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Thermodynamic self-consistency criterion in the mixed integral equation theory of liquid structure

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The insensitivity of the thermodynamically self-consistent mixed integral equation approach to the choice of and prescription for mixing the component closures is demonstrated using the square-well potential. Structures and mechanical properties are nearly identical among three different closure equations, which all compare well to Monte Carlo simulation data. These results suggest that future improvements will come from further applications of thermodynamic self-consistency arguments.

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Following the idea of Rowlinson [1], the thermodynamically self-consistent Rogers and Young (RY) [2] and HMSA [3] closures to the Ornstein-Zernike equation were formulated and deemed successful in part due to the mixing procedure, i.e., enforcing the hypernetted-chain (HNC) closure at large interparticle separations and the Percus-Yevick (PY) or soft-core mean-spherical (SMSA) approximations at short interparticle separations, respectively. The bridge diagrams deleted in the HNC approximation are of short range [4] and thus, one expects that the HNC approximation has to be enforced at large interparticle separations where those diagrams are insignificant. Alternatively, the PY closure, based on empirical evidence, is thought to be more accurate at short ranges where the strong repulsions act. It must be noted, however, that the existence of a solution that satisfies the self-consistency criterion is independent of these observations. The self-consistency criterion most commonly employed is that which enforces equality between isothermal compressibilities obtained via the fluctuation and virial routes

$$\chi^{\rm fluc} = \left(1 - \rho \int c(r) d\mathbf{r}\right)^{-1}, \tag{1a}$$

$$\chi^{\rm vir} = \beta^{-1} \left.\frac{\partial \rho}{\partial p}\right|_{\beta}, \tag{1b}$$

where ρ is the number density, $c(r)$ the direct correlation function, p the virial pressure, and $\beta = (k_B T)^{-1}$. This equality can be met whenever the following statement is satisfied by the mixed integral equation scheme

$$\chi_A^{\rm fluc}, \chi_B^{\rm vir} \lessgtr \chi_B^{\rm fluc}, \chi_A^{\rm vir}, \tag{2}$$

where A and B refer to two arbitrary closures. This statement applies to any interaction potential and any scheme that is constructed by mixing two individual clo-

TABLE I. Data for the $\lambda = 1.5$ square-well pressure, excess internal energy, and inverse isothermal compressibility for the HMSA and modified HMSA closures as functions of reduced density $\rho^* = \rho\sigma^3$ and reduced temperature $T^* = kT/\epsilon$. Monte Carlo (MC) data for T^*=5 is from Heyes [7] and for T^*=2 from Henderson Madden, and Fitts [6]. Note, data for the M2 closure have been omitted where no self-consistency can be achieved according to Eq. (2).

		$p/\rho kT$				$-U/N\epsilon$				χ^{-1}		
ρ^*	T^*	HMSA	M1	M2	MC	HMSA	M1	M2	MC	HMSA	M1	M2
0.1	5	1.119	1.120	1.119	1.11	0.617	0.617	0.618	0.615	1.264	1.265	1.263
0.2	5	1.292	1.294	1.292	1.30	1.262	1.260	1.265	1.25	1.717	1.725	1.709
0.3	5	1.544	1.548	1.543	1.52	1.945	1.943	1.950	1.95	2.494	2.510	2.468
0.4	5	1.919	1.924	1.916	1.87	2.672	2.671	2.679	2.70	3.809	3.833	3.753
0.5	5	2.483	2.491	2.478	2.40	3.440	3.440	3.445	3.475	6.004	6.040	5.894
0.6	5	3.336	3.348	3.326	3.45	4.224	4.226	4.224	4.27	9.607	9.673	9.370
0.7	5	4.620	4.643	4.599	4.65	4.984	4.988	4.967	5.045	15.43	15.57	14.84
0.8	5	6.537	6.585		6.61	5.667	5.673		5.75	24.76	25.07	
0.9	5	9.380	9.482		9.72	6.229	6.235		6.35	39.88	40.52	
0.5	2	1.344	1.353	1.356	1.35	3.622	3.622	3.625	3.636	3.802	3.837	3.784
0.6	2	1.967	1.972	1.974	1.97	4.400	4.400	4.399	4.415	7.214	7.238	7.176
0.7	2	3.109	3.115	3.116	3.20	5.166	5.168	5.161	5.174	13.22	13.27	13.09
0.8	2	5.013	5.038	5.008	5.08	5.848	5.854	5.806	5.861	23.03	23.24	22.10

1063-651X/96/53(3)/2968(4)/$10.00

sures. One expects then that the success of these mixing schemes depends on: (1) the nature and individual performance of the ingredient closures; (2) how they are mixed; and (3) the accuracy imparted by satisfying the self-consistency criterion. In this paper we will use the model square-well and Lennard-Jones 12-6 (LJ) fluids as examples to show that the latter decidedly dominates the accuracy of the solution, while the way in which the closures are mixed and the choice of closures only influences the range of convergence.

