Correctness of certain integral equation theories for core-softened fluids

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Integral equation approaches, based on the Ornstein-Zernike equation, provide a fast way to calculate phase diagrams and thermodynamic properties of systems as opposed to time-consuming and computationally expensive computer simulations. However, when employing integral equations it is necessary to introduce simplifications. The Ornstein-Zernike equation merely relates two unknown functions $h(r)$ and $c(r)$, and another relation (closer) between these two functions is needed. The latter function cannot be obtained in a closed form and it is always in some approximations. Various approximations exist with each of its own advantages and disadvantages. In this work we extensively tested hyper-netted chain, Percus-Yevick, Kovalenko-Hirata, and Rogers-Young closure on an interaction model with core-softened potential. Convergence domain was established for each method. We calculated pair distribution functions, pressure, and excess energy. Results were compared with Monte Carlo simulation results and literature data from molecular dynamics simulations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809744>]

I. INTRODUCTION

Theory of integral equations (IE) provides us with a fast and easy-to-implement method of calculating pair distribution function and thermodynamic properties that can be derived thereof.¹ As opposed to much more tedious molecular simulations that each yield one single point on a phase diagram, IE allows for a rather quick calculation of properties along the isotherms or isochores. Unfortunately, IE are in principle approximations that can produce wrong results. Caution must therefore be exercised to use IE with appropriate closures in regions where their use is justified.

In our study we investigate the fluid described by an isotropic repulsive core-softened potential. Core-softened potential with continuous shouldered well (CSW) was chosen because of its prominence, versatility, and difficulties it presents in analytic treatment. As it has been shown before, CSW and similar shouldered potentials are of particular importance for they can reproduce various fluid anomalies that are typical of water and other substances with angular dependent interactions,^{2–8} such as water, silica,^{3,9,10} silicon,¹¹ BeF₂.¹² CSW consists of five adjustable parameters that allow it to assume several quite distinct forms, ranging from deep double wells to repulsive ramp-like potentials. In our work we used original parameters as proposed by Franzese *et al.*^{13–15} Due to the presence of strongly repulsive wall, mildly repulsive shoulder and attractive well, CSW is rather difficult to treat with IE. As we show later, some standard procedures and closures fail or yield erroneous results.

We compare Monte Carlo simulation results with Ornstein-Zernike IE utilizing different closures. We study structure through pair distribution function, pressure and energy dependence upon density along several isotherms, and thermodynamic consistency of closures themselves.

II. THEORY

Ornstein-Zernike equation was proposed by Ornstein and Zernike in 1914¹⁶ and relates total correlation function, $h(r)$, with direct correlation function $c(r)$,

$$h(r) = c(r) + \rho \int h(r')c(|r - r'|)dr', \quad (1)$$

where ρ is the bulk density. From $h(r)$, pair distribution function, $g(r)$, can easily be calculated as $g(r) = h(r) + 1$, which is then used to obtain average thermodynamic and structural properties. We see that the total correlation consists of direct and indirect correlation parts; the latter is due to the influence of all other particles on any two particles in question. In order to solve this equation, one needs additional relation between $h(r)$ and $c(r)$. It can be shown¹ that there exists exact equation that describes relation between the two as

$$c(r) = h(r) - \ln[1 + h(r)] - \beta U(r) + B(r), \quad (2)$$

where $\beta = \frac{1}{kT}$ and $U(r)$ is the pair-wise potential. Here $B(r)$ denotes the bridge function, which is an infinite series of irreducible cluster diagrams. The bridge function is not known and even in principle cannot be calculated. Various approximations (known as closures) are employed instead. Their accuracy generally depends on the interaction potential. Hyper-netted chain approximation (HNC)^{17–19} assumes $B(r) = 0$, simplifying the closure relation to

$$c(r) = h(r) - \ln[1 + h(r)] - \beta U(r). \quad (3)$$

It is useful when long-range interactions (such as Coulomb forces) are present in the system. Another simple approximation was put forward by Percus and Yevick.^{20,21} The Percus-Yevick (PY) closure can be written as

$$c(r) = [1 + h(r)][1 - \exp(-\beta U(r))]. \quad (4)$$

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PY closure is suitable for systems with short-range potential. It is of particular importance because it can be solved analytically for a system of hard spheres.²²

Several other closures have been developed to address the shortcomings of HNC and PY, particularly in regard to the narrow region of convergence and inherent thermodynamic inconsistency. Kovalenko-Hirata closure (KH)²³ was constructed with such obstacles in mind as a more robust closure,

$$h(r) = \begin{cases} \exp[d(r)] - 1; & \text{for } d(r) \leq 0, \\ d(r); & \text{for } d(r) > 0, \end{cases} \quad (5)$$

where $d(r) = -\beta U(r) + h(r) - c(r)$.

