

Generating functionals, consistency, and uniqueness in the integral equation theory of liquids

R. Fantoni^{a)} and G. Pastore^{b)}

Dipartimento di Fisica Teorica dell'Università and Istituto Nazionale di Fisica della Materia, Strada Costiera 11, 34014 Trieste, Italy

(Received 21 April 2003; accepted 19 May 2003)

We discuss and illustrate through numerical examples the relations between generating functionals, thermodynamic consistency (in particular the virial-free-energy one), and uniqueness of the solution in the integral equation theory of liquids. We propose an approach for deriving closures automatically satisfying such characteristics. Results from a first exploration of this program are presented and discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1590642]

I. INTRODUCTION

Integral equation theories (IETs) of liquid-state statistical mechanics are valuable tools for studying structural and thermodynamic properties of pairwise interacting fluid systems.^{1,2} Many of these approximations to the exact relation between pair potential and pair correlation functions have been proposed in the last half century, starting from the pioneering works^{3–5} to the most refined and modern approximations^{6–10} which may approach the accuracy of computer simulation with a negligible computational cost.

The functional method in statistical mechanics¹ provides the most general and sound starting point to introduce IETs as approximations of the exact functional relations, and it is the classical statistical mechanics counterpart of the quantum density functional theory.

Notwithstanding the success of present IETs to describe the structure of simple one-component systems, considerable work is still devoted to derive improved approximations which could accurately describe the thermodynamics as well. Also applications to nonsimple or multicomponent systems are still subject of current studies.

Actually, the description of thermodynamics is one weak point of IET approaches: reasonable and apparently harmless approximations to the potential-correlation relations usually result in a dramatically inconsistent thermodynamics where many, if not all, among the exact sum rules derived from statistical mechanics, are violated.

The problem of thermodynamic inconsistency—i.e., the inequivalence between different routes to thermodynamics—actually plagues the IET approach to the point that the degree of inconsistency between different formulas for the same quantity is used as an intrinsic measurement of the quality of a closure.

In the past, some discussion of the thermodynamic consistency appeared in the literature. The hypernetted chain (HNC) approximation was recognized as a closure directly derivable from an approximation for the free-energy functional,¹¹ thus exhibiting consistency between the virial

formula and the thermodynamic expression for the pressure. However, this limited consistency is not enough to guarantee a unique and faithful description of the phase diagram. Apart from the problem of the remaining inconsistencies, the descriptions of the critical points and spinodal lines are seriously inadequate.

Extensive work on HNC (Refs. 12–14) showed that in place of a true spinodal line, it is more appropriate to describe the numerical results as due to a region in the thermodynamic plane where no real solution of the integral equation exists. In particular, Belloni¹² showed that the disappearance of the solution originates from a branching point where two solutions merge, instead of from a line of diverging compressibility. Thus, we have direct evidence that the HNC approximation may have multiple solutions, at least in part of the phase diagram.

Empirical improvements on HNC have been proposed^{6,9,10} providing in many cases excellent results for one-component simple fluids. However, although reduced, the thermodynamic inconsistency problem remains and the multiple-solution problem is completely untouched.

In this work we start an investigation of a new approach to IETs directly addressing the two points of uniqueness of the solution and thermodynamic consistency. The basic idea is to constrain the search for new closures within the class of generating functionals which are strictly convex free-energy functionals, thus enforcing the virial-energy consistency as well as the uniqueness of the solution.

In particular, in the present paper we try to answer the following questions: (i) Does at least one strictly convex free-energy functional of the pair correlation function exist? (ii) What is the nature of the resulting spinodal line (if any)? (iii) What is the quality of the resulting thermodynamic and structural results? (iv) Does the simultaneous requirement of consistency and uniqueness automatically provide improved results?

As we will show, we have a positive answer for (i), a thorough and interesting characterization for (ii), some interesting indications for (iii), and a partly negative answer for (iv).

However, we can show that it is possible to exploit the

^{a)}Electronic mail: rfantoni@ts.infn.it

^{b)}Electronic mail: pastore@ts.infn.it

control provided by the generating functional approach to easily generate new closures and we feel our procedure could be the basis of a more systematic approach to IETs.

In Sec. II we recall the connections between closures, generating functionals, thermodynamic consistency, and uniqueness of solutions and we illustrate them in the well-known case of HNC approximation. In Sec. III we introduce two straightforward extensions of the HNC approximation intended to cure its problems. In Sec. IV numerical results are presented and discussed. In Sec. V we show two possible improvements of the closures studied.

II. THERMODYNAMIC CONSISTENCY AND UNIQUENESS OF THE SOLUTION OF INTEGRAL EQUATIONS

Since the work by Olivares and McQuarrie,¹⁵ it is known the general method to obtain the generating functional whose extremum with respect to variations of the direct $[c(r)]$ or total $[h(r)]$ correlation functions results in the closure relation, provided the Ornstein–Zernike (OZ) equation is satisfied.

For example, if we have a closure of the form

$$\rho^2 c(r) = \Psi\{h(r), \beta\phi(r)\}, \quad (1)$$

where $\phi(r)$ is the pair interaction potential and Ψ is an arbitrary function, the functional

$$Q[h(r), \beta\phi(r)] = \frac{1}{2\beta\rho} \left(\int \frac{d\mathbf{k}}{(2\pi)^3} \{\rho h(k) - \ln[1 - \rho h(k)]\} - \int d\mathbf{r} h(r) \times \int_0^1 dt \Psi\{th(r), \beta\phi(r)\} + \text{const} \right) \quad (2)$$

is such that the extremum condition

$$\frac{\delta Q}{\delta h(r)} = 0 \quad (3)$$

is equivalent to

$$\rho^2 h(r) = \Psi\{h(r), \beta\phi(r)\} + \rho \int h(|\mathbf{r} - \mathbf{r}'|) \Psi\{h(r'), \beta\phi(r')\} d\mathbf{r}'. \quad (4)$$

Olivares and McQuarrie also showed how to find the generating functional if the closure is expressed in the form

$$\rho^2 h(r) = \Psi\{c(r), \beta\phi(r)\}. \quad (5)$$

In Appendix A we discuss the extension of their method to the case of a closure written as

$$\rho^2 c(r) = \Psi\{\gamma(r), \beta\phi(r)\}, \quad (6)$$

where $\gamma(r) = h(r) - c(r)$ is the indirect correlation function. Notice that most of the modern closures correspond to this last case.

The possibility of translating the original integral equation into an extremum problem allows us to get an easy control on two important characteristics of the approxima-

tion: thermodynamic consistency between energy and virial routes to the thermodynamics and uniqueness of the solution.

Indeed, once we get the generating functional Q , due to the approximations induced by the closure, there is no guarantee that its value at the extremum is an excess free energy. In order to be a free energy, the functional should satisfy the condition

$$\frac{\delta Q}{\delta \phi(r)} = \frac{\rho}{2} g(r), \quad (7)$$

where $g(r) = h(r) + 1$ is the pair distribution function.

Even if this condition is not new and mention to it is present in the literature,¹⁶ we discuss it in Appendix B as well as its consequences on the thermodynamic consistency between the virial pressure and the density derivative of the free energy.

