Statistical mechanics of rigid particles in an external field

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A new density functional is employed which simplifies and unifies the generalized van der Waals (GVDW) theory and the exact one-dimensional theory of hard particles in the presence of an external potential or solid walls. Numerical solution of density profiles in planar systems is made easy by introduction of the density functional. Numerical results for one- and three-dimensional fluids reveal that the GVDW theory fails at high chemical potentials by admitting negative densities. We have some evidence that the cause of the failure is a negative eigenvalue of the weighting function defining the local mean density or excluded volume in the theory. Density profiles of the exact one-dimensional theory are compared to those of the GVDW theory, those of the former exhibiting similar but stronger oscillations and of course no regions of negative density.

INTRODUCTION

The need for solvable theoretical models of fluids in the presence of confining external fields (in particular those resulting from solid walls or pores) has been intensified by the capacity of the new surface force apparatus to measure the force required to confine a molecularly thin fluid film between solids, and by the rapidly increasing power of Monte Carlo and molecular dynamics simulation afforded by supercomputers and large array processors. The generalized van der Waals (GVDW) theory, attractive for its simplicity and its kinship to the much studied van der Waals theory, has been developed by Nordholm and co-workers. The density distributions observed in computer simulations of simple fluids at solid walls have been adequately accounted for by the GVDW theory. Furthermore, the oscillatory behavior of the normal pressure vs film thickness observed with the surface force apparatus is qualitatively similar to that predicted by the GVDW theory.

The success of the GVDW theory led us to try to apply it to computer simulations and surface force measurements we have made on thin films of fluid mixtures confined between solid walls. We found, however, that under certain physically realizable conditions the theory predicts regions of negative density. Because the theory shows promise in some cases we believe a careful documentation of the nature of its failure is worthwhile.

In this paper we investigate hard-particle fluids in the presence of external fields or confining walls. The GVDW theory of hard particles between planar, reflecting walls in one and three dimensions is compared with the exact theory of hard rods. We use a new density functional that simplifies and unifies the mathematical structure of both the approximate and exact theories. The existence and uniqueness properties of the density distribution are revealed in especially simple form by the transformation. In the case of the exact theory, the transformation allows the reduction of the integral equation for the density profile to a pair of first order differential equations, which admit analytical solution.

THEORY

The configuration Helmholtz free energy of a D-dimensional fluid of hard particles in the presence of an external potential $u_e(r)$ is

$$ F_c = kT \int n(r) \left[ \ln \left( \frac{n(r)}{1 - v_0 \tilde{n}(r)} \right) + u_e(r) \right] d^D r $$

for the GVDW theory and the exact theory of hard rods. The quantity $v_0$ is a characteristic excluded volume per particle, $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $\tilde{n}(r)$ is a local mean density defined by

$$ \tilde{n}(r) = \int w(r,r') n(r') d^D r', $$

where $w(r,r')$ is a positive kernel obeying the condition

$$ \int w(r,r') d^D r' = 1. $$

Without further specifying $w(r,r')$ we can establish several relevant properties.

The chemical potential $\mu$ (relative to a convenient datum) is computed as $\delta F_c/\delta n(r)$, the first functional derivative of $F_c$ with respect to density$^{12}$:

$$ \mu = kT \ln \left( \frac{n(r)}{1 - v_0 \tilde{n}(r)} \right) + kT v_0 \int \frac{w(r,r') n(r')}{1 - v_0 \tilde{n}(r')} d^D r' + u_e(r). $$

The direct correlation function $C(r,r')$ can be obtained from the second derivative of $F_c$ with the aid of the formula

$$ C(r,r') = \frac{1}{n(r)} \delta (r - r') - \beta \frac{\delta^2 F_c}{\delta n(r) \delta n(r')}, $$

where $\beta = 1/kT$. The result is

$$ C(r,r') = -\frac{v_0 w(r,r')}{1 - v_0 \tilde{n}(r)} - \frac{v_0 w(r',r)}{1 - v_0 \tilde{n}(r')} - v_0^2 \int \frac{w(r'',r') n(r'') w(r'',r')}{1 - v_0 \tilde{n}(r'')} d^D r''. $$
Given the direct correlation function, the pair correlation function can be determined from the Ornstein-Zernike equation.\textsuperscript{13}