The aforementioned closures may suffer from thermodynamic inconsistency. Namely, because of underlying simplifications and approximations, virial and compressibility routes do not yield the same results for pressure, isothermal compressibility, etc. Rogers-Young closure (RY)²⁴ seeks to alleviate this problem by interpolating between HNC and PY closures based on equating the isothermal compressibilities from virial and compressibility routes (self-consistency condition),

$$h(r) = \exp[-\beta U(r)] \left[1 + \frac{\exp[f(r)[h(r) - c(r)]] - 1}{f(r)} \right] - 1, \quad (6)$$

where $f(r) = 1 - \exp(-\eta r)$. Parameter η varies with temperature and density and is chosen on the self-consistency condition,

$$\begin{aligned} (\rho k T \chi_T^v)^{-1} &= \left(\frac{\partial \beta P^v}{\partial \rho} \right) = 1 - \rho \int c(r) 4\pi r^2 dr \\ &= (\rho k T \chi_T^c)^{-1}, \end{aligned} \quad (7)$$

where virial pressures is evaluated as

$$\beta P^v = \rho - \frac{\beta \rho^2}{6} \int_0^\infty r \frac{dU}{dr} g(r) 4\pi r^2 dr. \quad (8)$$

Ornstein-Zernike system was solved with direct iterative method. For greater numerical stability of the algorithm, we defined function $t(r) = h(r) - c(r)$ and employed fast Fourier transform (FFT), simplifying Ornstein-Zernike equation into an algebraic equation

$$\tilde{t}(k) = \frac{\rho \tilde{c}^2(k)}{1 - \rho \tilde{c}(k)}. \quad (9)$$

Initially we set $t(r) = 0$ on 4096 grid points separated by $dr = 0.01$. $c(r)$ is calculated from closure and then subjected to fast Fourier transform. In three dimensions, FFT and reverse FFT between real and k -spaces yield

$$k \tilde{f}(k) = 4\pi \int_0^\infty r f(r) \sin(kr) dr \quad (10)$$

and

$$r f(r) = (2\pi^2)^{-1} \int_0^\infty k \tilde{f}(k) \sin(kr) dk. \quad (11)$$

dk was chosen so that $dk \cdot dr = \frac{\pi}{N}$.

By solving Ornstein-Zernike equation and utilising FFT again, new $t(r)$ is obtained. This process is repeated until sufficient convergence is achieved. After each step, new $t(r)$ is calculated as a weighted average of the old and the newly calculated value $t_i(r) = 0.999t_{i-1}(r) + 0.001t_{\text{new}}(r)$, thereby further increasing numerical stability. Convergence was estimated by the greatest difference $|t_{i-1}(r) - t_i(r)|$ for any particular r . When this difference fell below 10^{-5} calculation was deemed completed.

Calculations from Ornstein-Zernike equations were benchmarked against the results from Monte Carlo *NVT* simulations. In our simulations, the investigated system consisted of 1000 particles interacting pairwise via CSW potential (see below) in a cubic box with minimum image convention. System was equilibrated with 10 000 cycles and then run five times. Each run consisted of 10 000 cycles. One cycle is an attempted move of each particle.

III. MODEL

We studied the CSW potential that consists of identical spherical particles interacting by pair-wise potential function,

$$U(r) = \frac{U_R}{1 + \exp(\Delta(r - R_R)/a)} - U_A \exp\left(-\frac{(r - R_A)^2}{2\delta_A^2}\right) + \left(\frac{a}{r}\right)^{24}. \quad (12)$$

This function consists of three terms: a soft repulsive shoulder of height U_R , an attractive Gaussian well of depth U_A and width $2\delta_A\sqrt{2\ln 2}$, and a steep repulsive wall. R_R and R_A are the repulsive average radius and the distance of the attractive minimum, respectively, while a denotes the diameter of particles. Steepness of the repulsive shoulder is determined by the parameter Δ (see Figure 1).²⁵ In our work, we used the parameters as proposed in the original version of the potential:¹³ $U_R/U_A = 2$, $R_R/a = 1.6$, $R_A/a = 2$, $(\delta_A/a)^2 = 0.1$, and $\Delta = 15$.