Another issue where the generating functional approach is useful is the problem of multiple solutions of the integral equations.¹² In particular, the analysis of the convexity properties of the generating functional is a very powerful tool.^{17,18}

Let us illustrate this technique in the case of HNC closure. It is well known^{11,15} that the HNC equation, with closure

$$c(r) = h(r) - \ln[g(r)e^{\beta\phi(r)}], \quad (8)$$

can be derived from the variational principle

$$\frac{\delta \mathcal{F}[h]}{\delta h(r)} = 0, \quad (9)$$

where

$$\mathcal{F}[h] = \mathcal{F}_{OZ}[h] + \mathcal{F}_{HNC}[h], \quad (10)$$

with

$$\mathcal{F}_{OZ}[h] = \int \frac{d\mathbf{k}}{(2\pi)^3} \{\rho \hat{h}(k) - \ln[1 + \rho \hat{h}(k)]\}, \quad (11a)$$

$$\mathcal{F}_{HNC}[h] = \rho^2 \int d\mathbf{r} \{1 + g(r) (\ln[g(r)e^{\beta\phi(r)}] - 1) - h^2(r)/2\}. \quad (11b)$$

Let us call $\bar{h}(r)$ the extremum of \mathcal{F} , solution of the variational principle (9). It can be shown (see Appendix B) that, within an additive constant, $\mathcal{F}[\bar{h}]/(2\beta\rho)$ is the excess Helmholtz free energy per particle of the liquid. This ensures thermodynamic consistency between the route to the pressure going through the partial derivative of the free energy and the one going through the virial theorem (see Appendix B). In addition, it allows us to get a closed expression for the excess chemical potential without further approximations.^{19,20} This feature is highly desirable for applications of IETs to the determination of the phase diagrams.

Moreover, if we can prove that \mathcal{F} , defined on some convex set of trial correlation functions D_c , is a strictly convex functional, then we know that if a solution to Eq. (9) exists,

it corresponds to a minimum and is unique. A functional \mathcal{F} is strictly convex if, for all $y(r) \in D_c$ and $y(r) \neq 0$, we have

$$A = \int y(r) \frac{\delta^2 \mathcal{F}[h]}{\delta h(r) \delta h(r')} y(r') d\mathbf{r} d\mathbf{r}' > 0. \quad (12)$$

We calculate the second functional derivatives as follows:

$$\frac{\delta^2 \mathcal{F}_{OZ}[h]}{\delta h(r) \delta h(r')} = \rho^2 \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')} \frac{1}{[1 + \rho \hat{h}(k)]^2}, \quad (13a)$$

$$\frac{\delta^2 \mathcal{F}_{HNC}[h]}{\delta h(r) \delta h(r')} = \rho^2 \delta(\mathbf{r} - \mathbf{r}') \left(\frac{1}{g(r)} - 1 \right). \quad (13b)$$

Recalling that the static structure factor $S(k) = 1 + \rho \hat{h}(k)$, we find, for A ,

$$A/\rho^2 = \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hat{y}^2(k)}{S^2(k)} + \int d\mathbf{r} y^2(r) \left(\frac{1}{g(r)} - 1 \right). \quad (14)$$

Now, the most interesting results would be to show the strict convexity of the HNC functional over the convex set of all the admissible pair correlation functions [all the $h(r) \geq -1$ and properly decaying to zero at large distance].

However, this is not the case for HNC. It has not been possible to show the positive definiteness of Eq. (14) and it has been shown¹² that in some region of the thermodynamic plane the HNC approximation does exhibit multiple solutions.

The best we can do is to obtain a more limited result. Calling $g_1 = \sup g(r)$ ($g_1 > 1$ is the height of the first peak of the pair distribution function) and using Parseval theorem, we find

$$A/\rho^2 > \int \frac{d\mathbf{k}}{(2\pi)^3} \hat{y}^2(k) \left(\frac{1}{S^2(k)} - 1 + \frac{1}{g_1} \right), \quad (15)$$

from which we deduce that $A > 0$ on the following set of functions:

$$D = \{h(r) \mid 0 < S(k) < \sqrt{g_1/(g_1 - 1)} \forall k\}. \quad (16)$$

We conclude that \mathcal{F} defined on any convex set of functions $D_c \subset D$ is strictly convex. Near the triple point we are sure we are out from such set since the first peak of the pair distribution function for the Lennard-Jones fluid is $g_1 \approx 3$ (Ref. 21), so that $\sqrt{g_1/(g_1 - 1)} \approx 1.2$. The first peak of the static structure factor is also close to 3. Then we are not inside D and the HNC approximation may have multiple solutions.¹²

Instead, if we are in the weak-coupling regime, the previous conditions tell us that there is a range where the branch of solutions going to the perfect gas limit is unique and quite isolated from other solutions.

III. EXTENSIONS OF THE HNC APPROXIMATION

The generating functional approach can be used in a systematic way to look for better closures. We think that this way we can obtain a less empirical search method for improving closures.

In the following we report some preliminary analysis we have done. As a first test of our program, we have restricted

our investigations to simple modifications of the HNC functional. As we will discuss later, such a choice is certainly not optimal. However, we can learn enough to consider the approach worthwhile of further investigations and we feel the results are interesting in order to reveal more details about the characteristics of the solutions of the highly nonlinear IETs.

A. HNC/H2 approximation

We want to modify the HNC closure in order to have an integral equation with a generating functional which is strictly convex without having to restrict its definition domain. We choose, as our modified HNC (HNC/H2) closure,²²

$$c(r) = h(r) - \ln[g(r)] - \beta\phi(r) - \alpha h^2(r), \quad (17)$$

with α a parameter to be determined. The new closure generating functional is

$$\mathcal{F}_{HNC/H2}[h] = \rho^2 \int d\mathbf{r} \{1 + g(r) (\ln[g(r) e^{\beta\phi(r)}] - 1) - h^2(r)/2 + \alpha h^3(r)/3\}. \quad (18)$$

Its second functional derivative with respect to h is

$$\frac{\delta^2 \mathcal{F}_{HNC/H2}[h]}{\delta h(r) \delta h(r')} = \rho^2 \delta(\mathbf{r} - \mathbf{r}') \left[\frac{1}{g(r)} - 1 + 2\alpha h(r) \right]. \quad (19)$$

Recalling that $h = g - 1$ and $g(r) > 0$ for all r , we see that, for $\alpha = 1/2$,

$$\frac{1}{g} - 1 + 2\alpha h = \frac{(1-g)^2}{g} \geq 0 \quad \forall g. \quad (20)$$

Then $\mathcal{F}_{HNC/H2}$ is a convex functional, and since \mathcal{F}_{OZ} is unchanged and strictly convex (see Appendix C), their sum, the generating functional of the integral equation, is strictly convex.

Moreover, $\{\mathcal{F}_{OZ}[\bar{h}] + \mathcal{F}_{HNC/H2}[\bar{h}]\}/(2\beta\rho)$ continues to be the excess Helmholtz free energy per particle of the liquid since Eq. (7) holds (see Appendix B).

We have then an integral equation which is both thermodynamically consistent (the pressure calculated from the virial theorem coincides with that one calculated from the Helmholtz free energy) and with a solution which, when it exists, is unique.

