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Comments on the Variational Modified-Hypernetted-Chain Theory for Simple Fluids

Yaakov Rosenfeld[1]

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The variational modified-hypernetted-chain (VMHNC) theory, based on the approximation of universality of the bridge functions, is reformulated. The new formulation includes recent calculations by Lado and by Lado, Foiles, and Ashcroft, as two stages in a systematic approach which is analyzed. A variational iterative procedure for solving the exact (diagrammatic) equations for the fluid structure which is formally identical to the VMHNC is described, featuring the theory of simple classical fluids as a one-iteration theory. An accurate method for calculating the pair structure for a given potential and for inverting structure factor data in order to obtain the potential *and* the thermodynamic functions, follows from our analysis.

KEY WORDS: Modified-hypernetted-chain theory; bridge functions; local free energy functionals; diagrammatic expansion; structure factor.

1. INTRODUCTION

Recently Lado$^{(1)}$ and Lado, Foiles, and Ashcroft$^{(2)}$,[2] (LFA) used the Rosenfeld–Ashcroft$^{(3)}$ modified-hypernetted-chain (MHNC) scheme based on the universality of the bridge functions, and determined the optimum bridge function parameters by minimizing an approximate free energy functional. Solving the resulting MHNC integral equations with hard-sphere bridge functions of adjustable core size, they obtained excellent agreement with the simulation data for the structure and the thermodynamics of both the short-range Lennard-Jones and the long-range Coulomb potentials. The method they applied provides an entirely first

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[1] Nuclear Research Centre—Negev, P.O. Box 9001 Beer-Sheva, Israel.

[2] Note the difference notations: our B corresponds to $-B$ in Refs. 1 and 2.

principles approach to the theory of the structure and thermodynamics of simple classical liquids: it employs a *local* (i.e., without the need to integrate along an isotherm or isochore) free energy functional that determines by variation both the structure and the equation of state. The possibility of constructing an accurate approximate local free energy functional for simple classical fluids, its relation to the variational perturbation theory and additivity of equations of state, and its relevance to the problem of inverting structure factor data, have been recently analyzed in detail.$^{(4)}$

As examples of MHNC calculations are becomming available for increasing numbers and types of systems,$^{(5-11)}$ a systematic development of a local MHNC scheme is timely. In the present work we make a step in that direction by formulating a systematic variational MHNC (VMHNC) procedure within one particular successful representation for the bridge functions. As examples of the utility of the present formulation, we demonstrate how it is possible to feature the methods of Refs. 1 and 2 as two stages, of increasing accuracy, in a systematic "bootstrap" procedure based on the approximation of universality of the bridge functions, and to calculate analytically the term in the free energy which causes the improvement of the LFA results over those by Lado. This enables a simple pictorial analysis of the terms missing in the treatments by Lado$^{(1)}$ and by LFA,$^{(2)}$ without the need to perform any additional numerical calculations, and leads to a single, highly accurate recipe for both (a) calculating the pair functions and the equation of state for simple liquids of given pair potential, and (b) inverting pair structure data in order to obtain in the potential. Our bootstrap approach within the VMHNC scheme is analogous to that employed with the variational first-order thermodynamic perturbation theory (VPT) for which it was first proposed by Ross$^{(12)}$ and recently analyzed.$^{(13)}$

The new formulation of the VMHNC also enables us to draw direct conclutions regarding the diagrammatic iterative "build-up" of liquid state theory: We construct a variational diagrammatic iterative procedure which takes advantage of the similarity between the zero-order structure given by the HNC approximation, and the final result (presumably well) represented by the simulation data. Each iteration order is obtained from the previous one by a VMHNC-type calculation. It is argued on the basis of our analysis that the first such iteration beyond the "zero-order" HNC result is comparable in accuracy with present day simulation data. The theory of simple classical fluids thus exhibits the interesting property of being essentially a one-iteration theory as far as the pair structure and (noncritical) thermodynamics are concerned, provided this iteration is optimized.