For specified chemical potential, temperature, and external potential, the equilibrium density distribution \( n(r) \) is the solution to Eq. (4), a rather complicated nonlinear integral equation. The problem can be greatly simplified by introduction of the quantity \( h(r) \):

\[
h(r) \equiv \frac{n(r)}{1 - v_0 \rho(r)}. \tag{7}
\]

\( h(r) \) has units of density and qualitatively can be interpreted as the number of particles per unit of “free volume” in the spirit of van der Waals theory. Thus, we shall refer to \( h(r) \) as the free-volume density. Insertion of Eq. (7) into Eq. (4) yields the relatively simple integral equation

\[
h(r) = e^{\beta(\mu - u_c)} \exp \left\{ -v_0 \int w(t', r) h(t') \, dt' \right\}. \tag{8}
\]

From Eq. (8) it follows that \( h(r) = 0 \), the value \( h = 0 \) being attained only if \( \exp \left[ \frac{\beta(\mu - u_c)}{2} \right] = 0 \). The density distribution is related to \( h(r) \) by the equation

\[
n(r) + v_0 h(r) \int w(r', r) n(r') \, dr' = h(r). \tag{9}
\]

With the definitions \( t(r) = n(r) / \sqrt{h(r)} \) and \( m(r) = \frac{v_0 h(r)}{\sqrt{h(r)}}, \) this equation becomes

\[
(I + M)[t] = \sqrt{h}, \tag{10}
\]

where \( I \) is the identity operator and \( M \) is an integral operator with the kernel \( m(r, r') \).

An interesting relationship can be derived from Eq. (8). Differentiating \( h \) with respect to \( \beta \mu \) in Eq. (8), we obtain

\[
\frac{\partial h(t)}{\partial \beta \mu} + v_0 h(t) \int w(t', t) \frac{\partial h(t)}{\partial \beta \mu} \, dt' = h(r). \tag{11}
\]

Thus, if \( w(t, t') \) is symmetric, i.e., if \( w(t, t') = w(t', t) \), \( \partial h / \partial \beta \mu \) obeys the same equation as the density. In this case

\[
n(t) = \frac{\partial h(t)}{\partial \beta \mu}. \tag{12}
\]

Otherwise \( n \) and \( \partial h / \partial \beta \mu \) are related through adjoint problems.

The quantity \( t^+ = (I + M)^+[t] \) obeys to Eq. (10), namely,

\[
(I + M^+) t^+ = \sqrt{h}, \tag{13}
\]

where \( M^+ \) is the adjoint of \( M \), i.e., \( M^+ \) is an integral operator with kernel \( m^+(r, r') \).

We now turn to special cases. For the GVDW theory

\[
w(r, r') = \frac{3}{4 \pi \sigma^2} \eta(\sigma - |r - r'|) \tag{14}
\]

in three dimensions and

\[
w(x, x') = \frac{1}{2\sigma^2} \eta(\sigma - |x - x'|) \tag{15}
\]

in one dimension, where \( \sigma \) is the diameter of hard spheres or hard rods and \( \eta(x) \) is the Heaviside function (equal to zero if \( x < 0 \) and unity if \( x > 0 \)). For the GVDW model \( w(r, r') \) is symmetric and so \( n(r) \) can be computed from Eqs. (9) or (10), or as the derivative of \( h \) with respect to \( \beta \mu \). We consider hard planar walls, i.e., \( \mu \), depends only on distance \( x \) from the walls

\[
e^{-\beta \mu(x)} = 0, \quad 0 < x < L, \tag{16}
\]

\[
e^{-\beta \mu(x)} = 1, \quad x < 0 \text{ or } x > L.
\]

Thus, \( h \) and \( n \) depend only on \( x \) in the three-dimensional as well as the one-dimensional system. Equations (8) and (9) become

\[
h(x) = e^{\beta \mu} \exp \left\{ -v_0 \int_0^L \hat{w}(|x - x'|) h(x') \, dx' \right\}, \quad 0 < x < L
\]

[with \( h(x) = 0, x < 0, x > L \)] and

\[
n(x) + v_0 h(x) \int_0^L \hat{w}(|x - x'|) n(x') \, dx' = h(x), \tag{18}
\]

where \( \hat{w} \) is equal to \( w \) of Eq. (15) for a one-dimensional fluid and

\[
\hat{w}(|x - x'|) = \frac{3}{4 \sigma^2} \left[ \sigma^2 - (x - x')^2 \right] \eta(\sigma - |x - x'|) \tag{19}
\]

for a three-dimensional fluid. Equation (19) is obtained by integrating over the \( xy \) plane. Nordholm and co-workers recommend choosing \( v_0 = \sigma^2 \) for the three-dimensional case. Similarly, we set \( v_0 = \sigma \) for a one-dimensional fluid.