B. HNC/H3 approximation

In the same spirit as in Sec. III A we can try to add a term h^3 in the HNC/H2 closure

$$c(r) = h(r) - \ln[g(r)] - \beta\phi(r) - \alpha h^2(r) - \gamma h^3(r), \quad (21)$$

with α and γ parameters to be determined. We call this approximation HNC/H3. The closure generating functional is

$$\mathcal{F}_{HNC/H3}[h] = \rho^2 \int d\mathbf{r} \{1 + g(r) (\ln[g(r) e^{\beta\phi(r)}] - 1) - h^2(r)/2 + \alpha h^3(r)/3 + \gamma h^4(r)/4\}. \quad (22)$$

Its second functional derivative with respect to h is

$$\begin{aligned} \frac{\delta^2 \mathcal{F}_{HNC/H3}[h]}{\delta h(r) \delta h(r')} &= \rho^2 \delta(\mathbf{r}-\mathbf{r}') \left[\frac{1}{g(r)} - 1 + 2\alpha h(r) + 3\gamma h^2(r) \right] \\ &= \rho^2 \delta(\mathbf{r}-\mathbf{r}') \frac{1-g(r)}{g(r)} \{1 - 2\alpha g(r) + 3\gamma g(r)\} \\ &\quad \times [1 - g(r)]. \end{aligned} \quad (23)$$

In order to have the right-hand side of this expression positive for $g > 0$ the only choice we have is to set $\alpha = 1/2$. In this way,

$$(1-g)[1 - 2\alpha g + 3\gamma g(1-g)] = (1-g)^2(1 + 3\gamma g), \quad (24)$$

and we see that $\mathcal{F}_{HNC/H3}$ is a convex functional if we additionally choose $\gamma > -1/[3\text{sup}g(r)]$.

Once again $\{\mathcal{F}_{OZ}[\bar{h}] + \mathcal{F}_{HNC/H3}[\bar{h}]\}/(2\beta\rho)$ is the excess Helmholtz free energy per particle of the liquid and the thermodynamic consistency virial free energy is ensured.

IV. NUMERICAL RESULTS

To solve numerically the OZ plus closure system of nonlinear equations we used Zerah's algorithm²³ and Fourier transforms were done using fast Fourier transform. In the code we always work with adimensional thermodynamic variables $T^* = 1/(\beta\epsilon)$, $\rho^* = \rho\sigma^3$, and $P^* = P\sigma^3/\epsilon$, where σ and ϵ are the characteristic length and characteristic energy of the system, respectively. We always used 1024 grid points and a step size $\Delta r = 0.025\sigma$.

The thermodynamic quantities were calculated according to the statistical mechanics formulas for the excess internal energy per particle,

$$U^{exc}/N = 2\pi\rho \int_0^\infty \phi(r)g(r)r^2 dr; \quad (25)$$

the excess virial pressure

$$\beta P^v/\rho - 1 = -\frac{2}{3}\pi\beta\rho \int_0^\infty \frac{d\phi(r)}{dr} g(r)r^3 dr; \quad (26)$$

the bulk modulus calculated from the compressibility equation,

$$B_c = \frac{\beta}{\rho\chi_T} = \frac{1}{S(k=0)}, \quad (27)$$

where χ_T is the isothermal compressibility; and the bulk modulus calculated from the virial equation,

$$B_p = \beta \frac{\partial P^v}{\partial \rho}.$$

For the calculation of B_p once $g(r)$ and $c(r)$ had been calculated, Lado's scheme for Fourier transforms²⁴ was used to determine $\partial \hat{g}(k)/\partial \rho$. Even if slow, this allows us to explicitly calculate and later invert the coefficients matrix of the linear system of equations which enters the calculation of $\partial \hat{g}(k)/\partial \rho$.

TABLE I. We compare various thermodynamic quantities as obtained from the MC simulation of Hansen and Schiff, the RY, HNC, and HNC/H2 closures, for the inverse 12th-power fluid at the freezing point ($z=0.813$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^v/\rho - 1$ the excess virial pressure, and B_c and B_p are the bulk moduli calculated from the compressibility and the virial equations, respectively.

Closure	$U^{exc}/(N\epsilon)$	$\beta P^v/\rho - 1$	B_c	B_p
MC	2.675	18.7	-	72.7
RY ($\alpha=0.603$)	2.626	18.36	69.78	70.13
HNC	3.009	21.04	45.28	80.43
HNC/H2	3.200	22.37	52.66	87.26

A. Inverse power potentials

The general form of the inverse power potential is

$$\phi(r) = \epsilon \left(\frac{\sigma}{r} \right)^n, \quad (28)$$

where $3 < n < \infty$. For this class of fluids the thermodynamics depends only on the dimensionless coupling parameter

$$z = (\rho\sigma^3/\sqrt{2})(\beta\epsilon)^{3/n}. \quad (29)$$

In this paper we choose to fix $\rho^* = 1$ so that Eq. (29) gives the relation between z and T^* .

We performed our calculations on the $n=12, 6$, and 4 fluids at the freezing point. We compared three kind of closures: the one of Rogers and Young²⁵ (RY) with thermodynamic consistency virial compressibility and known to be very close to the simulation results, the hypernetted chain closure, and the HNC/H2 described in Sec. III A. In each case we compared our data with the Monte Carlo (MC) results of Hansen and Schiff.²⁶

1. Inverse 12th-power potential

The freezing point for this fluid is at $z = 0.813$. The RY α parameter to achieve thermodynamic consistency at this value of z is 0.603. Notice that we express α in units of σ and not of $a = (3/4\pi\rho)^{1/3}$ as in the original Rogers and Young's paper.²⁵

In Table I we compare various thermodynamic quantities (the excess internal energy per particle, excess virial pressure, bulk moduli) obtained from the MC simulation of Hansen and Schiff,²⁶ the RY, HNC, and HNC/H2 closures.

In Fig. 1 we compare the MC, HNC, and HNC/H2 results for the pair distribution function.

2. Inverse 6th-power potential

The freezing point for this fluid is at $z = 1.54$. The RY α parameter to achieve thermodynamic consistency at this value of z is 1.209.

In Table II we compare various thermodynamic quantities (the excess internal energy per particle, excess virial pressure, bulk moduli) obtained from the MC simulation of Hansen and Schiff,²⁶ the RY, HNC, and HNC/H2 closures.

3. Inverse 4th-power potential

The freezing point for this fluid is at $z = 3.92$. The RY α parameter to achieve thermodynamic consistency at this value of z is 1.794.

