Particle number fluctuations for the van der Waals equation of state

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Abstract
The van der Waals (VDW) equation of state describes a thermal equilibrium in a system of particles, where both repulsive and attractive interactions between them are included. This equation predicts the existence of the first order liquid–gas phase transition and the critical point. The standard form of the VDW equation is given by the pressure function in a canonical ensemble (CE) with a fixed number of particles. In this paper the VDW equation is derived within the grand canonical ensemble (GCE) formulation. We argue that this procedure can be useful for new physical applications, in particular, the fluctuations of the number of particles, which are absent in the CE, can be studied in the GCE. For the VDW equation of state in the GCE the particle number fluctuations are calculated for the whole phase diagram, both outside and inside the liquid–gas mixed phase region. It is shown that the scaled variance of these fluctuations remains finite within the mixed phase and goes to infinity at the critical point. The GCE formulation of the VDW equation of state can also be an important step for its application in the statistical description of hadronic systems, where numbers of different particle species are usually not conserved.

Keywords: particle number fluctuations, phase transitions, van der Waals equation

(Some figures may appear in colour only in the online journal)
1. Introduction

The statistical approach appears to be quite successful in the description of hadron multiplicities in high energy collisions. It leads to surprisingly good agreement between the results for the hadron resonance gas and the experimental data (see, e.g., [1–6]). The excluded volume (EV) model introduces the effects of hadron repulsion at short distances. The EV procedure substitutes a system volume $V$ by the available volume $V_{av} = V - bN$, where $b$ is the particle proper volume parameter and $N$ is the number of particles. This substitution can be performed easily in the canonical ensemble (CE) formulation, where the (conserved) particle number $N$ is an independent variable. The ideal gas pressure $p_{id}$ is then transformed to the EV pressure,

$$ p_{id}(V, T, N) = \frac{NT}{V} \rightarrow p_{ev}(V, N, T) = \frac{NT}{V - bN}, \quad (1) $$

which is the function of volume $V$, temperature $T$, and number of particles $N$. It has been shown [7, 8] that the substitution of $V$ by $V_{av}$ leads to a shift of the chemical potential $\mu$ and to a transcendental equation for the pressure function in the grand CE (GCE):

$$ p_{ev}(T, \mu) = p_{id}(T, \mu - p_{ev}(V, T, \mu)), \quad (2) $$

where $p_{id}(T, \mu)$ is the pressure of the ideal gas calculated in the GCE. The EV model (2) can be equivalently formulated in terms of the mean-field (see [9–11]). This makes it possible to incorporate other hadron interactions within the unified mean-field approach. The EV hadron equation of state is used for fitting the hadron multiplicities (see, e.g., [12, 13]) and for the hydrodynamic model calculations of nucleus–nucleus collisions (see, e.g., [14–16]).

In this paper the equation of state with both repulsive ($b > 0$) and attractive ($a > 0$) terms (see, e.g., [17, 18]),

$$ p(V, T, N) = \frac{NT}{V - bN} - a\frac{N^2}{V^2}, \quad (3) $$

is considered. The equation of state (3) was suggested by van der Waals (VDW) in 1873 and for his work he received the Nobel Prize in Physics in 1910. In this paper the VDW equation will be derived within the the GCE. The GCE formulation will then be used to calculate the particle number fluctuations in the VDW gas.

Normally, the GCE is the easiest one from the technical point of view. Thus, it is used more frequently and a typical problem in statistical mechanics is to transform GCE results to CE ones. However, the pressure functions of the EV (1) and VDW equation (3) have their simplest and most transparent forms only in the CE. A comparison of a simple analytical form (1) with a transcendental equation (2) elucidates this point. On the other hand, the CE pressure does not provide a complete thermodynamical description of the system. This is because the parameters $V$, $T$, and $N$ are not the natural variables for the pressure function.

Does one really need the GCE formulation for the statistical description of hadrons? There are at least three reasons for a positive answer to this question.

First, the CE pressure, e.g., (1) or (3), does not give any information concerning the particle mass $m$ and degeneracy factor $d$. However, the average energy of the system depends on the value of $m$, e.g., the thermal part of the energy per particle equals $m + 3T/2$ at $m \gg T$ and $3T$ at $m \ll T$.

Second, the number of hadrons of a given type is usually not conserved. For example, the number of pions cannot be considered as an independent variable and is a function of volume and temperature. The GCE formulation of the VDW equation can be therefore an important step in inserting the repulsive and attractive VDW interactions into the multi-component hadron gas.
Third, (1) and (3) of the CE give no answer about the particle number fluctuations. Formally, the number of particles does not fluctuate in the CE: the total number of particles \( N_0 \) is constant in the full volume \( V_0 \). However, the number of particles \( N \) starts to fluctuate if one considers a sub-system with \( V < V_0 \). If \( V \ll V_0 \) the \( N \)-fluctuations should follow the GCE results. For the EV model the particle number fluctuations were calculated in [19].