The present formulation and methods of analysis, made here with one particular choice for the bridge functions, can be readily extended to mixtures and to general bridge functions.

This paper is organized as follows: Section 2 and 3 give an exposition of the VMHNC procedure using specifically the Percus–Yevick hard-sphere bridge functions, of the signle parameter η, for which most MHNC calculations have been performed. Different representations for the correction to the free energy functional of Lado,(1) denoted by $\delta_{\phi}(\eta)$, are considered in Section 4. Analysis of the function $\delta_{\phi}(\eta)$. for different potentials $\phi(r)$, based on the results presented in Refs. 1 and 2 and on accumulated MHNC results for different types of pair interactions is given in Section 5. The variational iteration procedure for solving the exact diagrammatic equations for the pair structure is presented and discussed in Section 6. The concluding Section 7 includes the recipe for calculating the structure and thermodynamics of a simple fluid for a given pair potential, and for inverting structure factor data in order to obtain the potential *and* the free energy.

2. A SHORT RESUME OF THE MODIFIED-HNC SCHEME

The analysis of the density expansion of the pair correlation function $g(r)$ has led to the following equations(14):

$$h(x) = c(x) + \int d\mathbf{x}'\, h(|\mathbf{x} - \mathbf{x}'|)\, c(x') \tag{1}$$

$$c(x) = h(x) - \ln\{g(x) \exp[\beta\phi(x/\rho^{1/3}) + B(x)]\} \tag{2}$$

$$B(x) = -\sum_{E} h(x) = \mathscr{B}\{h(x)\} \tag{3}$$

The first equation is the Ornstein–Zernike (OZ) relation defining the direct correlation function $c(x)$ in terms of the total correlation function $h(x) = g(x) - 1$. In the second, a closure equation, $\phi(r)$ is the pair potential, $\rho = N/V$ is the number density, $\beta = (k_B T)^{-1}$ is the inverse temperature, and $B(x)$ is minus the sum of all elementary diagrams with $h(x)$ bonds that have at least triply connected field points, denoted by the functional $\mathscr{B}$. Throughout the paper we use the reduced length $x = r\rho^{1/3}$, and the "tilde" sign denotes Fourier transforms, e.g., $\tilde{h}(k)$.

The formal relation (3) cannot be utilized in practice, but the approximation embodied by the statement of "universality of the bridge functions" led, through the MHNC scheme, to an extremely accurate description of the available simulation data for a large class of simple classical fluids.(3,15–17) Consider, in particular, the one-parameter bridge functions obtained from the analytic solution of the Percus–Yevick (PY) equation for hard spheres,(18)

$$B(x, \eta) = y_{\mathrm{PY}}(x, \eta) - 1 - \ln y_{\mathrm{PY}}(x, \eta) \tag{4}$$

Within the PY theory for hard spheres, the function $y(x) = g(x) \exp[\beta\phi(x/\rho^{1/3})]$ is given by

$$y_{\mathrm{PY}}(x, \eta) = g_{\mathrm{PY}}(x, \eta), \qquad x > (6\eta/\pi)^{1/3} \tag{5}$$

$$y_{\mathrm{PY}}(x, \eta) = -c_{\mathrm{PY}}(x, \eta), \qquad x \leqslant (6\eta/\pi)^{1/2} \tag{6}$$

With the "optimum" value, $\eta = \eta_{\mathrm{UPY}}(\beta, \rho)$, obtained by requiring thermodynamic consistency between the equation of state obtained from the virial theorem and the compressibility equation, the solutions of Eqs. (1)–(4), denoted by "UPY," are essentially indistinguishable from the simulation data.(3,15–17)