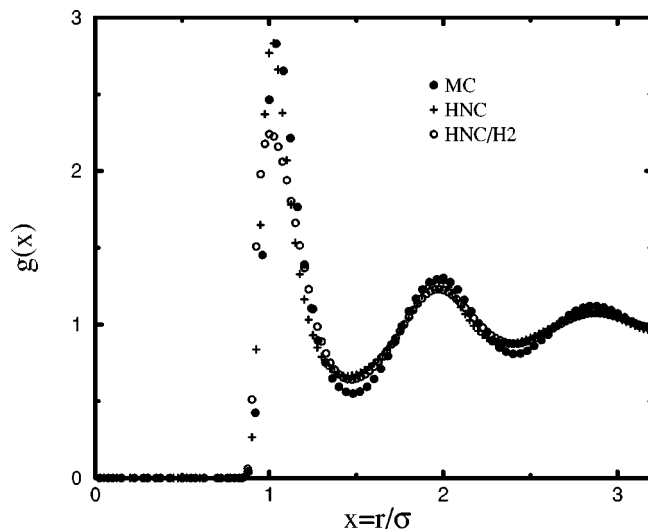


FIG. 1. Comparison of the Monte Carlo (MC), HNC, and HNC/H2 results for the pair distribution function of the inverse 12th-power fluid at $z = 0.813$.

In Table III we compare various thermodynamic quantities (the excess internal energy per particle, excess virial pressure, bulk moduli) obtained from the MC simulation of Hansen and Shiff,²⁶ the RY, HNC, and HNC/H2 closures.

In Fig. 2 we compare the MC, HNC, and HNC/H2 results for the pair distribution function.

B. Spinodal line

In this subsection we study a pair potential with a minimum. In particular we chose the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (30)$$

where ϵ and σ are positive parameters. The critical point for this fluid is at²⁷ $T_c^* = 1.3120 \pm 0.0007$, $\rho_c^* = 0.316 \pm 0.001$, and $P_c^* = 0.1279 \pm 0.0006$.

Integral equations usually fail to have a solution at low temperature and intermediate densities: i.e., in the two-phases unstable region of the phase diagram. In particular it is well known that the HNC approximation is unable to reproduce the *spinodal line*, the locus of points of infinite compressibility in the phase diagram.¹² This is due to the loss of solution as one approaches the unstable region on an isotherm from high or from low densities. The line of loss of solution, in the phase diagram, is called the *termination line*.

TABLE II. We compare various thermodynamic quantities as obtained from the MC simulation of Hansen and Shiff, the RY, HNC, and HNC/H2 closures, for the inverse 6th-power fluid at the freezing point ($z=1.54$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^{(v)}/\rho - 1$ the excess virial pressure, and B_c and B_p are the bulk moduli calculated from the compressibility and the virial equations, respectively.

Closure	$U^{exc}/(N\epsilon)$	$\beta P^{(v)}/\rho - 1$	B_c	B_p
MC	4.090	38.8	-	110.1
RY ($\alpha=1.209$)	4.114	39.03	111.0	111.4
HNC	4.235	40.18	84.02	113.7
HNC/H2	4.283	40.64	88.29	115.8

TABLE III. We compare various thermodynamic quantities as obtained from the MC simulation of Hansen and Shiff, the RY (notice that the bulk moduli were not given in the Rogers and Young's paper and the value of the virial pressure as reported in our table was not corrected to take into account the long-range nature of the potential), the HNC and HNC/H2 closures, for the inverse 4th-power fluid at the freezing point ($z=3.92$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^{(v)}/\rho - 1$ the excess virial pressure, and B_c and B_p are the bulk moduli calculated from the compressibility and the virial equations, respectively.

Closure	$U^{exc}/(N\epsilon)$	$\beta P^{(v)}/\rho - 1$	B_c	B_p
MC	8.233	107.7	-	156
RY ($\alpha=1.794$)	8.001	104.7	250.1	242.9
HNC	8.047	105.3	223.3	244.2
HNC/H2	8.068	105.5	227.0	257.7

According to the discussion of Sec. II, the loss of solution for the HNC approximation can be traced back to the loss of strict convexity of the generating functional.²⁸ Indeed, using the HNC approximation, we computed the bulk modulus from the compressibility equation B_c on several isotherms as a function of the density. At low temperatures we found that at both high density and low density we were unable to continue the isotherm at low values of B_c . Zerah's algorithm either could not get to convergence or it would converge at a nonphysical solution (with a pole in the structure factor at some finite wave vector k). Since HNC/H2 has, by construction, an always strictly convex generating functional, we expect it to be able to approximate a spinodal line (there should be no termination line).

In Fig. 3 we show the behavior of B_c on several isotherms as a function of density, calculated with the HNC/H2 approximation. We see that now there are no termination points. B_c never becomes exactly zero, and the low-temperature isotherms develop a bump in the intermediate-density region. The same plot for the bulk modulus calculated from the virial pressure B_p shows that at low temperatures this bulk modulus indeed becomes zero along the isotherms both at high and low densities.

In Fig. 4 the pressure is plotted as a function of the density on several isotherms for the HNC/H2 approximation. Apart from the fact that we find negative pressures, the isotherms have a van der Waals—like behavior.

The graphical analysis of the pressure plotted as a function of the chemical potential shows that the coexistence of the two phases (points where the curve crosses itself) is possible and is lost between $T^* = 1.1$ and $T^* = 1.2$. There generally are two points of coexistence.

V. IMPROVING THE CLOSURES

The numerical results for HNC/H2 exhibit interesting features as far as the coexistence region is concerned but show unambiguously a worst agreement with the MC structural data in correspondence with a marginal improvement in the thermodynamics.

We feel that the main problem is the difficulty of an accurate description of the bridge functions in terms of powers of the pair correlation function. Recent investigations of improved closures seem to point to the indirect correlation function $\gamma(r)$ or some renormalized version of it as the best

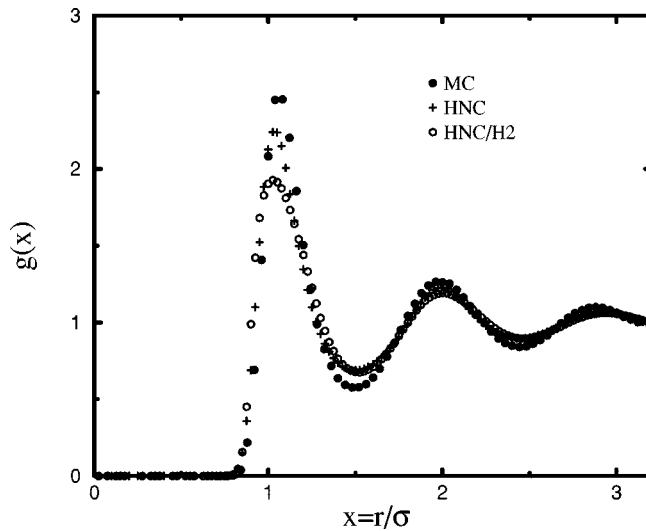


FIG. 2. Comparison of the Monte Carlo (MC), HNC, and HNC/H2 results for the pair distribution function of the inverse 4th-power fluid at $z=3.92$.

starting point for progress. However, before moving to more complex relations or functional dependences, we have explored two possible directions for improving the HNC/H2 closure. In the first approach we have tried to follow the reference hypernetted chain (RHNC) approach by Lado.²⁹ In the second we have explored the possibilities of optimization offered by the numerical coefficient of the cubic term in the generating functional.