This paper is organized as follows. In section 2 we discuss how to transform the CE pressure to the GCE. This procedure is illustrated by a derivation of the EV model for \( \rho_{ev}(T, \mu) \) in the GCE. In section 3 the VDW equation of state (3) is transformed to the transcendental equation for particle number density \( n(T, \mu) \) in the GCE. The particle number fluctuations and their behavior in the vicinity of the critical point are then analyzed in section 4. A summary in section 5 completes this paper.

2. From the CE to the GCE

In the GCE the macroscopic states of a thermal system are defined in terms of the grand potential \( \Omega \) which is a function of three physical variables—volume \( V \), temperature \( T \), and chemical potential \( \mu \). In a spatially homogeneous system the grand potential \( \Omega \) is straightforwardly connected to the system pressure [17]

\[
\Omega(V, T, \mu) = -p(T, \mu)V.
\]

Therefore, pressure \( p \) as a function of its natural variables, temperature \( T \) and chemical potential \( \mu \), gives a complete description of the equation of state. One calculates the entropy density \( s \), (conserved) number density \( n \), and energy density \( \varepsilon \) as

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

\[
\varepsilon(T, \mu) = Ts + \mu n - p.
\]

The thermodynamic potential in the CE is the free energy \( F(V, T, N) \) (or Helmholtz potential). The function \( F \) depends on its natural variables, volume \( V \), temperature \( T \), and number of particles \( N \), and it gives a complete thermodynamic description of the system’s properties. Entropy \( S \), pressure \( p \), chemical potential \( \mu \), and total energy \( E \) are calculated in the CE as [17]

\[
S(V, T, N) = -\left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad p(V, T, N) = -\left( \frac{\partial F}{\partial V} \right)_{T,N},
\]

\[
\mu(V, T, N) = \left( \frac{\partial F}{\partial N} \right)_{T,V}, \quad
\]

and

\[
E(V, T, N) = F + TS.
\]

If one knows \( p = p(V, T, N) \) in the CE it is not yet possible to find \( S(V, T, N) \), \( \mu(V, T, N) \), and \( E(V, T, N) \) in unique way. For a complete thermodynamic description in the CE one needs to reconstruct free energy \( F \), thus, the following equation should be solved:
The solution of (8) can be presented as
\[
F(V, T, N) = F(V_0, T, N) - \int_{V_0}^{V} dV' p(V', T, N).
\] (9)

To find \( F(V, T, N) \) one needs to know not only \( p(V, T, N) \) but, additionally, the free energy \( F(V_0, T, N) \) as the function of \( T \) and \( N \) at some fixed value of \( V = V_0 \). We assume that for fixed \( T \) the role of particle interactions becomes negligible at very small density \( N/V_0 \rightarrow 0 \). Thus, the ideal gas expression, \( F(V_0, T, N) \cong F_{id}(V_0, T, N) \), becomes valid at \( V_0 \rightarrow \infty \).

For a relativistic ideal Boltzmann gas the free energy reads [17]
\[
F_{id}(V, T, N) = -NT \left[ 1 + \ln \frac{V \phi(T; d, m)}{N} \right],
\] (10)

where
\[
\phi(T; d, m) = \frac{d}{2\pi^2} \int_{0}^{\infty} k^2 dk \exp\left( -\sqrt{k^2 + m^2/T} \right) = \frac{d m^2 T}{2\pi^2} K_2\left( \frac{m}{T} \right).
\] (11)

In (10) and (11), \( d \) is the degeneracy factor, \( m \) is the particle mass, and the quantity \( \phi \) has the physical meaning of the GCE particle number density at zero chemical potential.

Let us start with an example of the EV volume equation (1) in the CE. The particle proper volume parameter in (1) equals \( b = 4 \cdot (4\pi^3/3) \) with \( r \) being the corresponding hard sphere radius of the particle. This equation describes the repulsion between particles and can be rigorously obtained (in particular, a factor of 4 in the expression for \( b \)) for a gas of the hard balls at low density (see, e.g., [18]).

From (9) it follows that
\[
F(V, T, N) = -NT \left[ 1 + \ln \frac{V_0 \phi(T; d, m)}{N} \right] + \int_{V_0}^{V} dV' \frac{NT}{V' - bN},
\] (12)

where we have used that \((V_0 - bN)/V_0 \rightarrow 1 \) at \( V_0 \rightarrow \infty \). For the free energy (12) the chemical potential can be calculated as
\[
\mu = \left( \frac{\partial F}{\partial N} \right)_{V, T} = -T \ln \frac{(V - bN)\phi(T; d, m)}{N} + b \frac{NT}{V - bN}.
\] (13)

For particle number density \( n = N/V \) one finds from (13) for the ideal gas, i.e., at \( b = 0 \):
\[
\frac{N}{V} = n_{id}(T, \mu) = \exp \left( \frac{\mu}{T} \right) \phi(T; d, m).
\] (14)
At \(b > 0\) one can easily find from (13):

\[
\frac{N}{V} \equiv n_{ev}(T, \mu) = \frac{n_{id}(T, \mu^*)}{1 + b n_{id}(T, \mu^*)}, \quad \mu^* = \mu - b \frac{n_{ev}(T, \mu) T}{1 - b n_{ev}(T, \mu)},
\]

or equivalently,

\[
p_{ev}(T, \mu) = p_{id}(T, \mu^*), \quad \mu^* = \mu - b \frac{n_{ev}(T, \mu) T}{1 - b n_{ev}(T, \mu)} = \mu - b p_{ev}(T, \mu).
\]

Therefore, to solve the EV problem in the case of the Boltzmann statistics one has to obtain the solution of the transcendental equation (15) with respect to particle density \(n_{ev}(T, \mu)\) or of the transcendental equation (16) with respect to pressure \(p_{ev}(T, \mu)\) for every point in the \((\mu, T)\)-plane, i.e., in the GCE. These equations coincide with those suggested in [9–11] and in [7, 8], respectively.