For the exact theory of hard rods,\textsuperscript{9}

\[
h(x) = e^{\beta(\mu - \mu_c)} \exp \left\{ -\int_{x - \sigma}^{x + \sigma} h(x') \, dx' \right\}, \tag{20}
\]

where

\[
h(x) = \frac{n(x)}{1 - \int_{x - \sigma}^{x + \sigma} n(x') \, dx'}. \tag{21}
\]

Thus

\[
w(x, x') = \frac{1}{\sigma} \eta(x' - x) \eta(x + \sigma - x'). \tag{22}
\]

In the GVDW theory of hard rods \( w(x, x') \) is symmetric, whereas in the exact theory it is not. In both cases

\[
\int_{-\infty}^{\infty} w(x, x') \, dx' = 1.
\]

Differentiation of Eqs. (20) and (21) and rearrangement of the results yields

\[
h'(x) = -h(x) [\beta \mu_c(x) + h(x) - h(x - \sigma)] \tag{23}
\]

and

\[
l'(x) = h(x) l(x) - l(x + \sigma) h(x + \sigma), \tag{24}
\]

where \( l(x) \equiv n(x) / h(x) \). The primes on \( h' \), \( l' \), and \( \mu_c \) denote the first derivative with respect to \( x \).

Equations (23) and (24) have been solved analytically\textsuperscript{11} for potentials of the form

\[
e^{-\beta \mu(x)} = 0, \quad 0 < x < L, \tag{25}
\]

\[
e^{-\beta \mu(x)}, \quad 0 < x < L.
\]

\( \delta(x) \) being continuous and piecewise differentiable. The results are
\[ h(x) = h_j(x), \quad j\sigma < x < (j+1)\sigma, \quad j = 0, 1, \ldots \quad (26) \]

\[ l(x) = l_j(x), \quad L - (j+1)\sigma < x < L - j\sigma, \quad j = 0, 1, \ldots \quad (27) \]

and

\[ h_0(x) = \frac{e^{-\beta \phi(x)}}{e^{-\beta \phi(x)} + \int_0^x e^{-\beta \phi(x')} dx'}, \quad (28) \]

\[ l_0(x) = \exp \left[ \int_L^x h(x') dx' \right], \quad (29) \]

\[ h_j(x) = \frac{\exp \left[ -\beta \phi(x) + \int_{j\sigma}^x h_{j-1}(x' - \sigma) dx' \right]}{[e^{-\beta \phi(j\sigma)} h_{j-1}(j\sigma)] + \int_{j\sigma}^x \exp \left[ -\beta \phi(x') + \int_{j\sigma}^{x'} h_{j-1}(x' - \sigma) dx' \right] dx''}, \quad j > 0, \quad (30) \]

\[ l_j(x) = l_{j-1}(L - j\sigma) \exp \left[ \int_{L - j\sigma}^x h(x') dx' \right] + \int_{L - j\sigma}^{L - j\sigma} \exp \left[ -\int_x^{x'} h(x') dx' \right] l_{j-1}(x' + \sigma) h(x' + \sigma) dx'', \quad j > 0. \quad (31) \]

For hard walls, \( \phi(x) = 0 \), Eqs. (28) and (30) reduce to

\[ h_0(x) = \frac{1}{e^{-\beta \phi(x)} + x}, \quad (32) \]

and

\[ h_j(x) = \frac{h_{j-1}(j\sigma) \exp \left[ \int_{j\sigma}^x h_{j-1}(x' - \sigma) dx' \right]}{1 + h_{j-1}(j\sigma) \int_{j\sigma}^x \exp \left[ \int_{j\sigma}^{x'} h_{j-1}(x' - \sigma) dx' \right] dx''} \]

\[ = \frac{d}{dx} \ln \left[ 1 + h_{j-1}(j\sigma) \int_{j\sigma}^x \exp \left[ \int_{j\sigma}^{x'} h_{j-1}(x' - \sigma) dx' \right] dx'' \right], \quad j > 0. \quad (33) \]

