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Consistency Conditions for the Integral Equations of Liquid Structures[1]

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A thermodynamic consistency principle is established for the closure relations in integral equations that can yield accurate correlation functions as well as accurate thermodynamic properties. A brief *tour d'horizon* is given for existing consistency approaches. In addition to the common pressure consistency and the pressure–energy consistency, we introduce a third requirement based on the Gibbs–Duhem relation. We found that Gibbs–Duhem relation, mediated through the chemical potential, is instrumental in procuring accurate behavior of the bridge function and cavity function in the overlapping region ($0 < r < \sigma$). We test the Lennard–Jones fluid over wide ranges of T^* and ρ^* (T^* as low as 0.72 and ρ^* up to 0.90). For more than 15 state points we obtain excellent agreement in internal energy, pressure, and chemical potential. Comparison with Monte Carlo data on the bridge function and the radial distribution function also shows that the present approach is highly accurate.

KEY WORDS: bridge function; chemical potential; closure relation; Gibbs–Duhem relation; integral equations; Lennard–Jones potential; pressure consistency; thermodynamic consistency.

1. INTRODUCTION

Integral equation (IE) techniques have been used extensively to determine the structures of liquids and liquid mixtures [1] since the late 1950s and early 1960s. Most of the IEs, such as the Percus–Yevick (PY) [2] and

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the hypernetted-chain (HNC) [3] equations, are based on the Ornstein–Zernike (OZ) relation:

$$\gamma(r) \equiv h(r) - C(r) = \rho \int d\mathbf{r}'\, h(r')\, C(|\mathbf{r} - \mathbf{r}'|) \tag{1}$$

where $h(r)$ is the total correlation function (tcf); $C(r)$, the direct correlation function (dcf); $\gamma(r)$, the indirect correlation function (icf); and ρ, the number density. Knowledge of the tcf or, equivalently, the radial distribution function (rdf), $g(r) \equiv 1 + h(r)$, leads directly to the three thermodynamic quantities: pressure P (via the virial theorem), internal energy U, and isothermal compressibility χ_T:

$$\frac{\beta P^v}{\rho} = 1 - \frac{\rho}{6} \int d\mathbf{r}\, r \frac{\partial \beta u(r)}{\partial r} g(r) \tag{2}$$

$$\frac{\beta U'}{N} = \frac{\rho}{2} \int d\mathbf{r}\, \beta u(r)\, g(r) \tag{3}$$

$$\chi_T \equiv \left(\frac{\partial \beta P^c}{\partial \rho}\right)_T = 1 - \rho \int d\mathbf{r}\, C(r) \tag{4}$$

To solve Eq. (1), one needs a second condition, i.e., a *closure relation*, that relates the correlation functions to the pair potential $u(r)$. The closure relation can be given *formally* as

$$\ln y(r) \equiv \ln g(r) + \beta u(r) = h(r) - C(r) + B(r) \tag{5}$$

$B(r)$ is the bridge function, $y(r) = g(r) \exp(\beta u(r))$ is the cavity function, and $\beta \equiv 1/kT$ is the reciprocal temperature (k = Boltzmann constant). The cluster diagram of $B(r)$ is well-known [4]. However, to calculate "exactly" the bridge function according to the cluster integrals is mathematically a daunting task even for the simple hard-sphere fluid. Only a few low-density terms are known thereof. Approximate IEs make estimates of $B(r)$, thus producing approximate rdf's. For example, HNC simply sets $B(r) = 0$ identically. PY postulates

$$B_{\mathrm{PY}}(r) \approx \ln[1 + \gamma(r)] - \gamma(r) \tag{6}$$

The rdf's from these approximate IEs, when substituted into the thermodynamic expressions Eqs. (2–4), do not yield consistent values of P, U, and χ_T in the following sense. For example, the Helmholtz free energy A obeys the Gibbs–Helmholtz relation

$$d(\beta A) = U d\beta - (\beta P)\, dV, \qquad \beta = \frac{1}{kT} \tag{7}$$

In order for A to be an exact differential, the cross partial derivatives should be equal:

$$\left.\frac{\partial U}{\partial V}\right]_T = -\left.\frac{\partial \beta P}{\partial \beta}\right]_V \tag{8}$$

