Thermodynamically consistent Reference Interaction Site Model theory of the tangent diatomic fluid

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Abstract
Thermodynamic and structural properties of the tangent diatomic fluid are studied in the framework provided by the Reference Interaction Site Model (RISM) theory, coupled with a Modified Hypernetted Chain closure. The enforcement of the internal thermodynamic consistency of the theory is described in detail. The results we obtain almost quantitatively agree with available or newly generated simulation data. We envisage the possibility to extend the consistent RISM formalism to generic, more realistic molecular fluids.

Key words: Tangent diatomics, thermodynamic consistency, RISM, MHNC

Tangent diatomics, constituted by two identical hard spheres whose centre-to-centre distance is equal to the diameter $\sigma$ of each sphere, provide a relatively simple prototype model for molecular systems. They can be considered as a member of two more general classes, one constituted by hard dumbbells (or fused hard spheres), where each sphere composing the molecule can have a different $\sigma$ diameter and the bond length (elongation) is generally a fraction of $\sigma$, and the other one constituted by two or more freely jointed hard spheres, a model widely used as a basic representation for chain-like molecules.

The structural and thermodynamic properties of the tangent diatomic fluid including its phase behavior, have been widely analyzed until recently in terms of both computer simulations and liquid state theories. Early Monte Carlo calculations were carried out by Freasier et al. [1, 2]. In Ref. [3] Tildesley and Streett have used the Monte Carlo pressure to evaluate the constants entering an empirical analytic expression that accurately fits the compressibility factor as a function of the density. More recent simulations can be found in Refs. [4, 5, 6, 7]. The fluid-solid equilibrium has been investigated via Monte Carlo simulations and free energy calculations in Refs. [8, 9].

Theoretical studies have involved the Reference Interaction Site Model (RISM) theory of molecular fluids developed by Chandler and Andersen [10]. In particular, in Refs. [6, 11] the tangent diatomic fluid has been analyzed in the context of the Chandler-Silbey-Ladanyi "diagrammatically proper" formulation of RISM (CSL, [12]). Calculations based on the contracted formalism known as "polymer-RISM" are reported in Ref. [7]. Among other theoretical studies we mention a closed form analytic theory for the structural functions [13], an Ornstein-Zernike-type integral equation theory with a non-spherical bridge function [14], a modification of the

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Verlet theory for hard spheres [15], a scheme based on the Born-Green-Yvon integral equation theory [16]. The equation of state of tangent diatomics has been investigated via different formalisms (see [5, 17, 18] and references therein).

The aim of this Letter is to present the first (to the best of our knowledge) thermodynamically consistent study of the tangent diatomic fluid in the framework provided by the RISM theory. We document the accuracy of thermodynamic and structural properties obtained through such a scheme and envisage further applications to more realistic molecular fluids.

The RISM formalism [10] is a matrix generalization of the Ornstein-Zernike equation of simple fluids [19], relating the set of site-site pair distribution functions to the corresponding direct correlation functions. The molecular geometry enters the theory through a matrix of intramolecular correlations that takes into account the rigid bonds among the various interaction sites of the molecule (see Ref. [20] for a review of the method and applications). Because of the symmetry of the tangent diatomic molecule all site-site correlations are equal, so that the RISM equation assumes the simple form in $k$ space:

$$h(k) = [w(k) + 1] c(k) + 2\rho[w(k) + 1]c(k)h(k).$$

In Eq. (1) $\rho$ is the molecular number density, $h(r) = g(r) - 1$ and $c(r)$ are respectively the pair and direct correlation functions among any of the two sites of different molecules, and $g(r)$ is the site-site radial distribution function. The function $w(k)$, that takes into account the intramolecular correlations, is written as: $w(k) = \sin(kL)/kL$, where $L \equiv \sigma$ is the bond distance among the two spheres composing the model.

The RISM equation must be complemented by a closure relation, that is usually taken to be the Percus-Yevick (PY) or the Hypernetted Chain (HNC) [10, 21]. Going beyond these basic approximations, we suggest here to adopt a Modified Hypernetted Chain (MHNC) closure [22]; specifically, we assume that the well known exact expression for the radial distribution function of an atomic fluid [19],

$$g(r) = \exp[-\beta v(r) + h(r) - c(r) + E(r)],$$

may be employed for the site-site structural functions of a molecular fluid. In the equation above $v(r)$ is the interparticle potential, $\beta = 1/k_B T$ (where $k_B$ is the Boltzmann constant and $T$ the temperature) and $E(r)$ is the “bridge function”. The quotation marks are used in this context because the theoretical framework for a rigorous definition of the bridge diagrams is provided by the CSL proper formulation of RISM [12] (see also the recent developments in Refs. [11, 23]). As in the original MHNC scheme for atomic fluids [22], we then approximate $E(r)$ by $E_{HS}(r)$, namely the bridge function of a hard sphere fluid of some effective packing fraction $\eta_{HS}$, in the parametrization of simulation data provided by Verlet and Weis [24].