Evaluation of \( h_1(x) \) and \( h_2(x) \) yield

\[ h_1(x) = \frac{h_0(\sigma)[1 + (x - \sigma)e^{\beta \phi(x)}]}{1 + h_0(\sigma)[x - \sigma + 1/2(x - \sigma)^2 e^{\beta \phi(x)}]}, \quad (34) \]

and

\[ h_2(x) = \frac{h_1(2\sigma)[1 + h_0(\sigma)(x - 2\sigma)]}{1 + h_1(2\sigma)[x - 2\sigma] + h_0(\sigma)[1/2(x - 2\sigma)^2 + 1/6(x - 2\sigma)^3 e^{\beta \phi(x)}]}, \quad (35) \]

The general formula for the higher order terms can be established by application of the relationship

\[ \exp \left[ \int_{j\sigma}^x h_{j-1}(x' - \sigma) dx' \right] = 1 + h_{j-2}((j - 1)\sigma) \int_{(j - 1)\sigma}^{x - \sigma} \exp \left[ \int_{(j - 1)\sigma}^{x'} h_{j-2}(x' - \sigma) dx' \right] dx'', \quad (36) \]

obtained by integrating Eq. (33).

The general result for \( j > 1 \) is

\[ h_j(x) = \frac{d}{dx} \ln \left[ 1 + h_{j-1}(j\sigma) \left[ x - j\sigma + h_{j-2}((j - 1)\sigma) \left( \frac{(x - j\sigma)^2}{2!} + h_{j-3}((j - 2)\sigma) \left( \frac{(x - j\sigma)^3}{3!} + \cdots \right) \right] + h_1(2\sigma) \left( \frac{(x - j\sigma)^{j-1}}{(j - 1)!} + h_0(\sigma) \left[ \frac{(x - j\sigma)^{j+1}}{j!} + \frac{(x - j\sigma)^{j+1}}{(j + 1)!} e^{\beta \phi(x)} \right] \right) \right]. \quad (37) \]

**CALCULATIONS**

For the results reported in this section \( n \) and \( h \) are given in units of \( \nu_0^{-1} (v_0 = \sigma^3 \text{ in 3D and } \sigma \text{ in 1D}) \), \( L \) and \( x \) in units of \( \sigma \), and \( \mu \) in units of \( kT \).

Density profiles \( n(x) \) are shown in Figs. 1 and 2 for a three-dimensional GVDW fluid between hard walls separated by a distance \( L = 6 \) and at the chemical potential 4 and 10, respectively. At the higher chemical potential the theory admits negative densities in the profile. This is a general trend as is illustrated by Fig. 3, in which is plotted the chemical potential above which negative densities are predicted vs the separation of the hard walls. The same flaw occurs in the one-dimensional GVDW fluid as is also shown in Fig. 3.

The integral equations for \( h \) and \( n \) [Eqs. (17) and (18)] were solved by the finite element Schwartz–Wendroff technique using Newton’s method with continuation.\(^{14}\)

Density profiles computed from the exact hard-rod theory are compared in Figs. 4 and 5 with those of the one-dimensional GVDW theory. Although the profiles are somewhat similar, the profiles of the exact theory generally have more pronounced peaks. Since \( h \) is a positive function, it follows from Eqs. (29) and (31) that densities predicted by the exact hard-rod theory are never negative. This is of course to be expected. The exact and the approximate theory both predict that the first derivative of \( n(x) \) is discontinuous at \( x = \sigma \).
We investigated the question of uniqueness of the solutions of Eqs. (17) and (18) for $h$ and $n$ for the GVDW model. For $\beta \mu < 0$, Eq. (17) is a contraction mapping, and therefore has a unique solution $h(x)$ lying between 0 and 1. In this case, the operator $M$ has a norm less than 1. Thus, the equation for density has a unique solution. With the aid of the transformation discussed in the Appendix, we establish uniqueness of $h$ and $n$ for $\beta \mu < 0.857$ in one dimension and 2.858 in three dimensions. We do not have an analytic proof of uniqueness of $h$ for larger $\beta \mu$. However, we have shown numerically by eigenvalue analysis that $I + M$ is a positive definite operator up to $\beta \mu = 20$, the highest value we examined. This guarantees existence of a unique solution of the density equation. Since the eigenvalue of the Jacobian of the $h$ equation are the same as those of $I + M$, it follows that no turning points or bifurcation points are encountered in the family of $h$-solutions generated as $\beta \mu$ varies continuously from values of established uniqueness of $h$ to higher values.