The potential given and its variations have been extensively studied by molecular dynamics approach.^{2,13-15} Egorov²⁶ studied this model potential using integral equations with hybrid mean spherical approximation (HSMA) closure

FIG. 1. Comparison of CSW potential for various values of parameter Δ , which determines the steepness of the repulsive shoulder.

TABLE I. Convergence domains. Maximum density where a particular closure still displays convergence is shown. The lowest possible temperature, a medium temperature ($T^* = 2.5$) and a very high temperature ($T^* = 5.0$) were investigated. This is compared with MD results¹³ for gas-liquid critical points.

HNC		PY		KH		RY		MD critical point	
T^*	ρ^*	T^*	ρ^*	T^*	ρ^*	T^*	ρ^*	T^*	ρ^*
1.35	1.82	1.14	1.15	0.98	1.01	1.22	0.84	0.96 ± 0.06	0.085 ± 0.015
2.50	1.98	2.50	1.35	2.50	1.07	2.50	1.11	N/A	N/A
5.00	2.17	5.00	1.47	5.00	1.12	5.00	1.32	N/A	N/A

FIG. 2. Comparison of correlation function by IETs with MC and MD depicts molecular dynamic results from Egorov²⁶ for $\rho^* = 0.1$ at different temperatures.

FIG. 3. Same as Fig. 2, only for density $\rho^* = 0.3$.

FIG. 4. Same as Fig. 2, only for density $\rho^* = 0.7$.

in a limited phase region. To our knowledge, no Monte Carlo studies have been carried out so far.

IV. RESULTS AND DISCUSSION

For clarity and easiness of the comparison of results obtained with different methods, physical quantities are reported in dimensionless reduced units in terms of the particle diameter and the depth of the attractive well: $T^* = k_B T/U_A$, $\rho^* = \rho a^3$, and $p^* = p a^3/U_A$.

A. Convergence radius

Narrow radius of convergence of some closures represents a particular hindrance in employing Ornstein-Zernike integral equation. System of Ornstein-Zernike equation and closure relation cannot be solved analytically, except for very simple potentials and closures (such as hard spheres in PY²²). Instead, the solution has to be obtained iteratively. Unfortunately, for some regions of phase diagram the system equations may converge to physically meaningless solutions (such as the infamous “zig-zag pattern” or negative values of pair

FIG. 5. Comparison of density dependence of virial pressure by different IEs with MC results for different temperatures.

FIG. 6. Same as Fig. 5, only detailed comparison at low densities.

distribution function). In other regions, convergence can be lost altogether. Typically, the convergence is limited to relatively high temperatures and low to medium densities. In the vicinity of liquid-liquid or liquid-gas critical points, the solutions typically do not converge. It is also impossible to use Ornstein-Zernike equation below freezing point where crystalline structures form and long-range order appears. For each of the investigated closures, we identified the lowest possible temperature of convergence and approximate density dependence of convergence radius at higher temperatures.

As expected, KH proved to be a very robust closure. It converges above $T^* = 0.98$ up to the density $\rho^* = 1.01$. At higher temperatures, maximum density of convergence is only marginally increased. PY exhibits convergence above $T^* = 1.14$ up to the density $\rho^* = 1.15$. HNC proved to be very sensitive to temperature, requiring at least $T^* = 1.35$. However, it proved to be the most resilient in high density regime, converging up to $\rho^* = 1.82$. RY works above $T^* = 1.22$ but fails rather quickly as density reaches 0.84. Molecular dynamics results have reported gas-liquid critical point at

FIG. 7. Comparison of density dependence of compressibility pressure by different IETs with MC results for different temperatures.

FIG. 8. Same as Fig. 7, only detailed comparison at low densities.

FIG. 9. Mixing parameter η in RY closure as a function of temperature and density.

$T^* = 0.96 \pm 0.06$ and $\rho^* = 0.085 \pm 0.015$,¹³ and liquid-liquid critical point at $T^* = 0.49 \pm 0.01$ and $\rho^* = 0.247 \pm 0.008$. We can see that gas-liquid critical point is on the edge of KH closure convergence domain while liquid-liquid is well below the temperatures of convergence domain.

See Table I for information on the highest attainable density at higher temperatures ($T^* = 2.5$ and $T^* = 5.0$). It should be noted, however, that the convergence does not imply physical accuracy of the predictions. As we show later on, some closures converge to physically inaccurate results in regions of high density.