The most important feature of the UPY results (and thus of the similarly motivated VMHNC calculations) is that they give accurate predictions for the "screening" function $H(r) = \ln y(r)$ at $r = 0$, despite the fact that the calculated $g(r)$ and $c(r)$ are practically independent of the values of $B(r)$ in the region where $g(r) \cong 0$. This provides a crucial test for the validity of the assumption of universality within the diagrammatic contex.(15,19,20) This feature is unique for the self-consistency schemes based on the "universality." All other presently available self-consistency schemes(21–23) fail to give accurate $H(0)$ either because they treat only the long-range behavior of the bridge function,(21) or because they implicitly contain the usual PY approximation for the short-range behavior.(22) A systematic MHNC approach would be to maintain the UPY as the leading result and to seek the relatively small (nonuniversal) corrections, especially regarding the long-range behavior of the bridge functions.(8)

As originally predicted in Ref. 3, all MHNC calculations that use a self-consistency criterion in order to determine the bridge parameter $\eta(\beta, \rho)$ yield essentially identical results with either the PY hard sphere bridge functions or the Verlet–Weis–Grundke–Henderson(24,25) (VWGH) parametrized form for the "exact" hard sphere simulation results employed by LFA. In view of this, the fact that LFA improve upon the results by Lado is due to employing a better local choice of the parameter within essentially the same bridge function. Although not important thermodynamically, the analytic deficiencies of the VWGH parametrized bridge functions as encountered by LFA, have a significant effect on the structure. This undermines the basic contribution of the VMHNC approach, namely, the possibility it provides for inverting structure factor data. The PY bridge functions [Eqs. (4)–(6)] behave analytically better than the VWGH functions. In turn, the UPY results which provide as good a description as the VWGH parametrization for the system of hard spheres, should be also preferred heuristically since they are obtained without any resort to the simulations.

In view of the good analytic behavior of the PY bridge functions and the general high accuracy obtained by the UPY it is only natural that a first step in formulating a local theory would be to try it within the level of the UPY accuracy; i.e., we shall seek a simplified criterion for determining $\eta(\beta, \rho)$ locally yet still maintaining the UPY accuracy. The structure of the MHNC equations allows to regard the analytic PY results as being the exact results for some potential (somewhat different from hard spheres) thus enabling us to perform the study in a relatively simple manner. In particular, by adding a simple correction (which we calculate analytically) to the local free energy functional of Lado$^{(1)}$ we obtain the accuracy to LFA.$^{(2)}$

The scheme we follow is to construct a family of "virial-energy" consistent local free energy functionals sorting out the one which comes closest to satisfying also the "virial-compressibility" consistency (i.e., UPY).

3. VARIATIONAL MODIFIED-HNC PROCEDURE

Consider the parametric solution (η is the free parameter) of Eqs. (1)–(4) for some given potential $\phi(r)$, namely, $g_\phi(x, \beta, \rho, \eta)$. We define the MHNC free energy functional, f_ϕ^{MHNC}, and a correction term, Δ_ϕ, by

$$\begin{aligned} f_\phi^{\text{MHNC}}(\beta, \rho, \eta) = {} & \frac{1}{2}\int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta)[\beta\phi(x/\rho^{1/3}) + B(x, \eta)] \\ & - \frac{1}{2}\int d\mathbf{x}\left[\frac{1}{2}h_\phi^2(x, \beta, \rho, \eta) + h_\phi(x, \beta, \rho, \eta) \right. \\ & \left. - g_\phi(x, \beta, \rho, \eta)\ln g_\phi(x, \beta, \rho, \eta)\right] \\ & - \frac{1}{2}(2\pi)^{-3}\int d\mathbf{k}\{\ln[1 + \tilde{h}_\phi(k, \beta, \rho, \eta)] - \tilde{h}_\phi(k, \beta, \rho, \eta)\} \end{aligned} \tag{7}$$

$$\Delta_\phi(\beta, \rho, \eta) = \frac{1}{2}\int_0^\eta d\eta' \int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta')\frac{\partial B(x, \eta')}{\partial \eta'} \tag{8}$$