### 3. VDW equation of state in the GCE

#### 3.1. GCE formulation

The VDW equation for the system pressure is defined in the CE in the form of (3). Using (9) one obtains

\[
F(V, T, N) = F_{id}(V_0, T, N) + \int_0^{V_0} dV \left[ \frac{NT}{V - bN} - a \frac{N^2}{V^2} \right]
\]

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

The chemical potential then reads

\[
\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} = -T \ln \left( \frac{(V - bN)\phi(T; d, m)}{N} \right) + b \frac{NT}{V - bN} - 2a \frac{N}{V},
\]

and from (18) one obtains

\[
\frac{N}{V} \equiv n(T, \mu) = \frac{n_{id}(T, \mu^*)}{1 + b n_{id}(T, \mu^*)},
\]

\[
\mu^* = \mu - b \frac{n T}{1 - b n} + 2a n.
\]

The function \(n(T, \mu)\), which is the solution of transcendental equation (19), is reduced to \(n_{ev}(T, \mu)\) (15), if \(a = 0\), and to \(n_{id}(T, \mu)\) (14), if \(a = b = 0\). At fixed \(T\) and \(\mu\), the presence of the parameter \(b > 0\), which describes the repulsion between particles, leads to a suppression of particle number density \(n(T, \mu)\), while attractive interactions described by \(a > 0\) lead to its enhancement.

The energy density of the VDW gas can be calculated within the GCE from the pressure function, \(p(T, \mu)\),
\( \varepsilon(T, \mu) = T \left( \frac{\partial p}{\partial T} \right)_T + \mu \left( \frac{\partial p}{\partial \mu} \right)_\mu - p = \frac{\varepsilon_{id}(T, \mu^*)}{1 + b n_{id}(T, \mu^*)} - a n^2 \)

\[ \varepsilon_{id}(T; m) = \left[ \tau_{id}(T; m) - a n \right] n, \quad (20) \]

where \( \mu^* \) is defined in (19) and

\[
\tau_{id}(T; m) = \frac{\int_{0}^{\infty} k^2dk \sqrt{m^2 + k^2} \exp\left(-\sqrt{m^2 + k^2}/T\right)}{\int_{0}^{\infty} k^2dk \exp\left(-\sqrt{m^2 + k^2}/T\right)} = 3T + m \frac{K_1(m/T)}{K_2(m/T)} \quad (21)
\]

is the average energy per particle in the ideal gas. A comparison of the rhs of (20) with the corresponding ideal gas expression, \( \varepsilon_{id} = \tau_{id}(T; m)n_{id} \), demonstrates the role of the \( a \) and \( b \) parameters for the system energy density. Both the \( a \) and \( b \) parameters influence the particle number density and transform \( n_{id} \) into \( n \). \( a > 0 \) leads to an enhancement of particle number density and \( b > 0 \) to its suppression. Parameter \( b \) does not, however, contribute to the average energy per particle, whereas the mean field \(-a n\) created due to parameter \( a \) is added to the average energy per particle and changes it from \( \varepsilon_{id} \) to \( \varepsilon = \varepsilon_{id} - a n \).

It is also instructive to consider another derivation of (19) which is based on the procedure used in [20]. Introducing particle number density, \( n = N/V \), the VDW pressure function (3) can be written as

\[ p(T, n) = \frac{n T}{1 - b n} - a n^2. \quad (22) \]

For the particle number density in the GCE the following differential equation can be obtained

\[
n(T, \mu) = \left( \frac{\partial p(T, \mu)}{\partial \mu} \right)_T = \left( \frac{\partial p(T, n)}{\partial n} \right)_T \left( \frac{\partial n(T, \mu)}{\partial \mu} \right)_T = \left[ \frac{T}{(1 - b n)^2} - 2a n \right] \left( \frac{\partial n(T, \mu)}{\partial \mu} \right)_T. \quad (23)
\]

A general solution of (23) can be rewritten as

\[ \mu = \int dn \left[ \frac{T}{n(1 - bn)^2} - 2a \right] = T \ln \left[ \frac{n}{\phi(T; d, m)(1 - bn)} \right] + \frac{bT n}{1 - b n} - 2a n. \quad (24) \]

The temperature dependent integration constant in the solution (24) is defined in the form which guarantees the ideal gas solution (14) at \( b = a = 0 \). One can easily check that functions \( n(T, \mu) \) defined by (24) and (19) are identical.

