to a certain value of density. One has 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

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

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

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

$$\left(\frac{\partial\eta_q}{\partial T}\right)_{\rho,X} = -\frac{3}{T}\frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)}, \qquad \text{(B.3)}$$

and also, the relation between them,

$$\left(\frac{\partial\eta_q}{\partial\rho}\right)_{T,X} = -\frac{2T}{3\rho}\left(1 + \frac{3\rho}{2f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\left(\frac{\partial\eta_q}{\partial T}\right)_{\rho,X}. \qquad \text{(B.4)}$$

The above relation (B.4) results from the fact that after inverting Eq. (B.1), η_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's consider the function $\psi = \psi(\eta_q)$, which appears in the expression for the specific heat (8), namely,

$$\psi(\eta_q) \equiv \frac{5}{2}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)} - \frac{9}{2}\frac{J_{1/2}(\eta_q)}{J_{-1/2}(\eta_q)} =$$

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

It is readily apparent from Eq. (B.1) that the behavior of ψ 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 ρ, X) and high-temperature limit $\delta_q \gg 1$ ($T^{-1} \to 0$ at fixed ρ, X). Using Eq. (B.1) together with series (A.4) one derives ψ at a low-temperature limit,

$$\psi(\eta_q) = \left(\frac{\pi}{3\rho_q}\right)^{2/3}\frac{m_q^* T}{\hbar^2} + O\left(\frac{1}{\rho_q^2 \lambda\!\!\!^{-}{}_q^6}\right) = \left(\frac{\pi}{3}\right)^{2/3}\delta_q^2 + O\left(\delta_q^6\right). \qquad \text{(B.6)}$$

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

$$\psi(\eta_q) = \frac{3}{2} - \frac{3}{16}\rho_q\left(\frac{\pi\hbar^2}{m_q^* T}\right)^{3/2} +$$

$$+ O\left(\rho_q^2 \lambda\!\!\!^{-}{}_q^6\right) = \frac{3}{2} - \frac{3\pi^{3/2}}{16}\delta_q^{-3} + O\left(\delta_q^{-6}\right). \qquad \text{(B.7)}$$

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

$$-\frac{\rho^2}{T}\left(\frac{\partial\psi(\eta_q)}{\partial\rho}\right)_{T,X} = \frac{2\rho}{3}\left(1 + \frac{3\rho}{2f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\left(\frac{\partial\psi(\eta_q)}{\partial T}\right)_{\rho,X}, \qquad \text{(B.8)}$$

based on the relation (B.4). The second integration is confined to integrating ψ over T and can be easily carried out by using the very right-hand side equality of Eq. (B.5).

The correction ϕ_{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 the density of the integrand $\left(1+\frac{3\rho}{2f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\left(\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)}-1\right)\frac{d\rho}{\rho}$ as it follows from Eqs. (12) and (14). Taking Eq. (B.2) at fixed temperature ($dT=0$) and using the definition for the derivative of Fermi integral (A.2) one obtains

$$\left(1+\frac{3\rho}{2f_q}\left(\frac{\partial f_q}{\partial\rho}\right)_X\right)\left(\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)}-1\right)\frac{d\rho}{\rho}=$$

$$=\frac{1}{2}\frac{J_{-1/2}(\eta_q)}{J_{1/2}(\eta_q)}\left(\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)}-1\right)d\eta_q=$$

$$=d\left(\eta_q-\frac{2}{3}\frac{J_{3/2}(\eta_q)}{J_{1/2}(\eta_q)}-\ln\left(J_{1/2}(\eta_q)\right)\right). \quad \text{(B.9)}$$

Appendix C. Chemical potentials

The neutron, μ_n, and proton, μ_p, chemical potentials are defined as derivatives of the 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, μ_0, and isovector, μ_1, chemical potentials as

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

$$\mu_1=\left(\frac{\partial F}{\partial(N-Z)}\right)_{V,T,A}=\frac{\mu_n-\mu_p}{2}. \quad \text{(C.1)}$$

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

$$\mu_0(\rho,T,X)=\left(\frac{\partial\rho\phi}{\partial\rho}\right)_{T,X}-X\left(\frac{\partial\phi}{\partial X}\right)_{\rho,T},$$

$$\mu_1(\rho,T,X)=\left(\frac{\partial\phi}{\partial X}\right)_{\rho,T}. \quad \text{(C.2)}$$