B. Pair distribution function

Pair distribution function $g(r)$ was calculated for several densities and temperatures (Figures 2–4). We compared

FIG. 10. (Left) Relative difference between virial and compressibility pressure $((p_v - p_c)/\rho)$ for different densities in KH approach. (Right) Comparison of isotherms for virial and compressibility route with MC simulation data.

FIG. 11. (Left) Relative difference between virial and compressibility pressure $((p_v - p_c)/\rho)$ for different densities in HNC closure. (Right) Comparison of isotherms for virial and compressibility route with MC simulation data.

results from integral equations with PY, HNC, KH, and RY closures, our Monte Carlo simulation results and for $T^* = 1.7$ also molecular dynamic results from Egorov.²⁶

For low density $\rho = 0.1$ (Figure 2), only KH shows deviations from simulation data. KH underestimates the first peak at all temperatures while other closures yield consistent results. At intermediate density $\rho = 0.3$ (Figure 3), PY closure fails. KH continues to underestimate the first peak but the deviation is smaller than at lower densities. As density increases further to $\rho = 0.7$ (Figure 4), PY remains far off and KH again severely underestimates the first peak. HNC and RY manage to yield results that are in excellent agreement with simulation data. These was only expected for RY due to its thermodynamic consistency. HNC, on the other hand, is a very simple closure that only slightly overshoots the first peak at high densities. Our Monte Carlo simulations confirm the MD results of Egorov.²⁶

C. Pressure

PY, HNC, and KH yield different pressures when calculated via compressibility and virial route. Thus, we calculated pressure along four isotherms ($T^* = 1.3, 1.7, 1.9$, and 2.5) using integral equations and Monte Carlo simulation data.

Closure-independent relation for a spherical potential was used for HNC and KH,

$$\left(\frac{\partial p^c}{\partial \rho}\right)_T = kT \left(1 - \rho \int_0^\infty c(r) 4\pi r^2 dr\right). \quad (13)$$

FIG. 12. (Left) Relative difference between virial and compressibility pressure $((p_v - p_c)/\rho)$ for different densities in PY approximation. (Right) Comparison of isotherms for virial and compressibility route with MC simulation data.

This relation is somewhat impractical for it requires the integration of the compressibility equation over a range of densities. For PY closure, however, there exists a closed-form expression that can be used to evaluate compressibility pressure without integrating the compressibility equation:²⁷

$$\beta p_c = \rho - 4\pi\rho^2 \int_0^\infty cr^2 dr + 2\pi\rho^2 \int_0^\infty r^2 e(e-1)y^2 dr + \frac{1}{2\pi^2} \int_0^\infty k^2 [\rho \tilde{c}(k) + \ln(1 - \rho \tilde{c}(k))] dk, \quad (14)$$

where $e(r) = \exp(-\beta U(r))$ and $y(r) = \frac{g(r)}{e(r)}$.

Virial pressure for all closures was obtained as

$$\beta p_v = \rho - \frac{\beta\rho^2}{6} \int_0^\infty r \frac{dU}{dr} g(r) 4\pi r^2 dr. \quad (15)$$

As expected, in RY closure virial and compressibility pressures coincide.

Calculated pair distribution functions lead us to believe that HNC and RY would yield the best pressure estimates along the isotherm. When comparing calculations through virial (Figures 5 and 6) and compressibility (Figures 7 and 8) routes, interesting conclusions can be drawn. It seems that compressibility pressure in HNC closure the most accurately describes pressure dependence along an isotherm, surpassing even RY approximation. However, we have reasons to believe otherwise. Although there is excellent agreement at high densities, at lower densities HNC actually performs worse than all other closures. This is troublesome since integral equations generally exhibit better convergence and more accurate

FIG. 13. Ratio of virial pressure to match MC pressure in combination with compressibility pressure as function of density for various temperatures.

results at lower densities. Additionally, HNC is not thermodynamically consistent, yielding too high virial pressure.

RY performs in a more consistent way. Due to its nature, virial and compressibility approaches yield the same pressure, which is in fact quite close to the actual pressure from simulation data. For low pressures, agreement is quantitative, and even at high densities, it remains very good. Unfortunately, RY closure has a very limited density range of convergence. On the other hand, the KH closure works very good at low densities where its virial pressure follows simulation data the closest. However, as density increases above $\rho > 0.3$, KH approximation fails and predicts too high virial and compressibility pressures. PY approach seems to be only useful at extremely low densities, below $\rho < 0.1$.