This is called the *dU–dP* consistency by Martynov and Vompe [5]. This was the basis of another important rule: the Hiroike consistency [6] from the early 1960s. In addition, the virial pressure should be differentiable to give the isothermal compressibility

$$\left.\frac{\partial \beta P^v}{\partial \rho}\right]_T = \chi_T \tag{9}$$

This is called the *dPv–dPc* consistency [consistency between the virial theorem, Eq. (2) and the compressibility integral, Eq. (4)]. The HNC and PY theories, as approximations, do not satisfy either of these conditions. (HNC actually satisfies the Hiroike consistency! but not the *dPv–dPc* consistency). These inconsistencies then become a *measure* of the (lack of) soundness of the approximate theories. This prompts the questions: if we can formulate a closure relation [i.e., postulate a certain functional form for the bridge function $B(r)$, either empirically or theoretically] that ensures the *dU–dP* and *dPv–dPc* consistencies, would this $B(r)$ (a) *be a better bridge function*, compared to available "exact" machine simulation data on $B(r)$? or (b) *give more accurate thermodynamic properties* U, P, χ_T, etc. (possibly rivaling simulation results) and more accurate correlation functions: $g(r)$, $C(r)$, and $y(r)$? Question a is a fundamental question, while question b is a practical question. Both need to the asked.

In this paper, we set out to examine these questions by using not only the *dPv–dPc* consistency criteria, but also the Gibbs–Duhem relation: $\rho d\mu = dP$ at constant T. (*dU–dP* is not used for reasons stated below.) We compare with simulation data to answer question b. Of course, we are very interested in question a, being a more fundamental question, and examine a carefully.

It is appropriate to cite here other "consistency" criteria that have been employed in the literature. (A) The minimization of the free energy scheme of Lado et al. [7]. [This produced the successful reference hypernetted-chain (RHNC) equation.] (B) The free-energy variational principle —the existence and variations of an exact Helmholtz free energy *functional* [4, 8] yield all the definitions, the OZ relation, and the closure relations for the correlation functions as conditions of stationarity. The existence of this functional achieves the *ultimate* thermodynamic consistency in that all thermodynamic quantities derived therefrom are mutually consistent. The problem is that such functional exists only *formally* (in terms of, e.g., coupling parameter integrals) that cannot at the moment be evaluated for general pair potentials. Approximate Helmholtz functionals do exist [such as the one for HNC, where $B(r)=0$]. But these, again, give approximate rdf's and, consequently, inconsistencies. (C) Pressure consistency conditions of Rogers and Young [9] and Zerah and Hansen [10]. These rules are similar to the *dPv–dPc* consistency mentioned above. Their contribution lies in a *judicious* splitting of the pair potentials into a reference part u_r and a long-range part u_a: $u(r)=u_r(r)+u_a(r)$. (D) Consistency in thermodynamic properties. Recently Vompe and Martynov [5, 11] have proposed a comprehensive framework for "enforcing" the thermodynamic property consistencies (between *dPv–dPc* and *dU–dP*) by imposing conditions on the temperature and density derivatives of the correlation functions. In a general sense, our present approach belongs to approach D, with the exceptions that (i) we adopt the efficient Verlet form for the bridge function, (ii) we do not explicitly require the evaluation of the derivatives $\partial g(r)/\partial \rho$ and $\partial g(r)/\partial T$, and (iii) most importantly, we examine the *dμ–dP* (Gibbs–Duhem) consistency, which was not tested before. (Thus we use the *dPv–dPc* and *dμ–dP* consistencies.) We note that for pure fluids, only two independent consistencies are sufficient since other conditions are derivable from the first two and are dependent on them. The *dμ–dP* consistency has the important advantage that the chemical potential probes the short-range $(0 \leqslant r < \sigma)$ behavior of the cavity and bridge functions [12], while P and U only sample values of $B(r)$ within a short interval, $0.8 < r/\sigma < 1.3$. Using U and P only will not likely give correctly $B(r)$ for the overlapping region of r, especially for $B(r \to 0)$, where a number of zero-separation theorems must hold [13].