Note that f_ϕ^{MHNC} is a local functional which for $\eta = 0$ is just the usual "virial energy" (VE) consistent excess free energy for the HNC approximation. Using (1, 2) we find that the partial derivatives of f_ϕ^{MHNC} are given by[(26)]

$$\beta \left.\frac{\partial f_\phi^{\mathrm{MHNC}}(\beta, \rho, \eta)}{\partial \beta}\right|_{\rho,\eta} = u(\beta, \rho, \eta) \tag{9}$$

$$\rho \left.\frac{\partial f_\phi^{\mathrm{MHNC}}(\beta, \rho, \eta)}{\partial \rho}\right|_{\beta,\eta} = Z_v(\beta, \rho, \eta) - 1 \tag{10}$$

$$\left.\frac{\partial f_\phi^{\mathrm{MHNC}}(\beta, \rho, \eta)}{\partial \eta}\right|_{\beta,\rho} = \frac{1}{2} \int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta) \frac{\partial B(x, \eta)}{\partial \eta} \equiv \frac{\partial}{\partial \eta} \Delta_\phi(\beta, \rho, \eta) \tag{11}$$

where the potential energy, U, is given by (i.e., the "energy" equation of state)

$$U \equiv \frac{\beta U^{ex}}{N} = \frac{1}{2} \beta \int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta)\, \phi\left(\frac{x}{\rho^{1/2}}\right) \tag{12}$$

and the virial pressure equation of state is

$$Z_v \equiv \left(\frac{\beta P}{\rho}\right)_{\text{virial}} = 1 - \frac{\beta}{6} \int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta) \frac{x}{\rho^{1/3}} \phi'\left(\frac{x}{\rho^{1/3}}\right) \tag{13}$$

where $\phi'(r) = \partial\phi(r)/\partial r$.

Given the function $\eta(\beta, \rho)$, then the excess free energy, $f \equiv \beta F^{\mathrm{ex}}/N$, as obtained from U or Z_v is given, respectively, by

$$f_\phi^{\text{“E”}}(\beta, \rho) = f^{\mathrm{MHNC}}(\beta, \rho, \eta(\beta, \rho)) - \int_0^\beta d\beta' \left.\frac{\partial \eta(\beta', \rho)}{\partial \beta'} \frac{\partial \Delta_\phi(\beta', \rho, \eta)}{\partial \eta}\right|_{\eta = \eta(\beta', \rho)} \tag{14}$$

$$f_\phi^{\text{“V”}}(\beta, \rho) = f^{\mathrm{MHNC}}(\beta, \rho, \eta(\beta, \rho)) - \int_0^\rho d\rho' \left.\frac{\partial \eta(\beta, \rho')}{\partial \rho'} \frac{\partial \Delta_\phi(\beta, \rho', \eta)}{\partial \eta}\right|_{\eta = \eta(\beta, \rho')} \tag{15}$$

Suppose that the bridge parameter, $\eta = \eta(\beta, \rho)$, is obtained from any criterion of the type

$$\Delta_\phi(\beta, \rho, \eta) = \Delta_\phi^{(0)}(\eta) \tag{16a}$$

or

$$\frac{1}{2} \int d\mathbf{x}\, g_\phi(x, \beta, \rho, \eta) \frac{\partial B(x, \eta)}{\partial \eta} = \Delta_\phi^{(0)\prime}(\eta) \tag{16b}$$

where $\Delta_\phi^{(0)}(\eta)$ is a given function that vanishes at $\eta = 0$. The requirement that $\Delta_\phi^{(0)}(\eta = 0) = 0$ is a physical one and allows the MHNC results to include the correct low-density limit which is given accurately by the HNC approximation. For criteria of the type (16) we find that the MHNC result obeys virial-energy consistency

$$f_\phi^{\mathrm{E}} = f_\phi^{\mathrm{V}} = f_\phi^{\mathrm{VMHNC}}(\beta, \rho) \equiv f^{\mathrm{MHNC}}(\beta, \rho, \eta(\beta, \rho)) - \Delta_\phi^{(0)}(\eta(\beta, \rho)) \quad (17)$$

and f^{VMHNC} is a local functional like f^{MHNC}. A trivial choice of the type (16) is embodied, of course, in the HNC approximation. Moreover, in view of relations (9)–(11) we find that any MHNC procedure for which $\eta(\beta, \rho)$ is determined by a criterion of the type (16) may be cast in a variation form:

Considering the solutions $g_\phi(x, \beta, \rho, \eta)$ of Eqs. (1), (2) with a continuous one-parameter bridge function $B(x, \eta)$ that vanishes for $\eta = 0$ [e.g., the PY bridge function given by Eq. (4)], we construct the free energy functional

$$f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \eta) = f_\phi^{\mathrm{MHNC}}(\beta, \rho, \eta) - \Delta_\phi^{(0)}(\eta) \quad (18)$$

The variational condition

$$\frac{\partial}{\partial \eta} f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \eta) = 0 \quad (19)$$

yields Eq. (16b) for determining $\eta(\beta, \rho)$, and ensures that the energy obtained by $\beta U/N = \beta(df/d\beta)_\rho$ and the pressure obtained via $\beta P/\rho - 1 = \rho(df/d\rho)_\beta$ are given by Eqs. (12) and (13) with Hiroike's test$^{(27)}$

$$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$$

being satisfied since $\partial^2 f/\partial\beta\,\partial\rho = \partial^2 f/\partial\rho\,\partial\beta$. Here we wrote $f_\phi^{\mathrm{VMHNC}} = f$ in short notations.

The question is to what extent may a criterion of the type (16) [that is, Eq. (19)] accurately reproduce the UPY results which are based on "virial-compressibility" consistency and serve as our standard for the present analysis? In other words, is it possible to find a function $\Delta_\phi^{(0)}(\eta)$ such that the virial-compressibility consistency will be obeyed to a high degree of accuracy?

Note first that the structure and excess thermodynamic properties of the inverse power potentials, $\phi_n(r) = \varepsilon(\sigma/r)^n$, depend on the single reduced density-temperature variable, $\xi_n = (\pi/6)(\rho\sigma^3)(\beta\varepsilon)^{3/n}$ (corresponding to the packing fraction $\xi = \xi_\infty = (\pi/6)\rho\sigma^3$ for hard spheres). The VE consistency condition for these systems

$$U_n = \frac{3}{n}(Z_{v,n} - 1) \tag{20}$$

is automatically satisfied since $-r\phi_n'(r) = n\phi_n(r)$, to that the UPY criterion can be cast in the form (16). Indeed we may invert the monotonic relation $\eta = \eta_{\mathrm{UPY},n}(\xi_n)$ to get $\xi_{\mathrm{UPY},n}(\eta)$, and use Eq. (7) to calculate $\Delta_n(\xi_{\mathrm{UPY},n}(\eta), \eta)$, then the function given by $\Delta_n^{(0)}(\eta) = \Delta_n(\xi_{\mathrm{UPY},n}(\eta), \eta)$ reproduces by Eq. (19) the original UPY results. The available UPY results for the Lennard-Jones system(3,16) (which is a typical general test case for our purposes) obey to high accuracy the VE consistency, and to render Eq. (16) of the required accuracy we just have to find the best VE consistent results that lie closest to the UPY values. The high accuracy obtained by the variational perturbation theory (VPT) employing soft inverse power reference potentials,(13) and the apparent universality of the function(4) $s(\eta)$, where $s = -(\text{excess entropy})/Nk_B$, for the UPY results for various potentials, also provide strong indications of the possibility of recasting the UPY criterion in the variational form (19). Finally, and as analyzed below, the LFA(2) results represent the typical accuracy that may be obtained by a local UPY-oriented free energy functional that we seek.