3.2. Phase diagram for the VDW gas

The VDW equation of state contains a first order liquid–gas phase transition and has a critical point. The thermodynamic quantities at the critical point are equal to [18]:
The VDW equation (3) can then be rewritten in the following dimensionless (reduced) form:

$$T_c = \frac{8a}{27b}, \quad n_c = \frac{1}{3b}, \quad \rho_c = \frac{a}{27b^2}. \tag{25}$$

The VDW equation (3) can then be rewritten in the following dimensionless (reduced) form:

$$\tilde{p} = \frac{8 \tilde{T} \tilde{n}}{3 - \tilde{n}} - 3 \tilde{n}^2, \tag{26}$$

where $\tilde{n} = n/n_c$, $\tilde{p} = p/\rho_c$, and $\tilde{T} = T/T_c$. In the dimensionless presentation (26) the VDW equation has a universal form independent of the values of $a$ and $b$, and the critical point (25) is transformed to $\tilde{T_c} = \tilde{n_c} = \tilde{\rho_c} = 1$.

The dimensionless VDW isotherms are presented in figure 1(a) as functions of $\tilde{v} \equiv \tilde{n}^{-1}$. To describe the phase coexistence region below the critical temperature the VDW isotherms should be corrected by the well-known Maxwell construction of equal areas. These corrected parts of the VDW isotherms are shown by the solid horizontal lines. Figure 1(b) depicts the liquid–gas coexistence region on the $(\tilde{n}, \tilde{T})$-plane. The pure gaseous phase exists at all $\tilde{T} < 1$. However, it can be barely seen at $\tilde{T} \ll 1$ in figure 1(b). This is because of the very small admissible values of $\tilde{n}$ inside the pure gaseous phase at $\tilde{T} \to 0$, e.g., the largest value of the particle number density in the gaseous phase at $\tilde{T} = 0.25$ is $\tilde{n} \approx 5 \cdot 10^{-5}$. At any value of $\tilde{T} < 1$, the particle number density in the mixed phase is given by

$$n = \xi n_g + (1 - \xi) n_l, \tag{27}$$

where $\xi$ and $1 - \xi$ are the volume fractions of the gaseous and liquid components, respectively. The values of $n_g$ and $n_l$ in (27) are the particle densities of, respectively, the gaseous and liquid phases at the corresponding boundaries with the mixed phase. For example, at $\tilde{T} = 0.25$ one finds $\tilde{n}_g \approx 5 \cdot 10^{-5}$ and $\tilde{n}_l \approx 2.75$. For $\xi = 0.95$ (27) then gives $\tilde{n} \approx 0.95 \cdot 0.5 \cdot 10^{-5} + 0.05 \cdot 2.75 \approx 0.14$. Therefore, at $\tilde{n} = 0.14$ and $\tilde{T} = 0.25$ the gaseous component occupies 95% of the total volume of the mixed state but gives a negligible contribution to the total number of particles. Note also that $\tilde{n} = 3$ is an upper bound for the dimensionless particle density.

Let us consider the Maxwell rule in more detail. At each $\tilde{T} < 1$ VDW loops appear in the isotherm $\tilde{p}(\tilde{v})$. They are shown by the dashed lines in figure 1(a). Each loop consists of a
metastable part, where $\partial \bar{\rho} / \partial \bar{v} < 0$, and an unstable part, where $\partial \bar{\rho} / \partial \bar{v} > 0$. They are shown in figure 1(a) by the dashed-dotted and dotted lines, respectively. According to the Maxwell rule, the loop between values of $\bar{v}_1$ and $\bar{v}_2$ is substituted by the constant value $\bar{\rho}_0$ (the solid horizontal line in figure 1(a)), and the following condition should be fulfilled:

$$\int_{\bar{v}_1}^{\bar{v}_2} d\bar{v} \bar{\rho} = \bar{\rho}_0 (\bar{v}_2 - \bar{v}_1).$$  \hspace{1cm} (28)

It can be proven that the GCE formulation forbids the VDW loops and leads automatically to the Maxwell construction. Let us assume that the system can be divided into two parts—gas and liquid—with

$$N_g + N_l = N, \quad V_g + V_l = V, \quad \text{and} \quad \frac{N_g}{V_g} \neq \frac{N_l}{V_l}. \hspace{1cm} (29)$$

The free energy of the system can be then presented as

$$F(V, T, N) = F(V_g, T, N_g) + F(V_l, T, N_l),$$  \hspace{1cm} (30)

where the surface free energy is neglected in the thermodynamic limit $V \to \infty$. An equilibrium state corresponds to a minimum of the free energy. This leads to

$$\left( \frac{\partial F}{\partial V_g} \right)_{T, N_l} = 0, \quad \left( \frac{\partial F}{\partial N_g} \right)_{T, V_l} = 0.$$  \hspace{1cm} (31)

The relations in (31) are equivalent, respectively, to

$$p(T, V_g, N_g) = p(T, V_l, N_l), \quad \mu(T, V_g, N_g) = \mu(T, V_l, N_l).$$  \hspace{1cm} (32)

The first condition in (32) means that the VDW loop is transformed to the mixed phase region with equal pressures. The second condition in (32) leads in a unique way to the Maxwell rule of equal areas. The equilibrium conditions of phase coexistence are then fulfilled: both phases have the same temperature, pressure, and chemical potential in the coexistence region. These conditions are known as the Gibbs rules for a first order phase transition [18].