2. THEORETICAL APPROACH

In earlier studies [12], we have shown that the bridge function formula proposed by Verlet [14] is a very powerful one for hard-sphere fluids,

$$B(r) = -\frac{0.5\phi\gamma(r)^2}{1+\alpha\gamma(r)}, \quad \text{or} \quad = -\frac{0.5\phi\gamma^*(r)^2}{1+\alpha\gamma^*(r)}, \quad \text{where } \gamma^* \equiv \gamma - \beta u_a \tag{10}$$

where ϕ and α are parameters and, for hard spheres, assume the values 1 and 0.8, respectively. We refer to Eq. (10) as the VM (Verlet modified) closure. In this study, we test for the Lennard–Jones (LJ) fluid

$$u_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{11}$$

We then allow the VM parameters ϕ and α to vary with temperature and density (i.e., as functions of T and ρ). They should vary in such a way as to "enforce" the thermodynamic consistencies *dPv–dPc* and *dμ–dP*. For attractive potentials, Zerah–Hansen [10], Llano–Restrepo–Chapman [15], and Vompe–Martynov [11] have shown that a modified icf γ^* should be used in the closure Eq. (10) (namely, the icf stripped of its long-range attractive tail): $u_a(r)$ is the attractive part of the pair potential in the sense of Weeks–Chandler–Andersen (WCA) [16]. $u_a(r) = -\varepsilon$, for all $r < r_{\min}$, and $u_a(r) = u_{LJ}(r)$, for all $r \geqslant r_{\min}$, where $r_{\min} = \sqrt[6]{2}\,\sigma$. Thus the final closure form we adopt is the fraction with γ^* in Eq. (10).

3. RESULTS OF CALCULATIONS

We have carried out calculations for Lennard–Jones fluids under some 15 conditions from $T^* = kT/\varepsilon = 0.72$ to 1.556, and $\rho^* = \rho\sigma^3 = 0.4$ to 0.9. Table I gives a list of T^* and ρ^*, together with some of the parameter values ϕ and α determined in such a way that the *dPv–dPc* consistency is satisfied. We note that we used numerical differentation (Lagrange three-point or five-point formula) to get the derivatives: $\partial\beta P^v/\partial\rho$ with density grid size $d\rho \sim 0.0005$ or smaller. Usually more than one pair of values of α and ϕ will satisfy the *dPv–dPc* criterion! (They are correlated.) The *dμ–dP* consistency was then used to "fix" a particular pair of α and ϕ such that the derivative $\partial P/\partial\mu$ approaches the system density ρ (the Gibbs–Duhem relation). The chemical potential is evaluated with the closed and direct formula of Lee [12]:

$$\beta\mu' = \rho \int d\mathbf{r} \left[B(r) + \gamma(r) - h(r) + h(r)\, B(r) + \frac{h(r)\,\gamma(r)}{2} \right] - S^* \qquad (12)$$

where the star integral S^* is given by

$$S^* \equiv \rho \int d\mathbf{r} \left[\frac{h(r)}{\gamma^*(r)} \int_0^{\gamma^*} d\gamma^*\, B(\gamma^*) \right] \qquad (13)$$

The closure relation, Eq. (10), is used in Eq. (13).

The thermodynamic properties are displayed in Table I and compared with Monte Carlo (MC) data [17] as well as the acurate equation of state (EOS) for LJ fluids of Nicolas et al. [18]. The configurational internal energy is well reproduced by the consistent approach proposed here (U is usually very easy to reproduce by most closures). The consistent pressures (from $dPv = dPc$) are also very accurate for the data points tested. We now have $P^v \approx P^c$ due to the consistency requirement. Note that the density reaches as high as 0.9 and the temperature as low as 0.72. For the isotherm $T^* = 0.75$, we have also included comparison with the HMSA method of

Table I. Thermodynamic Properties from Consistent Integral Equations for Lennard-Jones Fluids