4. PERTURBATION REPRESENTATION FOR THE FITTING FUNCTIONS $\Delta_\Phi(\eta)$

With the UPY results serving as the standard of accuracy for the purpose of our analysis, the function $\Delta_\phi^{(0)}(\eta)$ may be regarded as a fitting function aiming to reproduce these results. In the spirit of perturbation theory for fluids we expect that $\Delta_\phi^{(0)}(\eta)$ will separate into a relatively large part that will not depend on the potential, and a relatively small ϕ-dependent part. In order to perform the analysis along such lines let us consider first the analytic solution of the PY equation for hard spheres.

Assume that the PY solution for hard spheres is interpreted as the VMHNC result for some potential (the "PY" potential) for which the functional [Eq. (18)] is given by the PY-virial (PYV) free energy

$$f_{\mathrm{PY}}^{\mathrm{VMHNC}}(\eta) = f_{\mathrm{PYV}}(\eta) = \frac{6\eta}{1-\eta} + 2\ln(1-\eta)$$

and thus the corresponding $\Delta_\phi^{(0)}(\eta)$ is given by

$$\Delta_{\mathrm{PY}}(\eta)=\int_0^\eta d\eta' \frac{1}{2}\int d\mathbf{x}\, g_{\mathrm{PY}}(x,\eta')\frac{\partial B(x,\eta')}{\partial\eta'} \tag{21}$$

These two relations define the PY potential.

The corresponding MHNC free energy functional, denoted $f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta)$, is given by

$$f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta)=f_{\mathrm{PYV}}(\eta)+\Delta_{\mathrm{PY}}(\eta) \tag{22}$$

Equations (21) and (22) represent a particular case of (18): Let $F(U,\rho,\eta)=f_\phi^{\mathrm{VMHNC}}(\beta,\rho,\eta)$ with $u=\beta\phi$, then $u(r/d)=\psi(r/d,\eta)$ and $\theta(\eta)=\rho_{\mathrm{PY}}$, where ψ and θ are two implicitly defined functions. Finally, $f_{\mathrm{PY}}^{\mathrm{VMHNC}}(\eta)=F(u_{\mathrm{PY}},\rho_{\mathrm{PY}},\eta)$.

Rewriting the criterion (16) in the perturbative form

$$\frac{1}{2}\int d\mathbf{x}\, g_\phi(x,\beta,\rho,\eta)\frac{\partial B(x,\eta)}{\partial\eta}=\frac{1}{2}\int d\mathbf{x}\, g_{\mathrm{PY}}(x,\eta)\frac{\partial B(x,\eta)}{\partial\eta}-\delta'_\phi(\eta) \tag{23}$$

i.e., defining $\delta_\phi(\eta)$ by

$$\Delta_\phi^{(0)}(\eta)=\Delta_{\mathrm{PY}}(\eta)-\delta_\phi(\eta) \tag{24}$$

the VMHNC free energy functional (18) is written as

$$f_\phi^{\mathrm{VMHNC}}(\beta,\rho,\eta)=[f_{\mathrm{PYV}}(\eta)+\delta_\phi(\eta)]+f^{\mathrm{MHNC}}(\beta,\rho,\eta)-f_{\mathrm{PY}}^{\mathrm{MHNC}} \tag{25}$$

with the variational condition (19) [i.e., (23)] taking the form

$$\frac{\partial f_\phi^{\mathrm{VMHNC}}}{\partial\eta}=\delta'_\phi(\eta)+\frac{1}{2}\int d\mathbf{x}[g_\phi(x,\rho,\rho,\eta)-g_{\mathrm{PY}}(x,\eta)]\frac{\partial B(x,\eta)}{\partial\eta}=0 \tag{26}$$

Notice at this stage that the results of Lado are obtained if we make the approximation $\delta_\phi(\eta)=0$, and their accuracy by comparison with the simulation data clearly displays δ_ϕ as the relatively small parameter in Eq. (24). Note also that with the approximation $\delta_\phi=0$, the VMHNC results for the system of hard spheres will be identical to the PY approximation for hard spheres, with f^{VMHNC} given by the PY-"virial" free energy.