4. Particle number fluctuations in the VDW gas

4.1. Particle number fluctuations in the pure phases

The variance of the total particle number in the GCE can be calculated as

$$\text{Var}[N] \equiv \langle N^2 \rangle - \langle N \rangle^2 = T \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = T V \left( \frac{\partial n}{\partial \mu} \right)_T,$$  \hspace{1cm} (33)

where the symbol $\langle \ldots \rangle$ denotes the GCE averaging and $n(T, \mu)$ is the particle number density in the GCE. The scaled variance for the particle number fluctuations is then

$$\omega^2[N] \equiv \frac{\text{Var}[N]}{\langle N \rangle} = T n \left( \frac{\partial n}{\partial \mu} \right)_T.$$  \hspace{1cm} (34)
It will be convenient to rewrite equation (19) as

\[ n = (1 - bn) \, n_{id}(T, \mu) \exp\left(-\frac{bn}{1 - bn}\right) \exp\left(\frac{2an}{T}\right). \]  

(35)

Taking the derivative of equation (35) with respect to \( \mu \) one obtains

\[ \frac{dn}{d\mu} = n \left[ \frac{1}{(1 - bn)^2} - \frac{2an}{T} \right]^{-1}. \]

(36)

Therefore, the scaled variance (34) equals

\[ \omega[N] = \left[ \frac{1}{(1 - bn)^2} - \frac{2an}{T} \right]^{-1}. \]

(37)

It is clearly seen from (37) that in the VDW gas the repulsive interactions suppress the particle number fluctuations, whereas the attractive interactions lead to their enhancement. Note that for \( a = 0 \) the value of \( \omega[N] \) (37) coincides with the result for the EV model obtained in [19].

The scaled variance (37) expressed in terms \( \tilde{n} \) and \( \tilde{T} \) equals to

\[ \omega[N] = \frac{1}{9} \left[ \frac{1}{(3 - \tilde{n})^2} - \frac{\tilde{n}}{4 \tilde{T}} \right]^{-1}. \]

(38)

In figure 2 the lines of the constant values of \( \omega[N] \) are shown on the \((\tilde{n}, \tilde{T})\) phase diagram outside the mixed phase region. At any fixed value of \( \tilde{T} \), the particle number fluctuations (38) approach those of the ideal gas, i.e. \( \omega[N] \approx 1 \), at \( \tilde{n} \to 0 \), and become small, \( \omega[N] \ll 1 \), at \( \tilde{n} \to 3 \). As it should be, the scaled variance (38) is always positive for all possible values of \( \tilde{n} \) and \( \tilde{T} \) outside the mixed phase region. At \( \tilde{T} \to 0 \) this is ensured by the simultaneous limiting behavior of \( \tilde{n} \to 0 \) in the pure gaseous phase and \( \tilde{n} \to 3 \) in the pure liquid phase.

At the critical point \((\tilde{T} = \tilde{n} = 1)\) the scaled variance of the particle number fluctuations diverges in the GCE. To study the behavior of \( \omega[N] \) in the vicinity of the critical point we introduce the quantities \( \tau = \tilde{T} - 1 \ll 1 \) and \( \rho = \tilde{n} - 1 \ll 1 \). Expanding (38) at small \( \tau \) and \( \rho \)
and keeping only the lowest orders of them one finds

$$\omega[N] \cong \frac{4}{9} \left[ \tau + \frac{3}{4} \rho^2 + \tau \rho \right]^{-1}. \quad (39)$$

In particular,

$$\omega[N] \cong \frac{4}{9} \tau^{-1} \quad \text{at} \quad \rho = 0, \quad \text{and} \quad \omega[N] \cong \frac{16}{27} \rho^{-2} \quad \text{at} \quad \tau = 0. \quad (40)$$

Note that the thermodynamic parameters $\tilde{T}$ and $\tilde{\rho}$ correspond to points outside the mixed phase region. Thus, in (40), parameter $\tau$ is positive, while $\rho$ can be both positive and negative.

As was mentioned above, the VDW equation of state permits the existence of metastable phases of super-heated liquid and super-cooled gas. These states are depicted by the dashed-dotted lines on the VDW isotherms in figure 1(a). In the metastable phases the system is assumed to be uniform and, therefore, one can use (38) to calculate the particle number fluctuations in these phases. In figure 3 the lines of the constant values of $\omega[N]$ are shown on the $(\tilde{\rho}, \tilde{T})$ phase diagram for both stable and metastable pure phases, while the unstable region is depicted by the gray area. It is seen that the scaled variance remains finite and diverges only at the boundary between the metastable and unstable regions. We recall that at this boundary $\partial \tilde{p} / \partial \tilde{n} = 0$, where $\tilde{p}$ is the dimensionless CE pressure (26). One can easily show using equations (26) and (38) that $\omega[N] \rightarrow \infty$ when $\partial \tilde{p} / \partial \tilde{n} = 0$. Note that the metastable regions of the equation of state can be reached within fast non-equilibrium processes, whereas the unstable region is physically forbidden. Note that the thermodynamic relations are not fulfilled in the unstable region, e.g., nonphysical behavior with $\omega[N] < 0$ is found in this region.