In the MHNC scheme for atomic fluids, $\eta_{HS}$ is adjusted to enforce the thermodynamic consistency of the theory, as for instance by requiring the equality between the virial and the compressibility equations of state. For a generic molecular fluid the virial equation of state cannot be deduced in terms of site-site radial distribution functions [25]; however, for hard dumbbells, and hence for the model at issue, an expression for the excess free energy per particle has been derived by Lowden and Chandler [26] in terms of an integral over $\sigma$ of the value of $g(r)$ at contact, $g(\sigma^*)$:

$$\frac{\beta A^e}{N} = 8\pi\rho \int_0^{\sigma^*} d\sigma' (\sigma')^2 g(r = \sigma^*; \rho, \sigma').$$

(3)
This expression for $A_{ex}$ leads, upon derivation with respect to the density, to a “virial-like” equation of state, that can be made equal (with a suitable choice of $\eta_{HS}$) to the pressure calculated from the compressibility route:

$$\frac{1}{\beta} \frac{\partial \rho}{\partial P} = 1 + \rho h(k = 0).$$

(4)

The coupled equations (1) and (2) have been solved through standard numerical methods. We employ a discrete grid of 8192 points, with a $r$ spacing $\Delta r = 0.005\sigma$. Complementary calculations with $2^{15}$ points and $\Delta r = 0.002\sigma$ show no appreciable difference with the smaller grid. In order to enforce the thermodynamic consistency, the calculations are repeated at each density for different values of $\eta_{HS}$ till the pressures coming from Eq. (3) and (4) coincide within a $\sim 2\%$ numerical accuracy.

We report in Fig. 1 the RISM/MHNC compressibility factor $\beta P/\rho$ for the tangent diatomic fluid, gauged against Monte Carlo data [3], and in comparison with the HNC approximation, (corresponding to the assumption $E(r) = 0$ in Eq. (2)) and the PY closure (in which one assumes $c(r) = 0$ outside the hard-sphere core). As visible, the thermodynamically consistent MHNC reproduces quite well the Monte Carlo equation of state over practically the whole fluid density range (the freezing threshold of the model being estimated at $\rho \sigma^3 \sim 0.53$ [8]). The HNC virial-like and compressibility equations of state bracket the simulation data; as an example, they exhibit an inconsistency of about 20% of their average value at $\rho \sigma^3 = 0.4$. The HNC pressure obtained from a closed expression derived in Ref. [27] (not shown in the Figure) is close to, but systematically above, the virial-like equation results. Both PY routes lay systematically close one to each other and slightly underestimate the simulation results. In order to complete our picture, the comparison with other microscopic theories shows that the MHNC approach and the compressibility route in the Born-Green-Yvon (BGY) theory (see Figure 5 of Ref. [16]) share the same level of accuracy for the pressure up to $\rho \sigma^3 \sim 0.4$, whereas the BGY virial route underestimates systematically the simulation data from $\rho \sigma^3 \sim 0.3$ onwards. The CSL approach reproduces quite well the Monte Carlo equation of state (see Figure 3 of Ref. [6]), although it is
slightly less predictive than the MHNC in the high density fluid regime.

The quality of our results can also be appraised from Figure 2 where we display the MHNC input functions for the consistency procedure, namely the excess free energy calculated from Eq. (3) and the $k \to 0$ limit of the static structure factor, $S(0)$ which constitutes the right hand side of Eq. (4). The MHNC results are presented along with the HNC and PY predictions, and compared with the corresponding analytical functions derived in Ref. [3] from an accurate fit of simulation data for the pressure. We observe that, although all closures give a relatively accurate reproduction of simulation data, the integration of the compressibility and the derivation of the free energy eventually give rise to the relative spread of theoretical predictions for the pressure already shown in Fig. 1.

MHNC and PY predictions for the site-site radial distribution function $g(r)$ are displayed in Figure 3 and compared with Monte Carlo data generated in this work. Standard Monte Carlo simulations are generally carried out on samples composed of $N = 500$ molecules enclosed in a cubic box with periodic boundary conditions. We have checked in these conditions the negligible influence of the box size and of the spatial mesh of structural functions through several runs with 4000 particles and by using spatial grids as fine as 0.001σ spacing. It appears from Figure 3 that in the intermediate-to-high density regime ($\rho \sigma^3 \geq 0.3$) the MHNC correlations are practically superimposed to the simulation results. Only at the highest density investigated, $\rho \sigma^3 = 0.5$, the "exact" $g(r)$ displays a shoulder before the cusp at $r = 2\sigma$ precluding to the freezing of the fluid, whereas the MHNC is less sensitive to this emerging feature. At $\rho \sigma^3 = 0.1/0.2$, the theoretical correlations agree with simulation data for distances around the cusp onwards, whereas they appear slightly distorted in the region $\sigma < r < 2\sigma$. This artifact is produced by too high a value of $\eta_{HS}$, necessary to impose the thermodynamic consistency. As a result, the contact value of $g(r)$ is slightly underestimated in the dilute fluid regime. The overall quite good reproduction of $g(r)$ at contact shown in Fig. 3 is noteworthy (the discrepancy with simulation data barely exceeding ~5% in the worst case investigated, i.e. at $\rho \sigma^3 = 0.1$), since $g(\sigma^+)$ constitutes an important parameter entering not only Eq. (3), but also other approximate expressions for the equation of state of tangent diatomics [16]. As visible from the figure, the MHNC and the
Figure 3: MHNC (full lines), PY (dashed lines) and Monte Carlo (symbols) site-site radial distribution functions for the tangent diatomic fluid at various densities. Theoretical predictions lay close to the corresponding simulation results and are superimposed at $\rho \sigma^3 = 0.3$.