As with the ordinary variational perturbation theory(13) we expect to obtain better results for soft (i.e., "physical") potentials if we start with a soft reference potential. To be specific we consider an inverse nth power potential. Using the mapping between ξ_n and η as defined by $\eta_{\mathrm{UPY},n}(\xi_n)$ or

$\xi_{\mathrm{UPY},n}(\eta)$, we write [in analogy to Eqs. (21), (22), and (24) for the "PY" potential]

$$\varDelta_n(\eta)=\int_0^{\eta} d\eta' \frac{1}{2}\int d\mathbf{x}\, g_n(x, \xi_{\mathrm{UPY},n}(\eta'), \eta')\frac{\partial B(x, \eta')}{\partial \eta'} \tag{27}$$

$$f_n^{\mathrm{MHNC}}(\eta)=f_n^{\mathrm{VMHNC}}(\xi_{\mathrm{UPY},n}(\eta), \eta)+\varDelta_n(\eta)\equiv f_n^{\mathrm{VMHNC}}(\eta)+\varDelta_n(\eta) \tag{28}$$

$$\varDelta_\phi^{(0)}(\eta)=\varDelta_n(\eta)+\delta_\phi^{(n)}(\eta) \tag{29}$$

In analogy with Eqs. (25) and (26) we now get

$$\begin{aligned} f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \eta)=&\,[f_n^{\mathrm{VMHNC}}(\xi_{\mathrm{UPY},n}(\eta), \eta)+\delta_\phi^{(n)}(\eta)]\\ &+f_\phi^{\mathrm{MHNC}}(\beta, \rho, \eta)-f_n^{\mathrm{MHNC}}(\eta) \end{aligned} \tag{30}$$

$$\begin{aligned} \frac{\partial f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \eta)}{\partial \eta}=&\,\delta_\phi^{(n)\prime}(\eta)+\frac{1}{2}\int d\mathbf{x}[g_\phi(x, \beta, \rho, \eta)\\ &-g_n(x, \xi_{\mathrm{UPY},n}(\eta), \eta)]\frac{\partial B(x, \eta)}{\partial \eta}=0 \end{aligned} \tag{31}$$

We expect that with a proper choice of the reference power "n," say $n=12$, for treating the Lennard-Jones LJ(12-6) potential, the perturbation approximation $\delta_\phi^{(n)}(\eta)=0$ in (30), (31) will yield better results, for a soft potential ϕ, than those based on the PY reference with $\delta_\phi(\eta)=0$ as originally used by Lado.

The analogy of our formulation above with the bootstrap procedure employed in the context of VPT becomes transparent once we note (see Appendix A) that the approximation $\delta_\phi^{(n)}(\eta)=0$ in Eqs. (30), (38) is identical to the one $\delta_\phi(\eta)=\delta_{\phi=r^{-n}}(\eta)\equiv\delta_n(\eta)$ in Eqs. (25), (26). In the language of VPT we may use the PY pair functions and introduce the Ross ad hoc corection to the entropy functional, i.e., write the VPT free energy functional

$$f_\phi^{\mathrm{VPT}}(\beta, \rho, \eta)=s_{\mathrm{Ross}}(\eta)+\frac{1}{2}\beta\int d\mathbf{x}\, g_{\mathrm{PY}}(x, \eta)\,\phi\left(\frac{x}{\rho^{1/3}}\right) \tag{32}$$

and determine $\eta(\beta, \rho)$ by requiring $\partial f_\phi^{\mathrm{VPT}}/\partial\eta=0$. The entropy function $s_{\mathrm{Ross}}(\eta)$ was chosen by Ross such that the same calculation for the inverse 12th power potential will fit the corresponding equation of state from simulations. It was shown however(13,22) that even better accuracy is obtained by starting with the inverse 12th power reference system proper, i.e., by using

$$f_\phi^{\mathrm{VPT},\text{“12”}}(\beta, \rho, \xi_{12})=s(\xi_{12})+\frac{1}{2}\beta\int d\mathbf{x}\, g_{12}(x, \xi_{12})\,\phi\left(\frac{x}{\rho^{1/3}}\right) \tag{33}$$

together with the variational condition $\partial f/\partial\xi_{12}=0$. Here $s(\xi_{12})$ is minus the excess entropy of the r^{-12} potential and no ad hoc correction is necessary.