Charge symmetry of nuclear forces governs the properties of μ_τ ($\tau=0$ 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 $(\partial\mu_0/\partial X)_{P,T}+$ $+X(\partial\mu_1/\partial X)_{P,T}=0$, the condition of chemical stability, Eq. (21), is rewritten as $(-1)^\tau(\partial\mu_\tau/\partial X)_{P,T}\le 0$ 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]

$$\left(\frac{\partial\mu_\tau}{\partial X}\right)_{P,T}=\left(\frac{\partial\mu_\tau}{\partial X}\right)_{\rho,T}-\left(\frac{\partial\mu_\tau}{\partial\rho}\right)_{X,T}\left(\frac{\partial P}{\partial X}\right)_{\rho,T}\left(\frac{\partial P}{\partial\rho}\right)_{X,T}^{-1}. \quad \text{(C.3)}$$

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

In Secs. 5, 6 various properties of nuclear matter are calculated using Skyrme EDF and simple model of van der Waals with correction for Fermi statistics. For the last case, the free energy per particle is defined as $\phi=\phi_{\text{vdW}}+\phi_{\text{stat}}$, see Eqs. (4) and (15). This suggests the following expressions for μ_0 and μ_1 determined from (C.2) taking into consideration the effective mass (20):

$$\mu_0=-2a_0\rho+T\frac{\eta_n+\eta_p}{2}+\frac{2bT}{3\pi^2}\left(\frac{2mT}{\hbar^2}\right)^{3/2}\frac{J_{3/2}(\eta_n)+J_{3/2}(\eta_p)}{2},\ \mu_1=-2a_1\rho X+T\frac{\eta_n-\eta_p}{2}. \quad \text{(C.4)}$$

REFERENCES

1. J.D. van der Waals. *Over de Continuiteit van den Gas- en Vloeistoftoestand* (Leiden: Sijthoff, 1873); J.S. Rowlinson. *J.D. Van Der Waals: On the Continuity of the Gaseous and Liquid States* (Amsterdam: Elsevier, 1988).
2. J.E. Mayer, M.G. Mayer. *Statistical Mechanics* (New York: Wiley, 1940).