D. Self-consistency

PY, HNC, and KH closures do not yield self-consistent results, i.e., thermodynamic quantities calculated via virial

and compressibility routes differ considerably. RY closure attempts to address this issue by using the mixing parameter η that interpolates between HNC and PY closures. As η increases, RY closure asymptotically approaches HNC. For $\eta = 0$, RY equals PY. η is calculated with bisection method for each point on a phase diagram in such a way that virial and compressibility routes yield the same isothermal compressibility. Consequently, pressures calculated by the two methods match, as well. As shown in Figure 9, η varies non-monotonically between 0 and 2.8 in the investigated phase region.

Albeit with rather inaccurate predictions, the KH ansatz exhibits a remarkably high self-consistency. Relative difference between calculated virial and compressibility pressures ($|(p_v - p_c)/\rho|$) is less than 1.0 for densities up to $\rho < 0.9$ (Figure 10). Unfortunately both results differ considerably from simulation data for higher pressures.

HNC closure shows a level of self-consistency up to densities $\rho < 0.5$ (Figure 11). As system grows even denser, virial pressure overshoots the simulation data. Curiously, compressibility pressure follows simulation data much more closely at higher densities than it does at lower.

As expected, PY approximation shows a very low degree of self-consistency (Figure 12). Moreover, calculations from virial route hint at a would-be phase transition, whereas compressibility route grossly overestimates the pressure from simulation data. For hard spheres, adding two thirds of exact solution of PY via compressibility route and one third via virial route (Carnahan-Starling equation²⁸) yields results that are in agreement with simulation data. We set out to calculate the appropriate virial and compressibility fractions for our system (Figure 13) to check if similar rules apply. At low densities, both pressures are too high. At intermediate densities, a large fraction of virial pressure and only a minuscule part of

FIG. 14. Comparison of excess energy per particle as obtained from MC simulations vs. IETs.

compressibility pressure ought to be used to obtain simulation data, clearly not following Carnahan-Starling rule.

E. Excess energy

Excess energy represents the difference between the translation internal energy of an ideal gas and the actual internal energy of a system (see Fig. 14). It is due to interactions between particles and can be evaluated as

$$\frac{U_{ex}}{N} = \frac{\rho}{2} \int_0^\infty U(r)g(r)4\pi r^2 dr. \quad (16)$$

At low densities (below $\rho^* < 0.4$), HNC, KH, and RY closures yield results that are in agreement with simulation data. However, as density increases, KH approach gives results that are too high. HNC and RY functions start to diverge from simulation as density reaches $\rho^* = 0.7$, but there is an important difference. HNC approximation predicts excess energy to further increase with increasing density, while RY one correctly predicts further decrease in energy. Agreement with our simulation results, however, is at high densities only qualitative.

V. CONCLUSION

We performed analysis of the Percus-Yevick, hypernetted chain, Kovalenko-Hirata, and Rogers-Young closures of Ornstein-Zenrike integral equations for the isotropic system of molecules with continuous shouldered well potential. Due to limited convergence domain of integral equations, we constrained our analysis to supercritical region of phase diagram. In this region, we investigated the system along several isotherms, from ultra-low to high ρ^* .

We confirmed the notion that RY closure describes the system far better than other closures. However, due to thermodynamic consistency requirement, which is mostly responsible for good results, calculations with RY approximation take an order of magnitude longer than with the other closures examined here. On an average computer, calculation of a single isotherm along the density range investigated in this paper takes approximately one day. With other closures, calculation is finished in a matter of minutes. HNC approximation proved to be a special case that requires a closer look. Although thermodynamically inconsistent, its compressibility pressure is in almost quantitative agreement with simulation data even for extremely high densities. Furthermore, radial distribution functions obtained from HNC and RY closures are virtually indistinguishable. However, further analysis showed that the remarkably good performance of HNC is coincidental. Discrepancy between virial and compressibility pressures grows large at high densities. Excess energy calculated with HNC is also wrong at high densities. In region above $\rho^* > 0.7$ all closures represent excess energy rather poorly, but only RY qualitatively captures the decreasing trend with increasing density.

It was expected to obtain good results with KH closure, but this was not the case. Despite its relatively high thermodynamic consistency (Figure 10) and robustness (broad convergence radius), results from KH were in poor agreement with our MC simulation results.

We have shown that RY closure works very well for CSW potential. Other closures are useful for low densities, but should be avoided at higher. Where computational cost is of the utmost importance, the HNC approximation may be considered instead of RY. Robustness of KH proves useful in regions, where other closures fail to exhibit convergence. PY approximation is not good and it should be avoided.

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