A. Pseudobridge functions for HNC/H2

From the graphical analysis of the pair distribution function it is known¹ that $g(r)$ may be written as

$$g(r) = \exp[-\beta\phi(r) + \gamma(r) + B(r)], \tag{31}$$

where $\gamma(r) = h(r) - c(r)$ is the sum of all the series-type diagrams and $B(r)$ the sum of bridge-type diagrams. If we take

$$B(r) = -\frac{1}{2}h^2(r) + G(r), \tag{32}$$

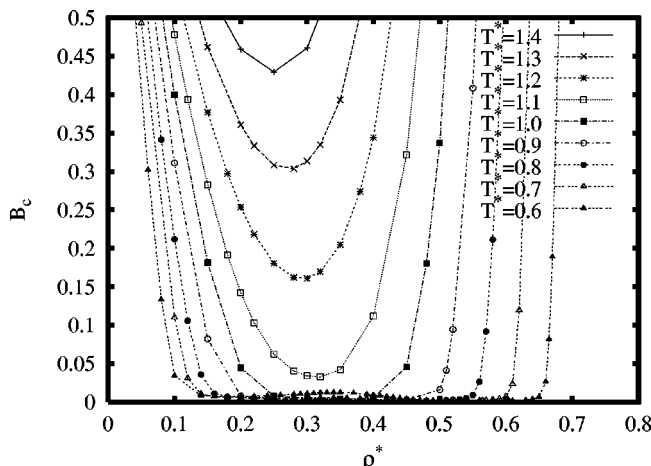


FIG. 3. Behavior of B_c of the Lennard-Jones fluid, on several isotherms as a function of the density for the HNC/H2 approximation.

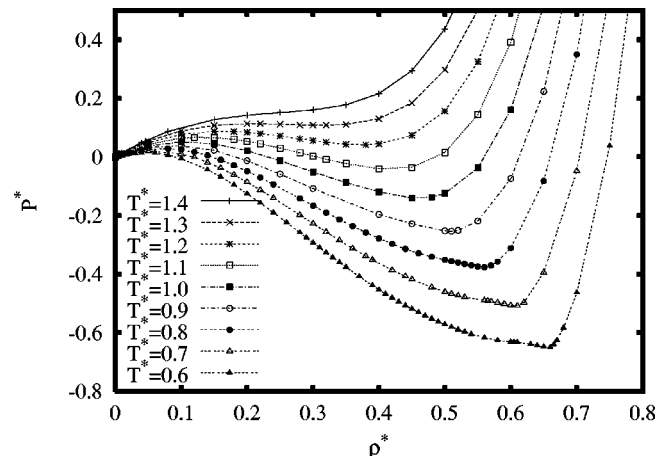


FIG. 4. Behavior of the pressure of the Lennard-Jones fluid, on several isotherms as a function of the density for the HNC/H2 approximation.

we have that our HNC/H2 approximation amounts to setting $G(r) = 0$. Rosenfeld and Ashcroft⁶ proposed that $B(r)$ should be essentially the same for all potentials $\phi(r)$. We now make a similar proposal for the G function, and we will refer to it as the *pseudobridge function*. In the same spirit of the RHNC approximation of Lado²⁹ we will approximate $G(r)$ with the G function of a short-range (reference) potential $\phi_0(r)$. Assuming known the properties of the reference system, we can calculate the G function as follows:

$$G_0(r) = \ln[g_0(r)e^{\beta\phi_0(r)}] - \gamma_0(r) + \frac{1}{2}h_0^2(r). \tag{33}$$

The reference HNC/H2 (RHNC/H2) approximation is then

$$g(r) = \exp\left(-\beta\phi(r) + \gamma(r) - \frac{1}{2}h^2(r) + G_0(r)\right). \tag{34}$$

An expression for the free-energy functional can be obtained *turning on* the potential $\phi(r)$ in two stages: first, from the noninteracting state to the reference potential $\phi_0(r)$ and then from there to the full potential $\phi(r)$. To this end we write

$$\phi(r; \lambda_0, \lambda_1) = \lambda_0\phi_0(r) + \lambda_1\Delta\phi(r), \tag{35}$$

with $\Delta\phi(r) = \phi(r) - \phi_0(r)$. Following the same steps as in Ref. 7 we obtain, for the excess free energy per particle,

$$f^{exc} = f_1 + f_2 + f_3^{(0)} + \Delta f_3, \tag{36}$$

where the first two terms were already encountered in Sec. II:

$$\beta f_1 = \frac{1}{2}\rho \int d\mathbf{r} \{1 + g(r)(\ln[g(r)e^{\beta\phi(r)}] - 1) - h^2(r)/2 + h^3(r)/6\}, \tag{37}$$

$$\beta f_2 = \frac{1}{2\rho} \int \frac{d\mathbf{k}}{(2\pi)^3} \{\rho\hat{h}(k) - \ln[1 + \rho\hat{h}(k)]\}. \tag{38}$$

The third term is assumed known:

$$\begin{aligned} \beta f_3^{(0)} &= -\frac{1}{2}\rho \int d\mathbf{r} \int_0^1 d\lambda_0 G(r; \lambda_0, 0) \frac{\partial g(r; \lambda_0, 0)}{\partial \lambda_0} \\ &= \beta(f^{(0)} - f_1^{(0)} - f_2^{(0)}); \end{aligned} \tag{39}$$

here, $f^{(0)}$ is the excess free energy per particle of the refer-

ence system and $f_1^{(0)}, f_2^{(0)}$ are defined as in Eqs. (37), (38) for the reference potential and its corresponding correlation functions. The last term is

$$\beta\Delta f_3 = -\frac{1}{2}\rho \int d\mathbf{r} \int_0^1 d\lambda_1 G(r; 1, \lambda_1) \frac{\partial g(r; 1, \lambda_1)}{\partial \lambda_1}. \quad (40)$$

According to our proposal, G is insensitive to a change in potential from ϕ_0 to ϕ . We may then approximate this last term as follows:

$$\beta\Delta f_3 \approx -\frac{1}{2}\rho \int d\mathbf{r} G_0(r) [g(r) - g_0(r)]. \quad (41)$$

Now that we have the free energy we may consider it as a functional of both $h(r)$ and $G_0(r)$ and take its variation with respect to these functions. We find

$$\begin{aligned} \beta\delta f^{exc} = & \frac{1}{2}\rho \int d\mathbf{r} \{c(r) - h(r) + h^2(r)/2 + \ln[g(r)e^{\beta\phi(r)}] \\ & - G_0(r)\} \delta h(r) - \frac{1}{2}\rho \int d\mathbf{r} [g(r) - g_0(r)] \delta G_0(r). \end{aligned} \quad (42)$$

It follows that the free energy is minimized when both the RHNC/H2 closure [Eq. (34)] is satisfied and when the constraint

$$\int d\mathbf{r} [g(r) - g_0(r)] \delta G_0(r) = 0 \quad (43)$$

is fulfilled.

Taking the second functional derivative of f^{exc} with respect to $h(r)$ we find that also this free energy is a strictly convex functional of the total correlation function. This property was lacking in the RHNC theory and constitutes the main feature of the RHNC/H2 closure. As already stressed in Sec. III A it ensures that if a solution to the integral equation exists it has to be unique.