PY predictions are indistinguishable at $\rho \sigma^3 = 0.3$. The PY is slightly less accurate than the MHNC outside this density range, and in particular, as already observed in Ref. [6], tends to overestimate (underestimate) the contact value of $g(r)$ at lower (higher) densities. In comparison with our predictions, results from BGY [16] and CSL [8] theories show a better agreement with simulations data only in the low density regime.

The body of theoretical results presented in this Letter appears of remarkable accuracy, especially in consideration of the relative simplicity of the scheme adopted. The thermodynamically consistent MHNC improves on previous RISM results and exhibits an accuracy similar to the more rigorous but comparatively more complex CSL formalism. We have also several evidences testifying that the MHNC approach positively predicts the thermodynamic and structural properties of hard dumbbells for generic elongations other than $L = \sigma$ [28]. The present study paves the way for further applications to more realistic systems. In fact, although a consistency procedure for a generic molecular model cannot hinge on Eq. (3), since this relationship holds strictly for the hard-dumbbell fluid, other consistency schemes, based e.g. on the “energy route” to thermodynamics, can be implemented in such cases. Investigations on these topics are currently underway.

References

[1] B.C. Freasier, Chem. Phys. Lett. 35 (1975) 280.
[2] B.C. Freasier, D. Jolly, R.J. Bearman, Mol. Phys. 31 (1976) 255.
[3] D. J. Tildesley, W. B. Streett, Mol. Phys. 41 (1980) 85.
[4] I. Nezbeda, S. Labik, A. Malijevsky, Collect. Czech. Chem. Comun. 54 (1989) 1137.
[5] A.A. Archer, G. Jackson, Mol. Phys. 73 (1991) 881.
[6] A. Yethiraj, Mol. Phys. 80 (1993) 695.
[7] A. Yethiraj, C.K. Hall, J. Chem. Phys. 93 (1990) 5315.
[8] C. Vega, E.P.A. Paras, P.A. Monson, J. Chem. Phys. 96 (1992) 9060.
[9] E.G. Noya, M.M. Conde, C. Vega, J. Chem. Phys. 129 (2008) 104704.
[10] D. Chandler, H.C. Andersen, J. Chem. Phys. 57 (1972) 1930.
[11] Y. Duda, L.L. Lee, Y. Kalyuzhnyi, W.G. Chapman, P.D. Ting, Chem. Phys. Lett. 339 (2001) 89.
[12] D. Chandler, R. Silbey, B.M. Ladanyi, Mol. Phys. 46 (1982) 1335.
[13] G.P. Morriss, P.T. Cummings, Mol. Phys. 49 (1983) 1103.
[14] S. Labik, W.R. Smith, R. Pospisil, A. Malijevsky, Mol. Phys. 69 (1990) 649.
[15] S. Labik, A. Malijevsky, W.R. Smith, Mol. Phys. 73 (1991) 87.
[16] M.P. Taylor, J.E.G. Lipson, J. Chem. Phys. 100 (1994) 518.
[17] T. Boublík, I. Nezbeda, Chem. Phys. Lett. 46 (1976) 315.
[18] A. Dominik, P. Jain, W.G. Chapman, Mol. Phys. 103 (2005) 1387.
[19] J.-P. Hansen, I.R. McDonald, Theory of Simple Liquids, 2nd ed., Academic Press, London, 1986.
[20] P.A. Monson, G.P. Morriss, Adv. Chem. Phys. 77 (1990) 451.
[21] F. Hirata, P.J. Rossky, Chem. Phys. Lett. 83 (1981) 329.
[22] Y. Rosenfeld, N.W. Ashcroft, Phys. Rev. A 20 (1979) 1208.
[23] L. Lue, D. Blankschtein, J. Chem. Phys. 102 (1995) 5427.
[24] L. Verlet, J.J. Weis, Phys. Rev. 45 (1972) 939.
[25] P.T. Cummings, G.P. Morriss, C.C. Wright, Mol. Phys. 43 (1981) 1299.
[26] L.J. Lowden, D. Chandler, J. Chem. Phys. 59 (1973) 6587; erratum: J. Chem. Phys. 62 (1975) 4246.
[27] S.J. Singer, D. Chandler, Mol. Phys. 55 (1985) 621.
[28] G. Munaò, D. Costa, C. Caccamo, in preparation (2008).