Figure 3. The lines of the constant values of the scaled variance $\omega[N]$ are shown on the $(\tilde{\rho}, \tilde{T})$ phase diagram for both stable and metastable pure phases. The boundary between the stable and metastable phases is depicted by the thick black line and the unstable region is depicted by the gray area.
4.2. Particle number fluctuations in the mixed phase

Let us consider a point \((n, T)\) inside the mixed phase. The volume \(V\) is then divided into the two parts, \(V_g = \xi V\) occupied by the gaseous phase with particle number density \(n_g\) and \(V_l = (1 - \xi) V\) occupied by the liquid phase with particle number density \(n_l\). The total number of particles \(N\) equals \(N_g + N_l\). The average value and scaled variance for the \(N\)-distribution are

\[
\langle N \rangle = \langle N_g \rangle + \langle N_l \rangle = V \left[ \xi n_g + (1 - \xi) n_l \right],
\]

\[
\omega[N] = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle N_g^2 \rangle - \langle N_g \rangle^2}{\langle N \rangle} + \frac{\langle N_l^2 \rangle - \langle N_l \rangle^2}{\langle N \rangle} + 2 \left[ \frac{\langle N_g N_l \rangle - \langle N_g \rangle \langle N_l \rangle}{\langle N \rangle} \right].
\]

In calculating the variations of the \(N_g\) and \(N_l\) distributions inside the the mixed phase, one should take into account the fluctuations of the corresponding volumes \(V_g = \xi V\) and \(V_l = (1 - \xi) V\). In fact, these are the fluctuations of the parameter \(\xi\). In the thermodynamic limit \(V \to \infty\), one finds:

\[
\frac{\langle N_g^2 \rangle - \langle N_g \rangle^2}{\langle N \rangle} = \frac{\langle N_g \rangle}{\langle N \rangle} \omega_\xi[N_g] + \frac{n_g^2}{n} V \left[ \langle \xi^2 \rangle - \langle \xi \rangle^2 \right],
\]

\[
\frac{\langle N_l^2 \rangle - \langle N_l \rangle^2}{\langle N \rangle} = \frac{\langle N_l \rangle}{\langle N \rangle} \omega_\xi[N_l] + \frac{n_l^2}{n} V \left[ \langle \xi^2 \rangle - \langle \xi \rangle^2 \right],
\]

\[
\frac{\langle N_g N_l \rangle - \langle N_g \rangle \langle N_l \rangle}{\langle N \rangle} = -2 \frac{n_g n_l}{n} V \left[ \langle \xi^3 \rangle - \langle \xi \rangle^3 \right].
\]

where \(\omega_\xi[N_g]\) and \(\omega_\xi[N_l]\) in (43) and (44) correspond to the fixed value of \(\xi\), and can be calculated using (33) and (34). One finds

\[
\omega[N] = \frac{\xi_0 n_g}{n} \left[ \frac{1}{(1 - bn_g)^2} - \frac{2an_g}{T} \right]^{-1} + \frac{(1 - \xi_0) n_l}{n} \left[ \frac{1}{(1 - bn_l)^2} - \frac{2an_l}{T} \right]^{-1} + \frac{(n_g - n_l)^2 V}{n} \left[ \langle \xi^3 \rangle - \langle \xi \rangle^3 \right].
\]

where the equilibrium value \(\langle \xi \rangle \equiv \xi_0\) is defined as

\[
\xi_0 = \frac{n_l}{n_1} - \frac{n}{n_1 - n_g}.
\]

To calculate the variance \(\langle \xi^2 \rangle - \langle \xi \rangle^2\) in (46) we can return to the CE formulation and use (30) rewriting it as the following

\[
F(V, T, N; \xi) = F(\xi V, T, N_g) + F[(1 - \xi) V, T, N_l].
\]

Note that in the limit \(V \to \infty\) assumed in our study the particle number densities \(n_g\) and \(n_l\) in the GCE are identical to their CE values as a consequence of thermodynamic equivalence.
The probability distribution \( W(\xi) \) is proportional to \( \exp[-F(V, T, N; \xi)/T] \). The function \( F \) is given by (48) and as a function of \( \xi \) it can be presented as a power series expansion over \( \xi - \xi_0 \) in the vicinity of the equilibrium value \( \xi_0 \). This gives the \( \xi \) normalized probability distribution \( C \) is a normalization factor) in the form

\[
W(\xi) = C \exp \left[ -\frac{1}{2T} \frac{\partial^2 F}{\partial \xi^2} |_{\xi = \xi_0} (\xi - \xi_0)^2 \right] = C \exp \left[ -\frac{(\xi - \xi_0)^2}{2\sigma^2} \right],
\]

where

\[
\sigma^2 = T \left( \frac{\partial^2 F}{\partial \xi^2} \right)^{-1} |_{\xi = \xi_0} = \frac{T}{V^2} \left[ \left( \frac{\partial \rho_g}{\partial V} \right) + \left( \frac{\partial \rho_f}{\partial V} \right) \right]^{-1}
\]

\[
= \frac{T}{V} \left( \frac{n_g T}{\xi_0 (1 - bn_g)} - \frac{2an_g^2}{\xi_0} + \frac{n_1 T}{(1 - \xi_0)(1 - bn_1)} - \frac{2an_1^2}{1 - \xi_0} \right)^{-1}. \tag{50}
\]