The constraint, as for RHNC, gives a certain thermodynamic consistency to the theory (see Ref. 7). If we choose a hard sphere reference potential $\phi_0(r) = \phi_0(r; \sigma)$ which depends on the length scale σ , the optimum values of the parameters that makes the generating functional a free energy can be determined by the constraint (43) which becomes

$$\int d\mathbf{r} [g(r) - g_0(r)] \frac{\partial G_0(r)}{\partial \sigma} = 0. \quad (44)$$

However, neither the hard-sphere pseudobridge functions nor some empirical attempt to model the unknown function via a Yukawa function provided useful results.

B. Optimized HNC/H3 approximation

For $\gamma=0$ HNC/H3 reduces to HNC/H2. For $\gamma>0$ the first peak of the pair distribution function is dumped with respect to the one of the pair distribution function calculated with HNC/H2. For $\gamma<0$ the first peak increases giving in general a better fit to the simulation data.

In Fig. 5 we compare the pair distribution function of the Lennard-Jones fluid near its triple point, calculated with a molecular dynamic simulation,²¹ the HNC/H2 approxima-

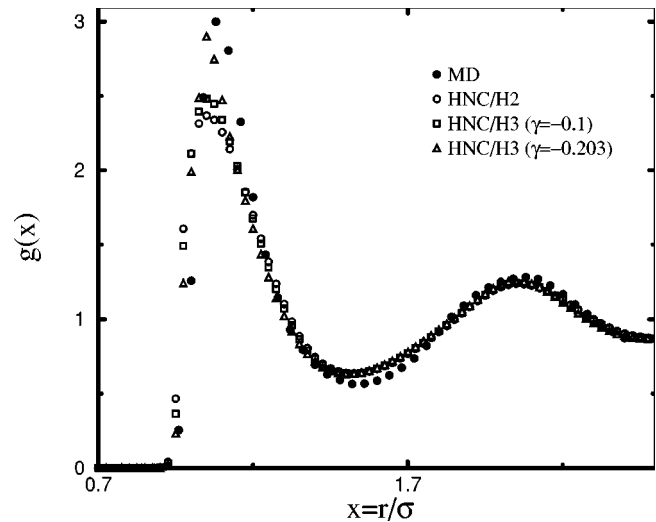


FIG. 5. Comparison of the pair distribution function of a Lennard-Jones fluid at $\rho^*=0.85$ and $T^*=0.719$, computed from the molecular dynamic (MD) simulation of Verlet, the HNC/H2 approximation, and the HNC/H3 approximation. For HNC/H3 we present results obtained setting $\gamma=-0.1$ (when the generating functional of the approximation is still strictly convex) and $\gamma=-0.203$ (which gives the best fit possible to the simulation data but does not ensure the strict convexity of the generating functional).

tion, the approximation HNC/H3 with $\gamma=-0.203$ (at lower values of γ Zerah's algorithm would fail to converge), and the approximation HNC/H3 with $\gamma=-0.1$ (when the generating functional of HNC/H3 is still strictly convex). As we can see HNC/H3 fits the simulation data better than HNC/H2 even if the first peak is still slightly displaced to the left of the simulation data, a well-known problem of the HNC approximation.⁶

The best results are given by HNC/H3 with $\gamma=-0.203$. Note that the HNC/H3 generating functional at this value of γ is not strictly convex (strict convexity is lost for $\gamma \leq -1/9$). The first peak of the static structure factor is at $k\sigma \approx 6.75$ and has a magnitude of 2.41, a quite low value for a liquid near the triple point. We have calculated the pressure and the internal energy. We found $\beta P/\rho \approx 3.87$ and $U^{exc}/(N\epsilon) \approx -5.72$ [very close to the HNC results $\beta P/\rho \approx 3.12$ and $U^{exc}/(N\epsilon) \approx -5.87$] to be compared with the simulation results³⁰ 0.36 and -6.12 , respectively. The bulk moduli are $B_c \approx 11.74$ and $B_p \approx 36.61$ which shows that at the chosen value of γ we do not have the thermodynamic consistency virial compressibility and we do not improve on HNC inconsistency (using HNC we find $B_c \approx 7.09$ and $B_p \approx 32.72$).

VI. CONCLUSIONS

In this paper we have analyzed the relations between generating functionals, thermodynamic consistency, and uniqueness of the solution of the integral equations of liquid-state theory. We think that the requirement of deriving from a free energy and the uniqueness of the solution are two important ingredients to enforce in the quest for better closures. The former requirement is of course crucial to get virial-energy consistency. But it is also important to get integral equations able to provide a closed formula for the chemical potential without additional approximations. This last issue

looks highly desirable for applications of IET to the determination of phase diagrams. The latter is certainly a useful constraint from the numerical point of view but it is also a very strong condition, probably able to avoid some non physical behavior in the coexistence region, although this point would deserve further investigation. Most of the existing closures fail to satisfy the condition of uniqueness of the solution. Among them, only the optimized random phase approximation by Andersen and Chandler^{18,31} satisfies both constraints although they were not used in the original derivation of the approximation. One obvious question is whether the enforcement of these constraints automatically results in improved closures.

In this work, we have started an exploration of the capabilities of the combined requirement of consistency and uniqueness, starting with simple modifications to the HNC closure, corresponding to the addition of a square and a cubic power of $h(r)$ in the HNC functional. We found a couple of approximations (HNC/H2 and HNC/H3), which have built in the virial-free-energy thermodynamic consistency and have a unique solution.

We numerically tested these closures on inverse power and the Lennard-Jones fluid. From the tests on the inverse-power potential fluids one can see that the HNC/H2 approximation is comparable to HNC for the thermodynamic quantities and performs worse than RY and even HNC for structural properties. The tests on the Lennard-Jones fluid revealed that this approximation does not suffer from the presence of a termination line (present in HNC and almost all the existing closures). This allowed us to follow isotherms from the low-density to the high-density region, and this behavior would be very useful in the study of the phase coexistence. However, the thermodynamic results show only a marginal improvement on HNC and the structure is definitely worse.

Our trials to improve HNC/H2 in the same spirit of the modified HNC approaches did not succeed. We feel that the main reason is in the difficulty of modeling the real bridge functions through a polynomial in the function $h(r)$. In this respect, approaches based on generating functionals depending on the indirect correlation function $\gamma(r)$ look more promising but we have not tried them yet.

Much better results for the structure are found with HNC/H3 as is shown in Fig. 5. However, probably for the same reasons just discussed, one has to give up to have an approximation with a strictly convex generating functional depending on $h(r)$. The thermodynamics reproduced by HNC/H3 is not yet satisfactory: due to the slight left shift of the main peak of the $g(r)$, the calculated pressure misses the simulation result. Nonetheless, the presence of the free parameter γ in HNC/H3 leaves open the possibility of imposing the thermodynamic consistency virial compressibility. If the value of the parameter needed to have the consistency is bigger than $-1/[3\text{supg}(r)]$, then we would have an approximation which is completely thermodynamically consistent and have a unique solution. This strategy may eventually lead us to discover that the price we have to pay to have a completely thermodynamically consistent approximation is the loss of strict convexity of the generating functional.