To close the Ornstein-Zernike equation

$$g(r) - 1 = c(r) + \rho \int [g(|\mathbf{r} - \mathbf{s}|) - 1]\, c(s) d\mathbf{s} \qquad (3)$$

we will consider the following two modifications to the HMSA closure equation

M1:

$$g(r) = e^{-\beta\phi_1(r)} \left(1 + \frac{1}{f(r)}[e^{f(r)[\gamma(r) - \beta\phi_2(r)]} - 1]\right), \qquad (4a)$$

$$f(r) = 1 - e^{-1/\alpha r}; \qquad (4b)$$

M2:

$$g(r) = e^{-\beta\phi_1(r)} \left(1 + \frac{1}{f(r)}\{[1 + f(r)\gamma(r)]e^{-f(r)\beta\phi_2(r)} - 1\}\right), \qquad (5a)$$

$$f(r) = 1 - e^{-\alpha r}. \qquad (5b)$$

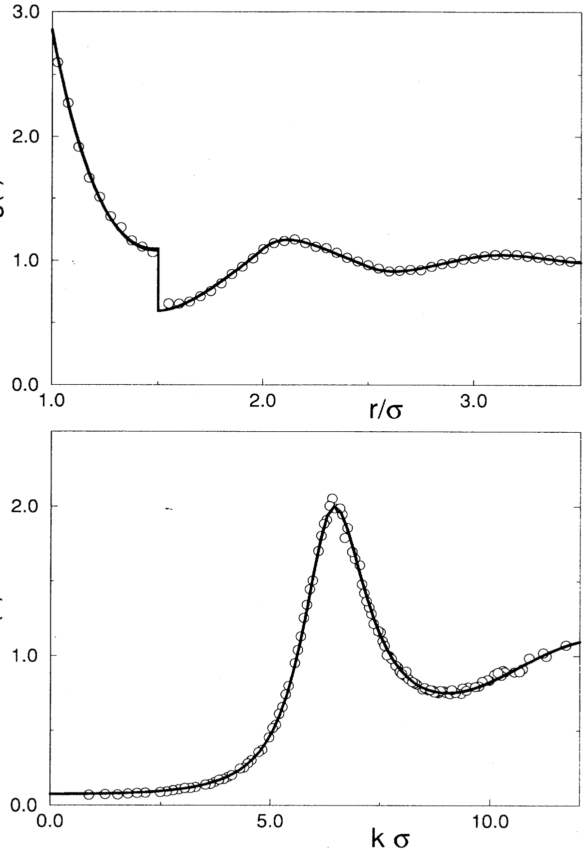

FIG. 1. (a) λ=1.5 square-well g(r) and (b) $S(k)$ for T^*=2 and ρ^*=0.7: points are 256 particle Monte Carlo data and the (indistinguishable) lines are HMSA, M1 and M2 predictions. Note that in (b), the $k \to 0$ limit is related to the isothermal compressibility via $S(0) = \chi$.

In these equations $\phi_1(r)$ and $\phi_2(r)$ are the repulsive and attractive parts of the pair potential as defined by some prescription, such as that of Weeks, Chander, and Andersen [5]; $\gamma(r) = g(r) - c(r) - 1$ with $g(r)$, the radial distribution function; $f(r)$ is a switching function in which the α parameter is adjusted to meet the self-consistency criterion. In the first modified closure, referred to hereafter as M1, the original HMSA closure [Eq. (4a)] is left intact while the switching function [Eq. (4b)] is altered from the RY form [Eq. (5b)]. According to the interpretation of Rogers and Young [2] and Zerah and Hansen [3], this would suggest that the modified closure interpolates between HNC at short interparticle separations and SMSA

TABLE II. Data for the Lennard-Jones pressure, excess internal energy, and inverse isothermal compressibility for the HMSA and RY integral equation schemes compared to simulation data (MC/MD) from Zerah and Hansen [3] and references cited therein.

		$p/\rho kT$			$U/N\epsilon$			χ^{-1}	
ρ^*	T^*	HMSA	RY	MC/MD	HMSA	RY	MC/MD	HMSA	RY
0.5	20	1.94	1.94	1.93	0.58	0.58	0.52	3.43	3.42
1.333	20	7.91	7.90	8.00	18.6	18.6	18.86	25.81	25.64
0.5	5	1.86		1.867	-2.37		-2.37	3.78	
1.0	5	6.32	6.27	6.43	-2.30	-2.35	-2.285	22.79	21.99
1.279	5	13.00	12.83	13.44	1.68	1.48	2.18	54.05	52.89
0.55	2.74	1.65		1.65	-3.21		-3.21	4.17	
1.0	2.74	7.11	6.97	7.37	-4.33	-4.44	-4.19	30.60	28.55
1.1	2.74	9.90	9.65	10.17	-3.86	-4.00	-3.70	44.40	42.03

at large interparticle separations, an exact reversal of the original HMSA closure. In the second modified closure, referred to hereafter as M2, we have linearized part of the exponential in the original HMSA closure equation to obtain a closure [Eq. (5a)] that interpolates between SMSA and now PY instead of the HNC closure, while maintaining the RY form for the switching function.