Using the \( \xi \)-distribution (49) one finds

\[
\langle \xi^2 \rangle - \langle \xi \rangle^2 = \sigma^2
\]

and, finally,

\[
\omega[N] = \frac{\xi_0 n_g}{n} \left[ \frac{1}{(1 - bn_g)^2} - \frac{2an_g}{T} \right]^{-1} + \frac{(1 - \xi_0) n_1}{n} \left[ \frac{1}{(1 - bn_1)^2} - \frac{2an_1}{T} \right]^{-1}
\]

\[
+ \frac{(n_g - n_1)^2}{n} \left[ \frac{n_g}{\xi_0 (1 - bn_g)^2} - \frac{2an_g}{\xi_0 T} + \frac{n_1}{(1 - \xi_0)(1 - bn_1)^2} - \frac{2an_1}{(1 - \xi_0)T} \right]^{-1}. \tag{52}
\]

Introducing dimensionless variables (26) one can rewrite (52) as

\[
\omega[N] = \frac{\xi_0 \bar{n}_g}{9\bar{\eta}} \left[ \frac{1}{(3 - \bar{n}_g)^2} - \frac{\bar{n}_g}{4\bar{T}} \right]^{-1} + \frac{(1 - \xi_0) \bar{n}_1}{9\bar{\eta}} \left[ \frac{1}{(3 - \bar{n}_1)^2} - \frac{\bar{n}_1}{4\bar{T}} \right]^{-1}
\]

\[
+ \frac{(\bar{n}_g - \bar{n}_1)^2}{9\bar{\eta}} \left[ \frac{\bar{n}_g}{\xi_0 (3 - \bar{n}_g)^2} - \frac{\bar{n}_g}{\xi_0 4\bar{T}} \right]
\]

\[
+ \frac{\bar{n}_1}{(1 - \xi_0)(3 - \bar{n}_1)^2} - \frac{\bar{n}_1}{(1 - \xi_0) 4\bar{T}} \right]^{-1}. \tag{53}
\]

In figure 4 the lines of the constant values of \( \omega[N] \) (53) are shown on the (\( \bar{\eta} \), \( \bar{T} \)) phase diagram inside the mixed phase. At small \( \bar{T} \), the particle number fluctuations inside the mixed phase are small, \( \omega[N] \ll 1 \), almost everywhere. This is because the main contribution to (53) comes from the liquid component of the mixed state and the corresponding fluctuations inside the liquid phase are always small at small \( \bar{T} \). However, even at \( \bar{T} \to 0 \), the scaled variance (53) remains close to the ideal gas value, \( \omega[N] \approx 1 \), in a small region near the boundary with
the gaseous phase. This region is not seen in figure 4 because of very small $\bar{\rho}$-values. Part of this region with $0.2 < \bar{T} < 0.4$ (both inside and outside of the mixed phase) is shown in figure 5.

To study the behavior of (53) in the vicinity of the critical point we introduce $0 < \rho_0 = 1 - \bar{n}_g \ll 1$, $0 < \rho_1 = \bar{n}_l - 1 \ll 1$, and $0 < t = 1 - \bar{T} \ll 1$. At $t \to 0$ one finds $\rho_0 = \rho_1 = 2 \sqrt{t}$ and

$$\omega[N] \approx \frac{16}{9} t^{-1}. \quad (54)$$
Finally, the scaled variance $\omega [N]$ is shown in figure 6 for all possible values of $\vec{n}$ and $\tilde{T}$, both inside and outside the mixed phase. It is interesting to compare (53) for the scaled variance calculated inside the mixed phase and (38) outside the mixed phase. These two equations give the same results at the phase boundary. At the boundary between the gaseous and mixed phase (i.e., $\xi_0 = 1$) both the second and third terms on the rhs of (53) become equal to zero, and the first term in (53) coincides with (38). Similarly, at the boundary between the liquid and mixed phase (i.e., $\xi_0 = 0$) both the first and third terms on the rhs of (53) become equal to zero, and the second term in (53) coincides with (38). It might seem from figure 6 that at small temperatures fluctuations have a discontinuity at the boundary between the liquid and mixed phase. This is, however, not the case: as mentioned above, when approaching the boundary from inside the mixed phase ($\xi_0 \to 0$), the third term in the rhs of (53) vanishes, but at small temperatures it vanishes rapidly and only in the very vicinity of the phase boundary. Consequently, this behavior is seen poorly on the scale used in figure 6.