APPENDIX A: GENERATING FUNCTIONALS OF γ

Often in the numerical solution of the OZ plus closure integral equation use is made of the auxiliary function $\gamma(r) = h(r) - c(r)$. Suppose that the closure relation can be written as

$$\rho^2 c(r) = -\Psi\{\gamma(r)\}, \tag{A1}$$

where Ψ is a local function of the function γ and has a dependence on the value of the pair potential not explicitly shown.

We want to translate the integral equation into a variational principle involving functionals of $\gamma(r)$. Then we introduce a closure functional $\mathcal{F}_{cl}[\gamma]$ such that

$$\frac{\delta \mathcal{F}_{cl}[\gamma]}{\delta \gamma(r)} = \Psi\{\gamma(r)\} \tag{A2}$$

and an OZ functional $\mathcal{F}_{OZ,c}[\gamma]$ such that, when $c(r)$ and $\gamma(r)$ satisfy the OZ equation, we have

$$\frac{\delta \mathcal{F}_{OZ,c}[\gamma]}{\delta \gamma(r)} = \rho^2 c(r). \tag{A3}$$

Then when both the closure and the OZ relations are satisfied, the functional $\mathcal{F} = \mathcal{F}_{cl} + \mathcal{F}_{OZ,c}$ is stationary with respect to variations of $\gamma(r)$: i.e.,

$$\frac{\delta \mathcal{F}[\gamma]}{\delta \gamma(r)} = 0. \tag{A4}$$

This is the variational principle sought.

Now, we want to find $\mathcal{F}_{OZ,c}$. The OZ equation in k space is

$$\rho \hat{c}^2(k) + \rho \hat{\gamma}(k) \hat{c}(k) - \hat{\gamma}(k) = 0. \tag{A5}$$

When we solve it for \hat{c} we find two solutions

$$\hat{c} = \frac{-\hat{\Gamma} \pm \sqrt{\hat{\Gamma}^2 + 4\hat{\Gamma}}}{2\rho}, \tag{A6}$$

where $\hat{\Gamma}(k) = \rho \hat{\gamma}(k)$ is always positive since

$$\hat{\Gamma} = \rho^2 \hat{h} \hat{c} = \rho^2 \frac{\hat{h}^2}{1 + \rho \hat{h}} = \rho^2 \frac{\hat{h}^2}{S(k)}, \tag{A7}$$

$S(k)$ being the liquid static structure factor which is positive definite for all k . Since $\hat{c}(k)$ is a function which oscillates around 0, where \hat{c} is negative we have to choose the solution with the minus sign, where it is positive the one with the plus sign. In particular, if the isothermal compressibility of the liquid χ_T is smaller than the one of the ideal gas, χ_T^0 , we have that

$$\hat{c}(0) = \frac{1}{\rho} \left(1 - \frac{\chi_T^0}{\chi_T} \right) < 0, \tag{A8}$$

and we have to start with the minus sign.

The functional we are looking for is then [see Eq. (30) in Ref. 15, with the constant set equal to zero]

$$\mathcal{F}_{Oz,c}[\gamma] = \int_0^1 dt \int d\mathbf{r} \gamma(r) \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\rho}{2} e^{i\mathbf{k}\cdot\mathbf{r}} \times [-t\hat{\Gamma}(k) + s_c(k) \sqrt{t^2\hat{\Gamma}^2(k) + 4t\hat{\Gamma}(k)}], \quad (\text{A9})$$

where $s_c(k)$ is +1 when $\hat{c}(k) \geq 0$ and -1 when $\hat{c}(k) < 0$. Rearranging the integrals and making the change of variable $y = t\hat{\Gamma}$ we find

$$\begin{aligned} \mathcal{F}_{Oz,c}[\gamma] &= \frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \int_0^{\hat{\Gamma}(k)} dy [-y + s_c(k) \sqrt{y^2 + 4y}] \\ &= \int \frac{d\mathbf{k}}{(2\pi)^3} \{ -\hat{\Gamma}^2/4 + s_c(k) \\ &\quad \times ((1 + \hat{\Gamma}/2) \sqrt{(1 + \hat{\Gamma}/2)^2 - 1} \\ &\quad - \ln[1 + \hat{\Gamma}/2 + \sqrt{(1 + \hat{\Gamma}/2)^2 - 1}]) \}. \quad (\text{A10}) \end{aligned}$$

If the closure relation has the form

$$\rho^2 h(r) = -\Psi\{\gamma(r)\}, \quad (\text{A11})$$

we can derive the corresponding functional using the same procedure. The final result is a functional $\mathcal{F}_{Oz,h}[\gamma]$ which differs from Eq. (A10) for a plus sign in front of the first term in the integral.

However, by examining their second functional derivatives, we notice that both $\mathcal{F}_{Oz,c}[\gamma]$ and $\mathcal{F}_{Oz,h}[\gamma]$ are not certainly convex or concave. Thus, any check of the convexity properties of generating functionals of the $\gamma(r)$ function should be done on the full functional.

APPENDIX B: THERMODYNAMIC CONSISTENCY

For a homogeneous liquid interacting through a pair potential $\phi(r)$, the Helmholtz free energy per particle, f , can be considered a functional of ϕ . Indeed, in the canonical ensemble, one has

$$\beta f[\phi] = \beta f_0 - \frac{1}{N} \ln \left(\frac{1}{V^N} \int \exp \left[-\beta \frac{1}{2} \sum_{i \neq j} \phi(\mathbf{r}_{ij}) \right] d\mathbf{r}_1 \cdots d\mathbf{r}_N \right), \quad (\text{B1})$$

where f_0 is the free energy per particle of the ideal gas ($\phi=0$) and V is the volume of the liquid. Taking the functional derivative with respect to $\beta\phi(r)$ one finds

$$\frac{\delta\beta f[\phi]}{\delta\beta\phi(r)} = \frac{\rho}{2} g(r). \quad (\text{B2})$$

Imagine that we found a functional $\mathcal{A}([h],[\phi],\rho,\beta)$ that has an extremum for those correlation functions that solve the OZ and the closure system of equations. Suppose further that such functional has the property

$$\frac{\delta\beta\mathcal{A}}{\delta\beta\phi(r)} = \frac{\rho}{2} g(r), \quad (\text{B3})$$

which can be rewritten more explicitly as follows:

$$\left. \frac{\delta\beta\mathcal{A}}{\delta\beta\phi(r)} \right|_{[h],\rho,\beta} + \int d\mathbf{r}' \left. \frac{\delta\beta\mathcal{A}}{\delta h(r')} \right|_{[\phi],\rho,\beta} \frac{\delta h(r')}{\delta\beta\phi(r)} = \frac{\rho}{2} g(r). \quad (\text{B4})$$

Evaluating this expression on the correlation function \bar{h} solution of the OZ plus closure system of equations, which is an extremum for \mathcal{A} , we find

$$\left. \frac{\delta\beta\mathcal{A}}{\delta\beta\phi(r)} \right|_{[\bar{h}],\rho,\beta} = \frac{\rho}{2} \bar{g}(r). \quad (\text{B5})$$