3. J. Frenkel. *Kinetic theory of liquids* (Oxford: Clarendon Press, 1946).
4. L.D. Landau, E.M. Lifshitz. *Statistical Physics.* Part 1 (Oxford: Pergamon Press, 1980) 449 p.
5. J. Pochodzalla et al. Probing the nuclear liquid-gas phase transition. Phys. Rev. Lett. 75 (1995) 1040.
6. J.B. Natowitz et al. Limiting temperatures and the equation of state of nuclear matter. Phys. Rev. Lett. 89 (2002) 212701.
7. J.B. Natowitz et al. Caloric curves and critical behavior in nuclei. Phys. Rev. C 65 (2002) 034618.
8. V.A. Karnaukhov et al. Critical temperature for the nuclear liquid-gas phase transition. Phys. Rev C 67 (2003) 011601(R).
9. H. Jaqaman, A.Z. Mekjian, L. Zamick. Nuclear condensation. Phys. Rev. C 27 (1983) 2782.
10. S.N. Fedotkin, A.G. Magner, M.I. Gorenstein. Effects of quantum statistics near the critical point of nuclear matter. Phys. Rev. C 100 (2019) 054334.
11. H.A. Bethe. Theory of nuclear matter. Ann. Rev. Nucl. Sci. 21 (1971) 93.
12. J.W. Negele, D. Vautherin. Density-Matrix Expansion for an Effective Nuclear Hamiltonian. Phys. Rev. C 5 (1972) 1472.
13. T.H.R. Skyrme. CVII. The nuclear surface. Phil. Mag. 1 (1956) 1043.
14. T.H.R. Skyrme. The effective nuclear potential. Nucl. Phys. 9 (1959) 615.
15. D. Vautherin, D.M. Brink. Hartree-Fock Calculations with Skyrme's Interaction. I. Spherical Nuclei. Phys. Rev. C 5 (1972) 626.
16. V. Vovchenko, D.V. Anchishkin, M.I. Gorenstein. Van der Waals equation of state with Fermi statistics for nuclear matter. Phys. Rev. C 91 (2015) 064314.
17. R.V. Poberezhnyuk et al. Noncongruent phase transitions in strongly interacting matter within the quantum van der Waals model. Phys. Rev. C 99 (2019) 024907.
18. J.S. Rowlinson. The Properties of Real Gases. In: *Thermodynamics of Gases* (Berlin: Springer-Verlag, 1958) p. 1.
19. S.I. Sandler, H. Orbey. Mixing and Combining Rules. In: *Equations of State for Fluids and Fluid Mixtures.* Part I. (Amsterdam: Elsevier, 2000) p. 321.
20. W.A. Küpper, G. Wegmann, E.R. Hilf. Thermostatic properties of symmetric nuclear matter. Ann. Phys. 88 (1974) 474.
21. M. Brack, C. Guet, H.-B. Håkansson. Selfconsistent semiclassical description of average nuclear properties – a link between microscopic and macroscopic models. Phys. Rep. 123 (1985) 275.
22. V.M. Kolomietz, S. Shlomo. Static properties of nuclei. In: *Mean Field Theory* (Singapore: World Scientific, 2020) p. 130.
23. F. Perey, B. Buck. A non-local potential model for the scattering of neutrons by nuclei. Nucl. Phys. 32 (1962) 353.
24. G.E. Brown, J.H. Gunn, P. Gould. Effective mass in nuclei. Nucl. Phys. 46 (1963) 598.
25. S. Shlomo, V.M. Kolomietz. Hot nuclei. Rep. Prog. Phys. 68 (2005) 1.
26. V.M. Kolomietz, A.I. Sanzhur, S. Shlomo. Self-consistent mean-field approach to the statistical level density in spherical nuclei. Phys. Rev. C 97 (2018) 064302.
27. C. Mondal et al. Interdependence of different symmetry energy elements. Phys. Rev. C 96 (2017) 021302(R).
28. Tuhin Malik et al. Nucleon effective mass and its isovector splitting. Phys. Rev. C 98 (2018) 064316.
29. J.S. Rowlinson, F.L. Swinton. The thermodynamics of liquid mixtures. In: *Liquids and Liquid Mixtures* (London: Butterworth Scientific, 1982) p. 86.
30. R.V. Poberezhnyuk et al. Quantum van der Waals and Walecka models of nuclear matter. Int. J. Mod. Phys. E 26 (2017) 1750061.
31. D.H. Youngblood, H.L. Clark, Y.-W. Lui. Incompressibility of nuclear matter from the giant monopole resonance. Phys. Rev. Lett. 82 (1999) 691.
32. G. Bonasera, M.R. Anders, S. Shlomo. Giant resonances in ^{40,48}Ca, ^{68}Ni, ^{90}Zr, ^{116}Sn, ^{144}Sm, and ^{208}Pb. Phys. Rev. C 98 (2018) 054316.
33. H. Müller, B.D. Serot. Phase transitions in warm, asymmetric nuclear matter. Phys. Rev. C 52 (1995) 2072.
34. M. Dutra et al. Skyrme interaction and nuclear matter constraints. Phys. Rev. C 85 (2012) 035201.
35. B.K. Agrawal, S. Shlomo, V. Kim Au. Determination of the parameters of a Skyrme type effective interaction using the simulated annealing approach. Phys. Rev. C 72 (2005) 014310.
36. L.G. Cao et al. From Brueckner approach to Skyrme-type energy density functional. Phys. Rev. C 73 (2006) 014313.
37. A.W. Steiner et al. Isospin asymmetry in nuclei and neutron stars. Phys. Rep. 411 (2005) 325.
38. M. Rashdan. A Skyrme parametrization based on nuclear matter BHF calculations. Mod. Phys. Lett. A 15 (2000) 1287.
39. P.A.M. Guichon et al. Physical origin of density dependent forces of Skyrme type within the quark meson coupling model. Nucl. Phys. A 772 (2006) 1.
40. M.A. Anisimov et al. Crossover to global critical phenomena in fluids. Physica A 188 (1992) 487.
41. F.J. Fernández Velicia. New functional expansions for the Fermi-Dirac functions. Phys. Rev. A 30 (1984) 1194.
42. E.C. Stoner. XXIV. The thermodynamic functions for a Fermi-Dirac gas. Phil. Mag. 28 (1939) 257.
43. A. Sommerfeld. Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik. Z. Phys. 47 (1928) 1.

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РІВНЯННЯ СТАНУ ВАН ДЕР ВААЛЬСА
ДЛЯ АСИМЕТРИЧНОЇ ЯДЕРНОЇ МАТЕРІЇ

Розглянуто застосування рівняння ван дер Ваальса до асиметричної ядерної матерії в області критичного стану. Виходячи з виразу ентропії у наближенні Томаса - Фермі, який забезпечує виконання теореми Нернста, отримано поправки до тиску та вільної енергії ван дер Ваальса, що виникають за рахунок статистики Фермі. Отримані поправки враховують ефективну масу нуклона та нейтрон-протонну асиметрію. Параметри рівняння стану ван дер Ваальса одержані виходячи з експериментального значення критичної температури симетричної ядерної матерії та порівняння моделі ван дер Ваальса з теорією функціоналу густини енергії Скірма. Розглядається критична лінія в просторі тиску, температури і нейтрон-протонного складу. Визначається коефіцієнт нестисливості вздовж критичної лінії в залежності від складу ядерної матерії. Обговорюється стрибок питомої теплоємності при перетині критичної лінії.

Ключові слова: асиметрична ядерна матерія, рівняння стану, критична лінія.

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