				$\beta P/\rho$		$-\beta U'/N$	
T^*	ρ^*	ϕ	α	This work	EOS[a]	This work	EOS[a]
1.556	0.4	0.5356	1.0	0.517	0.507 (0.553)[b]	1.707	1.704 (1.724)[b]
1.556	0.6	1.00	1.055	0.956	0.883 (0.955)	2.517	2.523 (2.526)
1.556	0.8	1.23	1.00	2.77	2.804 (2.768)	3.17	3.25 (3.273)
1.5	0.4	0.5356	1.0	0.453	0.447 (0.41)	1.784	1.781
1.5	0.6	1.00	1.055	0.853	0.791	2.614	2.635
1.5	0.7	1.12	1.0	1.51	1.479	3.04	3.046
1.5	0.8	1.00	0.815	2.71	2.72	3.404	3.4
1.5	0.9	1.00	0.76	4.56	4.72	3.66	3.657
1.0	0.8	1.00	0.815	1.4	1.309 (1.53)	5.502	5.522
0.81	0.8	1.00	0.79	0.375	0.204 (0.06)	7.0	7.027
0.75	0.84	—	0.6	0.445	0.441[c] 0.464[d] 0.449[e]	8.031	8.032[c] 8.029[d] 8.028[e]
0.75	0.85	—	0.6	0.693	0.692[c] 0.712[d] 0.705[e]	8.114	8.112[c] 8.113[d] 8.109[e]
0.75	0.86	—	0.6	0.957	0.952[c] 0.976[d] 0.977[e]	8.196	8.179[c] 8.195[d] 8.188[e]
0.75	0.87	—	0.6	1.237	1.244[c] 1.256[d] 1.268[e]	8.276	8.256[c] 8.275[d] 8.265[e]
0.72	0.85	1.00	0.731	0.671	0.490[a] (0.36)[b]	8.454	8.431[a]

[a] From the equation of state of Ref. 18.
[b] In parentheses from MC of Ref. 17.
[c] From MC of Ref. 20.
[d] From HMSA of Zerah-Hansen [10].
[e] From RHNC of Lado [7].

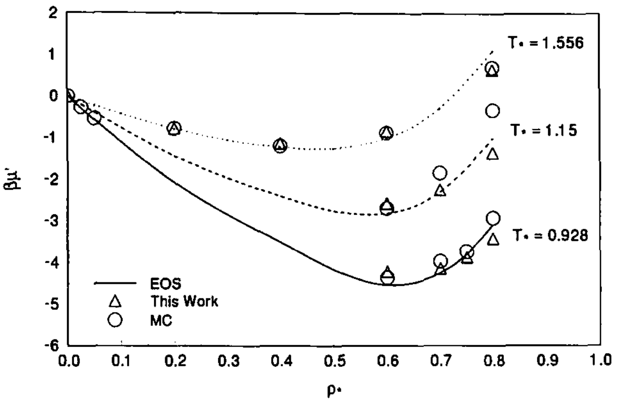

Fig. 1. The configurational chemical potential μ' of a Lennard–Jones fluid as a function of density at three isotherms: $T^* = 0.928$, 1.15, and 1.556. EOS (lines) are from Nicolas et al. [18], MC, (circles) from [17]. The self-consistent results (triangles) are from the closure Eq. (10) and Eqs. (12) and (13).

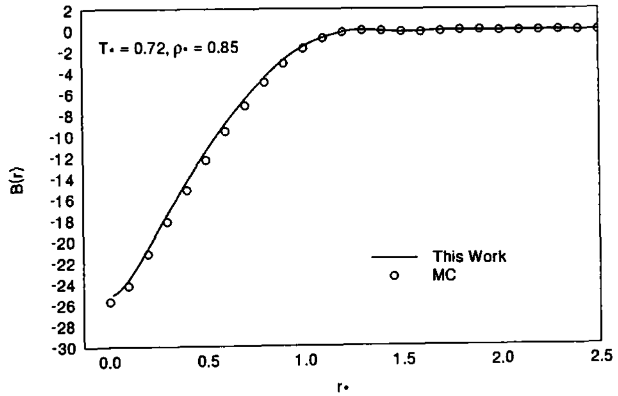

Fig. 2. The bridge function of a Lennard–Jones fluid at $T^* = 0.72$ and $\rho^* = 0.85$. MC (circles) are from Llano-Restrepo et al. [15]. The self-consistent results (line) are form Eq. (10) and the *dPv–dPc* and *dμ–dP* consistent relations. Note that at $r = 0$, MC gives $B(0) = -25.7$, while consistency gives $B(0) = -25.3$.

Zerah–Hansen and with the RHNC method of Lado. To do the structures at $T^* = 0.75$ (and $\rho^* \sim 0.86$) we found $\alpha \sim 0.6$, and we optimized ϕ as $\phi = a \exp(-\eta r)$, where a and η were parameters to be determined by consistency conditions. These measures were used only for the isotherm $T^* = 0.75$. In all cases, the thermodynamic properties are very accurately given by the present consistent approach. A special comparison with the chemical potential is presented in Fig. 1. We see that the chemical potential is closely given by Eq. (12), except at higher densities ($\rho^* > 0.7$) for the low-temperature isotherms. We surmise two possible sources of errors: (i) the formula, Eq. (13), is not valid for high densities; and/or (ii) the closure, Eq. (10), is not robust enough. We now put more onus on source ii (for reasons already stated in Ref. 12).