Then we can write

$$\begin{aligned} \beta\mathcal{A}([\bar{h}],[\phi],\rho,\beta) &= \int d\mathbf{r} \left. \frac{\delta\beta\mathcal{A}}{\delta\beta\phi(r)} \right|_{[\bar{h}],\rho,\beta} \beta\phi(r) \\ &\quad + \mathcal{D}([\bar{h}],\rho,\beta), \quad (\text{B6}) \end{aligned}$$

with \mathcal{D} a functional independent of ϕ . Changing variables to adimensional ones, $\mathbf{r} = \mathbf{r}^* \rho^{-1/3}$ and using Eq. (B5) we find

$$\begin{aligned} \beta\mathcal{A}([\bar{h}^*],[\phi],\rho,\beta) &= \frac{1}{2} \int d\mathbf{r}^* \bar{g}^*(r^*) \beta\phi(r^* \rho^{-1/3}) \\ &\quad + \mathcal{D}([\bar{h}^*],\rho,\beta), \quad (\text{B7}) \end{aligned}$$

where we defined new distribution functions $g^*(r^*) = g(r^* \rho^{-1/3})$. If \mathcal{D} has no explicit dependence on ρ , then one readily finds

$$\begin{aligned} \rho \frac{\partial\beta\mathcal{A}([\bar{h}^*],[\phi],\rho,\beta)}{\partial\rho} &= -\frac{\rho}{6} \int d\mathbf{r}^* \bar{g}^*(r^*) \beta\phi'(r^* \rho^{-1/3}) r^* \rho^{-4/3} \\ &= -\frac{\rho}{6} \int d\mathbf{r} \bar{g}(r) \beta\phi'(r) r = \beta P^{exc}/\rho, \quad (\text{B8}) \end{aligned}$$

where again we used the fact that \mathcal{A} has an extremum for $h = \bar{h}$. We used a prime to denote a derivative with respect to the argument, and P^{exc} is the excess pressure of the liquid.

If \mathcal{D} has no explicit dependence on β , we also find

$$\frac{\partial\beta\mathcal{A}([\bar{h}^*],[\phi],\rho,\beta)}{\partial\beta} = \frac{\rho}{2} \int d\mathbf{r} \bar{g}(r) \phi(r) = U^{exc}/N, \quad (\text{B9})$$

where U^{exc} is the excess internal energy.

If \mathcal{D} has no explicit dependence on both β and ρ , $\mathcal{D}([\bar{h}^*],\rho,\beta) = \mathcal{D}([\bar{h}^*])$, we conclude from Eqs. (B8) and (B9) that

$$\mathcal{A}([\bar{h}^*],[\phi],\rho,\beta) = f^{exc}(\rho,\beta) + \text{const}, \quad (\text{B10})$$

where f^{exc} is the excess free energy per particle of the fluid. Under these circumstances we see from Eq. (B8) that we have thermodynamic consistency between the route to the pressure going through the partial derivative of the free energy and the route to the pressure going through the virial theorem.

APPENDIX C: STRICT CONVEXITY OF $\mathcal{F}_{OZ}[h]$

It can be proved that the functional

$$\mathcal{F}_{OZ}[h] = \int \frac{d\mathbf{k}}{(2\pi)^3} \{ \rho \hat{h}(k) - \ln[1 + \rho \hat{h}(k)] \}, \quad (\text{C1})$$

defined on the convex set

$$D_c = \{ h(r) | S(k) > 0 \quad \forall k \}, \quad (\text{C2})$$

is a strictly convex functional. The strict convexity is a trivial consequence of the strict convexity of the integrand in Eq. (C1).

It remains to prove that D_c is a convex set. Given two elements of this set h' and h'' , we need to show that $h = \lambda h' + (1 - \lambda)h''$ is an element of D_c for all $\lambda \in [0, 1]$. Since

$$\begin{aligned} S(k) &= 1 + \rho \hat{h}(k) \\ &= 1 + \rho [\lambda \hat{h}'(k) + (1 - \lambda) \hat{h}''(k)] \\ &= 1 + \lambda [S'(k) - 1] + (1 - \lambda) [S''(k) - 1] \\ &= \lambda S'(k) + (1 - \lambda) S''(k) > 0 \quad \forall \lambda \in [0, 1], \end{aligned} \quad (\text{C3})$$

then D_c is a convex set.

¹J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, London, 1986).

²C. Caccamo, Phys. Rep. **274**, 1 (1996).

³M. Born and H. S. Green, Proc. R. Soc. London, Ser. A **188**, 10 (1946).

⁴J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).

⁵J. M. J. van Leeuwen, J. Groenvelde, and J. De Boer, Physica **25**, 792 (1959).

⁶Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A **20**, 1208 (1979).

⁷F. Lado, S. M. Foiles, and N. W. Ashcroft, Phys. Rev. A **28**, 2374 (1983).

⁸L. Verlet, Mol. Phys. **41**, 183 (1980).

⁹G. A. Martynov and G. N. Sarkisov, Mol. Phys. **49**, 1495 (1983).

¹⁰D.-M. Duh and A. D. J. Haymet, J. Chem. Phys. **103**, 2625 (1995).

¹¹T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, 537 (1961).

¹²L. Belloni, J. Chem. Phys. **98**, 8080 (1993).

¹³P. D. Poll and N. W. Ashcroft, Phys. Rev. A **35**, 5167 (1987).

¹⁴A. Schlijper, M. Telo de Gama, and P. Ferreira, J. Chem. Phys. **98**, 1534 (1989).

¹⁵W. Olivares and D. A. McQuarrie, J. Chem. Phys. **65**, 3604 (1976).

¹⁶S. Høye and G. Stell, J. Chem. Phys. **67**, 439 (1977).

¹⁷G. Pastore, Mol. Phys. **63**, 731 (1988).

¹⁸G. Pastore, O. Akinlade, F. Matthews, and Z. Badir Khan, Phys. Rev. E **57**, 460 (1998).

¹⁹R. Kjellander and S. Sarman, J. Chem. Phys. **90**, 2768 (1989).

²⁰L. Lee, J. Chem. Phys. **97**, 8606 (1992).

²¹L. Verlet, Phys. Rev. **165**, 201 (1968).

²²Our first trial should really be $c = -\ln g - \beta\phi$, which should be called HNC/H1. We have tested numerically this closure, and we found that it performed worse than HNC/H2 for both the structure and thermodynamics of the system under examination.

²³G. Zerah, J. Comput. Phys. **61**, 280 (1985).

²⁴F. Lado, J. Comput. Phys. **8**, 417 (1971).

²⁵F. J. Rogers and D. A. Young, Phys. Rev. A **30**, 999 (1984).

²⁶J. P. Hansen and D. Shiff, Mol. Phys. **25**, 1281 (1973).

²⁷J. J. Potoff and A. Z. Panagiotopoulos, J. Chem. Phys. **109**, 10914 (1998).

²⁸P. G. Ferreira, R. L. Carvalho, M. M. Telo de Gama, and A. G. Schlijper, J. Chem. Phys. **101**, 594 (1994).

²⁹F. Lado, Phys. Rev. A **8**, 2548 (1973).

³⁰L. Verlet, Phys. Rev. **159**, 98 (1967).

³¹H. C. Andersen and D. Chandler, J. Chem. Phys. **57**, 1918 (1972).