We have evaluated the mechanical properties of the above modified closures as well as the original HMSA closure. Table I contains pressure, excess internal energy, and isothermal compressibility data for two supercritical isotherms, as well as Monte Carlo data [6, 7] for comparison. As shown, the integral equation results compare favorably with the Monte Carlo data and the data from the different closures are nearly indistinguishable. Only at the highest densities do we see differences as high as 5%. This agreement can be traced to the fact that the closures produce equilibrium structures which are nearly identical. As seen in Fig. 1 the $g(r)$ and the corresponding $S(k)$ predictions are indistinguishable among the different closures.

For subcritical temperatures we find that the isothermal compressibility along the liquid spinodal behaves (classically) as $\chi \sim \Delta\rho^{-2}$ for the M2 closure, whereas the HMSA and M1 closures are less well behaved and yield $\chi \sim \Delta\rho^{-1}$, but only well below the critical temperature [8]. All the mixed closures yield square-root branch-point singularities along the vapor branch as do the PY [9] and HNC closures [10] themselves.

These observations hold for other square-well widths and, in addition, they hold for the Lennard-Jones fluid. In Fig. 2 we show that, according to Eq. (2), there are thermodynamically self-consistent solutions to both the HMSA and RY integral equation schemes for the LJ fluid. Solutions to the RY scheme are also found for the square-well potential, indicating that the presence of the attraction in the potential does not preclude the use of the RY closure as previously postulated [3]. The existence of a solution to the RY and other schemes depends on the form of the potential only to the extent that the potential affects the compressibilities of the component closures. Hence, the regions in the phase diagram where solutions are found may be restricted as seen in Fig. 2 for the RY closure applied to the LJ fluid. However, as demonstrated for the LJ fluid in Table II, when thermodynamically self-consistent solutions are found, they yield thermodynamic properties in good agreement with simulation data independent of the choice of component closures.

In conclusion, the technique of enforcing thermodynamic self-consistency of solutions to the Ornstein-Zernike equation through mixed integral equations is a powerful tool for predicting accurate fluid structures. Irrespective of the choice of and prescription for mixing the closures, converged solutions to the mixed integral equation scheme yield equivalent fluid structures, and hence, equivalent thermodynamic properties, that also agree well with data from simulations. Interpreting the mixing of closures to ensure thermodynamic self-consistency to be somehow simply related to interpolating between the structures resulting from the pure component closures is incorrect. These results suggest that attempting to simultaneously satisfy higher-order consistency relationships [11], or attempting to produce closures that

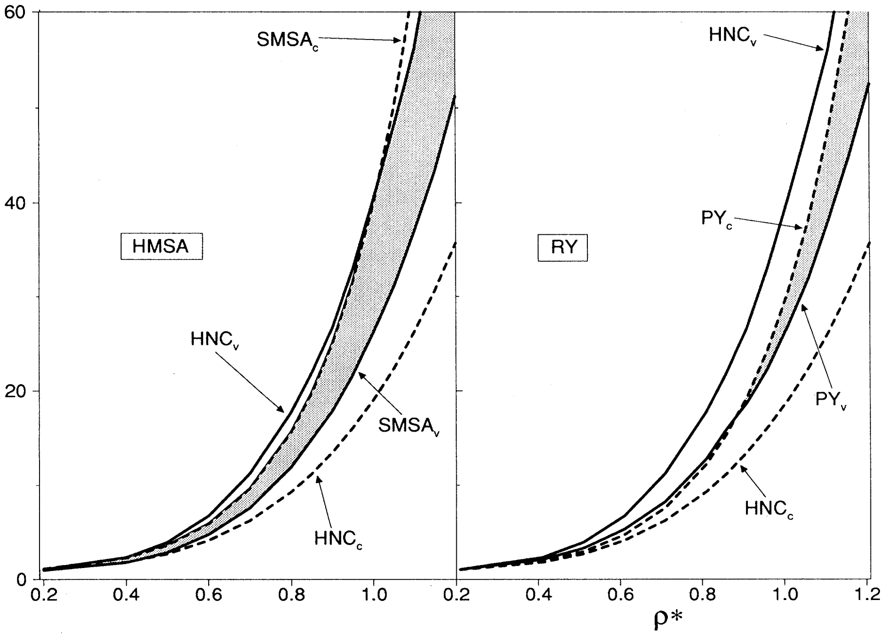

FIG. 2. Inverse isothermal compressibility as a function of reduced density for the HMSA and RY mixed integral equation schemes at $T^*=2.74$. The dashed lines are the compressibilities from the fluctuation route and the solid lines are from the virial route for the component closures. The shaded area indicates regions of overlap where the HMSA/RY compressibility will be located.

meet the consistency criterion "globally" (equality between pressures) [12], can be fruitful, more so than attempting to improve the ingredient closures. The choice of closures, though not the way in which they are mixed, should be made to ensure that a solution exists according to Eq. (2). This choice, it must be noted, also dictates the existence of and form of the critical behavior.

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