To test the consistent bridge functions produced from Eq. (10), we plot $B(r)$ for the state $\rho^* = 0.85$ and $T^* = 0.72$ in Fig. 2 with the MC data of Llano-Restrepo et al. [15]. It is seen that excellent reproduction of the MC $B(r)$ is achieved from small $r \to 0$ to longer ranges. This agreement by far exceeds that attained by Vompe–Martynov [11] [refer to their Figs. 6 and 7, 1994 where $B(0)$ was much overestimated]. To test the correlation functions further, we compared the consistent rdf with the molecular dynamics (MD) data on LJ fluids from Verlet [19] at $T^* = 0.72$ and $\rho^* = 0.85$ in Fig. 3. Excellent agreement is in evidence. This is not an isolated instance. Comparison at other states where MC data are available shows a similarly good agreement.

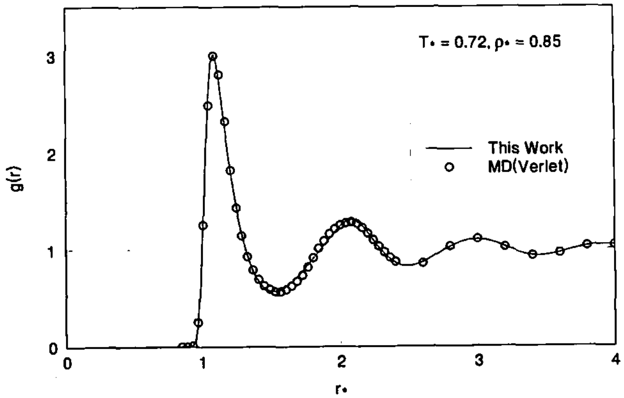

Fig. 3. The radial distribution function of a Lennard–Jones fluid at $T^* = 0.72$ and $\rho^* = 0.85$. MD (molecular dynamics results in circles) are from Verlet [19]. The self-consistent results (line) are from Eq. (10) and the *dPv–dPc* and *dμ–dP* consistent relations.

4. CONCLUSIONS

In this work, we explore the possibility of employing the macroscopic thermodynamic consistencies *dPv–dPc* and *dμ–dP* to determine the liquid structures of Lennard–Jones fluids. We use a flexible and robust closure: the Verlet form, Eq. (10), for this task. The goal is to obtain nearly "exact" correlation functions through the integral equation method. Comparison with conventional consistency approach shows that the present approach gives (i) accurate small-r behavior for correlation functions not achieved by other methods; (ii) accurate and consistent pressures ($P^v = P^c$) and energy values; and (iii) prediction of values of chemical potential [which depends to a large extent on the overlapping region ($r^* < 1$) of the correlation functions] accurate up to $\rho^* \sim 0.7$.

On different thermodynamic constraints, pressure consistency (*dPv–dPc*) is relative straightforward to employ. The consistency (*dU–dP*) turns out to be difficult to enforce under the present setup [Eqs. (8) and (10)]. We conjecture that it will be difficult to enfoce for any trial closures that might be employed simply because U and P derive most their contributions from the rdf at the same contact region (e.g., $0.8 < r^* < 1.3$). This causes numerical insensitivity. The Gibbs–Duhem relation ($\partial P/\partial\mu = \rho$), on the other hand, goes through the chemical potential. According to Lee 1992 [12], μ derives major contributions from the short-range values ($0 < r < \sigma$) of $y(r)$ and $B(r)$. We have shown that the advantage of the *dμ–dP* criterion, despite the numerical noises, ensures correct asymptotic values $r \to 0$ of the bridge function. We can now answer question b, that the thermodynamic properties are accurately reproduced, in the affirmative. As to question a, that $B(r)$ is more accurate, we have shown that the thermodynamic property consistencies can yield extremely accurate bridge functions, if the right closure form and the right consistency conditions are used. At least for the cases studied, this conclusion is confirmed.

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