5. Summary

The VDW pressure function (3) has a simple and familiar form in the CE. However, there are some reasons for its reformulation in the GCE. First of all, the CE pressure does not give a complete thermodynamic description of the system. In addition, the GCE has clear advantages if one tries to extend the VDW model to a multi-component hadron gas. The GCE formulation is also necessary to find the particle number fluctuations in the VDW gas.

In this paper we consider the procedure of a transformation of the CE pressure function to the GCE equation of state. This procedure has the form of a first order differential equation for the free energy $F$ as a function of $V$. A general solution of this equation includes the boundary condition at $V = V_0$ which is taken in the form of the ideal gas free energy in the limit of $N/V_0 \to 0$. This adds to the GCE formulation information of the particle masses and degeneracy factors which was absent in the CE pressure function. Following this procedure we transform the CE VDW pressure (3) to the transcendental equation (19) for the particle
number density in the GCE. Other thermodynamic functions of the VDW gas in the GCE can then be obtained in a unique way.

The particle number fluctuations are calculated for the VDW gas in the GCE formulation. An analytical expression for the scaled variance of particle number fluctuations is derived in terms of dimensionless particle number density $\tilde{n} = n/n_c$ and temperature $\tilde{T} = T/T_c$. It clearly demonstrates that in the VDW gas the repulsive interactions suppress the particle number fluctuations, whereas the attractive interactions lead to their enhancement. In the pure phases far away from the critical point the particle number fluctuations approach those of the ideal gas, i.e., $\omega[N] \approx 1$, at $\tilde{n} \ll 1$, and become small, $\omega[N] \ll 1$, at $\tilde{n} \to 3$. The scaled variance $\omega[N]$ increases in a vicinity of the critical point and diverges at the critical point $\tilde{n} = \tilde{T} = 1$. Admitting the presence of metastable states, one observes that the scaled variance $\omega[N]$ also diverges at the boundary between the metastable and unstable regions, where $\partial \omega / \partial \tilde{n} = 0$.

The fluctuations of partial volumes $V_g$ and $V_l$ occupied by the gaseous and liquid components have an influence on the particle number fluctuations in the mixed phase. However, the particle number fluctuations remain finite in the mixed phase. They start to increase in the vicinity of the critical point and diverge at the critical point reached from inside the mixed phase.

We hope that this study of the VDW equation of state within the GCE formulation can be useful for several applications in hadron physics. In particular, it looks promising for considering nuclear matter with the VDW equation of state corrected by the Fermi statistics effects. It is also interesting to study the particle number fluctuations for hadronic systems in the vicinity of the critical point.

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References

[1] Cleymans J and Satz H 1993 Z. Phys. C 57 135
[2] Becattini F, Cleymans J, Keranen A, Suhonen E and Redlich K 2001 Phys. Rev. C 64 024901
[3] Braun-Munzinger P, Magestro D, Redlich K and Stachel J 2001 Phys. Lett. B 518 41
[4] Rafelski J and Letessier J 2003 Nucl. Phys. A 715 98c
[5] Andronic A, Braun-Munzinger P and Stachel J 2006 Nucl. Phys. A 772 167
[6] Becattini F, Manninen J and Gazdzicki M 2006 Phys. Rev. C 73 044905
[7] Gorenstein M I, Petrov V K and Zinovjev G M 1981 Phys. Lett. B 106 327
[8] Rischke D H, Gorenstein M I, Stoecker H and Greiner W 1991 Z. Phys. C 51 485
[9] Anchishkin D V 1992 Sov. Phys. JETP 75 195
[10] Anchishkin D V 1992 Zh. Eksp. Teor. Fiz. 102 369 in Russian
[11] Anchishkin D and Suhonen E 1995 Nucl. Phys. A 586 734–54
[12] Anchishkin D and Vovchenko V 2014 arXiv:1411.1444 [nucl-th]
[13] Yen G D, Gorenstein M I, Greiner W and Yang S N 1997 Phys. Rev. C 56 2210
[14] Yen G D and Gorenstein M I 1999 Phys. Rev. C 59 2788
[15] Braun-Munzinger P, Heppe I and Stachel J 1999 Phys. Lett. B 465 15
[16] Hama Y, Kodama T and Socolowski O Jr. 2005 Braz. J. Phys. 35 24
[17] Werner K, Karpenko Iu, Pierog T, Bleicher M and Mikhailov K 2010 Phys. Rev. C 82 044904
[16] Satarov I. M., Dmitriev M. N. and Mishustin I. N. 2009 Phys. Atom. Nucl. 72 1390
Merdeev A. V., Satarov I. M. and Mishustin I. N. 2011 Phys. Rev. C 84 014907
[17] Greiner W., Neise L. and Stöcker H. 1995 Thermodynamics and Statistical Mechanics
(New York: Springer)
[18] Landau L. D. and Lifshitz E. M. 1975 Statistical Physics (Oxford: Pergamon)
[19] Gorenstein M. I., Hauer M. and Nikolajenko D. O. 2007 Phys. Rev. C 76 024901
[20] Kostyuk A., Gorenstein M., Stöcker H. and Greiner W. 2001 Phys. Lett. B 500 273