A failure of the GVDW theory previously noted by Tarazona\textsuperscript{15} is that except in the limit of zero density, the pair correlation function predicted by the theory allows hard
spheres to interpenetrate. Since the theory is based on a mean field free energy model, one might still hope that qualitatively correct trends in density profiles and multicomponent adsorption could be obtained. It is clear from the calculations presented here that this hope is certainly dashed at higher chemical potentials. We have also found that addition of attraction between fluid particles and the wall and the fluid particles themselves makes matters worse: negative densities occur at even lower chemical potentials.

A suspicion we have is that the occurrence of negative densities is related to the fact that the kernels, Eqs. (15) and (19), have negative eigenvalues as discussed in the Appendix. To support this thesis we have examined the GVDW model in one and three dimensions with the modified kernel \[ \hat{w}(x-x') + \lambda \delta(x-x') \] \[ \lambda = \text{positive number greater than the minimum eigenvalue of } \hat{w}(x-x') \]. The result is that negative densities were not found numerically up to chemical potentials \( \beta \mu = 20 \), the highest value studied. We are currently examining alternative approximations of the weighting function \( w(r,r') \), including the density functional suggested by Robledo and Tarazona to see whether the simplicity of the GVDW theory can be kept when its qualitative failures are removed.

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Appendix

Consider the equation

\[ f = e^{-Kf}, \]  
(A1)

where \( K \) is a self-adjoint, completely continuous integral operator with positive kernel in a Hilbert space. Any solution \( f \) of Eq. (A1) is positive and bounded by unity. Thus, we need to consider only functions such that \( 0 < f < 1 \) in seeking solutions to Eq. (A1). We made the added assumption that the minimum eigenvalue \( \lambda_0 \) of \( K \) is greater than \(-1/2\).

With the transformation

\[ \zeta = (I+K)f, \]  
(A2)

Eq. (A1) can be rearranged as

\[ \zeta = A(\zeta), \]  
(A3)

where

\[ A(\zeta) = K(I+K)^{-1} \zeta + e^{-K(I+K)^{-1}\zeta}. \]  
(A4)

Differentiating \( A((1-\alpha)\zeta_1 + \alpha \zeta_2) \) with respect to \( \alpha \) and integrating the result over \( \alpha \) from 0 to 1, we obtain

\[ A(\zeta_2) - A(\zeta_1) = \int_0^1 \left[ 1 - \exp\left(-K(I+K)^{-1}\right) \right] \times \left[ (1-\alpha)\zeta_1 + \alpha \zeta_2 \right] \times K(I+K)^{-1}(\zeta_2 - \zeta_1) d\alpha. \]  
(A5)

Since \( f \) is restricted to positive functions less than one, the norm of the quantity \( K(I+K)^{-1}(1-\alpha)\zeta_1 + \alpha \zeta_2 \) is positive and less than \( K(1) \), and so

\[ 1 - \exp\left(-K(I+K)^{-1}\right) \times \left[ (1-\alpha)\zeta_1 + \alpha \zeta_2 \right] < 1 - e^{-K(1)} \times (1-\alpha)\zeta_1 + \alpha \zeta_2 \leq 1 - e^{-K_{\max} \equiv \eta}, \]  
(A6)

where

\[ K_{\max} = \max_r \int_\Omega k(r,r')d^d r'. \]  
(A7)

From Eqs. (A5) and (A6) it follows that

\[ \|A(\zeta_2) - A(\zeta_1)\| < \eta \|K(I+K)^{-1}(\zeta_2 - \zeta_1)\|, \]  
(A8)

where \( \eta < 1 \). \( \| \zeta \| \) denotes the norm of \( \zeta \). Using the spectral norm, we have

\[ \|K(I+K)^{-1}\| = \max_\sigma \left| \frac{\lambda_n}{\lambda_\sigma + \lambda_n} \right|. \]  
(A9)

If \( \lambda_0 > -1/2 \), the right-hand side of Eq. (A9) is less than 1. Thus, since \( \|K(I+K)^{-1/2} \| < \|K(I+K)^{-1/2} \| \| \zeta \| \), we find

\[ \|A(\zeta_2) - A(\zeta_1)\| < \eta \|\zeta_2 - \zeta_1\| \]  
(A10)

since \( \lambda_0 > -1/2 \) by hypothesis.

Equation (A9) is the Lipschitz condition establishing that \( A \) is a contraction mapping and that as a consequence Eq. (A3) possesses a unique solution. Since \( (I+K)^{-1} \) is a positive definite operator Eq. (A1) has a unique solution if Eq. (A3) does.

It remains to establish that Eq. (A1) is equivalent to Eq. (8) and to find the range of chemical potentials for which \( \lambda_0 > -1/2 \). With the transformation \( f = h \exp(-\beta \mu) \) and \( k(r,r') = w(r,r') \exp(\beta \mu) \), Eq. (8) takes the form of Eq. (A1) for hard walls and the GVDW model. To obtain a lower bound on the eigenvalues of \( K \) we set \( f(r) \equiv 0 \) for \( r \) outside \( \Omega \), the volume of interest. Then we can express \( Kf \) in the form

\[ Kf = \delta \int \hat{w}(k) \hat{f}(k)e^{ik \cdot r} d^d k, \]  
(A11)

where \( \hat{w}(k) \) and \( \hat{f}(k) \) denote the Fourier transforms of \( w(r-r') \) and \( f(r) \). The smallest eigenvalue of \( K \) can then be given the bound

\[ \lambda_{\min} (\hat{f},\hat{f}) = \min_\hat{f} \frac{\int \hat{w}(k) \hat{f}(k) |d^d k|}{\int |\hat{f}(k)|^2 d^d k}, \]  
(A12)

or

\[ \lambda_{\min} (\hat{f},\hat{f}) = (2\pi)^{d/2} \int \hat{w}(k). \]  
(A13)

\( (\hat{f},\hat{v}) \) denotes the inner product of \( \hat{f} \) and \( \hat{v} \).

For the one- and three-dimensional GVDW fluid Eq. (A13) yields the bounds
\[
\lambda_0 e^{\beta_0} \min_k \left[ \frac{\sin k\sigma}{k\sigma} \right] = -\frac{2}{3\pi} e^{\beta_0} \tag{A14}
\]
and
\[
\lambda_0 e^{\beta_0} \min_k \left[ \frac{\sin k\sigma - k\sigma \cos k\sigma}{(k\sigma)^3} \right] = -\frac{8}{9\pi^3} e^{\beta_0}. \tag{A15}
\]

Thus, Eq. (A3) is a contraction in one dimension if $\beta_0 < 0.857$ and in three dimensions if $\beta_0 < 2.858$.

As the system increases in size, $\lambda_0$ converges to the bounds set by Eqs. (A14) and (A15). Already at $L = 6$, the numerically determined smallest eigenvalue of $K$ in one dimension is $-0.1967 \exp(\beta_0)$, fairly close to the bound $(-2/3\pi) \exp(\beta_0)$.

We can also show that $(I + M)^{-1}$ exists if $\lambda_0 > -1$.

From the definition of $M$ it follows that
\[
(u, Mu) = e^{-\beta_0 (\sqrt{h} u, K \sqrt{h} u)} > \lambda_0 e^{-\beta_0 (\sqrt{h} u, \sqrt{h} u)} \geq 0
\]
if $\lambda_0 > 0$,
\[
> \lambda_0 (u, u) \text{ if } \lambda_0 < 0. \tag{A16}
\]

The inequality for $\lambda_0 < 0$ follows from the fact that $h$ is positive and bounded from above by $\exp(\beta_0)$. Equation (A16) establishes that the self-adjoint operator $I + M$ has an inverse and, therefore, the density equation, Eq. (13), has a unique solution when $\lambda_0 > -1$. This result guarantees a unique density distribution for a given $h$ when $\beta_0 < 1.55$ and $3.55$ in the case of a one- and three-dimensional GVDW fluid, respectively.