The nice feature of the VMHNC scheme as formulated above is that these two stages (and more) of the VPT bootstrap procedure can be obtained by using simple fitting functions which are capable of fitting, by the single parameter, both the structure and the equation of state. Indeed if in Eq. (32) we write $s_{\rm Ross}(\eta)=f_{\rm PYV}(\eta)+\Delta s(\eta)$; then $\delta_{n=12}(\eta)$ in Eqs. (25), (26) is the VMHNC analog of the "Ross" correction $\Delta s(\eta)$. Similarly, $\delta_\phi^{(n=12)}(\eta)=0$ (with $n=12$), in Eqs. (30), (31) is analogous to the VPT calculation based on Eq. (31). This feature of the VMHNC has already enabled a general analysis of the VPT entropy function, i.e., a derivation of Ross-type ad hoc corrections with a pictorial display of their respective accuracy.(4)

5. ANALYSIS OF THE FITTING FUNCTION $\delta_\Phi(\eta)$

In order to analyze the functions $\delta_\phi(\eta)$ with the help of the available results of Refs. 1 and 2 we write Eqs. (25) and (26) in the following form:

$$f_\phi^{\rm VMHNC}(\beta,\rho,\eta)=f_\phi^{(0)}(\beta,\rho,\eta)+\delta_\phi(\eta) \tag{34}$$

$$\frac{\partial f_\phi^{\rm VMHNC}(\beta,\rho,\eta)}{\partial\eta}=I_{\rm PY}(\beta,\rho,\eta)+\delta'_\phi(\eta)=0 \tag{35}$$

where [see Eq. (24)]

$$f_\phi^{(0)}(\beta,\rho,\eta)=f_{\rm PYV}(\eta)-f_{\rm PY}^{\rm MHNC}(\eta)+f_\phi^{\rm MHNC}(\beta,\rho,\eta) \tag{36}$$

and we define

$$I_{\rm PY}(\beta,\rho,\eta)\equiv\frac{\partial f_\phi^{(0)}(\beta,\rho,\eta)}{\partial\eta}=\frac{1}{2}\int d\mathbf{x}[g_\phi(x,\beta,\rho,\eta)-g_{\rm PY}(x,\eta)]\,\frac{\partial B(x,\eta)}{\partial\eta} \tag{37}$$

In other words, we look for the function $\delta_\phi(\eta)$, for different potentials ϕ, such that the solution of Eq. (35), i.e.,

$$I_{\rm PY}(\beta,\rho,\eta)=-\delta'_\phi(\eta) \tag{38}$$

will be in good agreement with the UPY (i.e., simulation) results, noting the fact that $\delta_\phi(\eta)=0$ (and thus $I_{\rm PY}=0$) corresponds to the already reasonably accurate results of Lado.(1)

The situation we face is schematically, but quite generally, represented by Fig. 1 where we plot $u(\beta, \rho, \eta)$, $Z_v(\beta, \rho, \eta)$, $f^{\mathrm{VMHNC}}(\beta, \rho, \eta)$, $I_{\mathrm{PY}}(\beta, \rho, \eta)$ and the inverse compressibility

$$K_c^{-1} \equiv \beta \left(\frac{\partial P}{\partial \rho} \right)_\beta = 1 - \int d\mathbf{x}\, c(x, \beta, \rho, \eta) \tag{39}$$

for given β, ρ as function of the parameter η. For $\eta = 0$ the plotted functions have their respective values as obtained in the HNC approximation. As a rule (see Ref. 3) manifesting the general characteristic

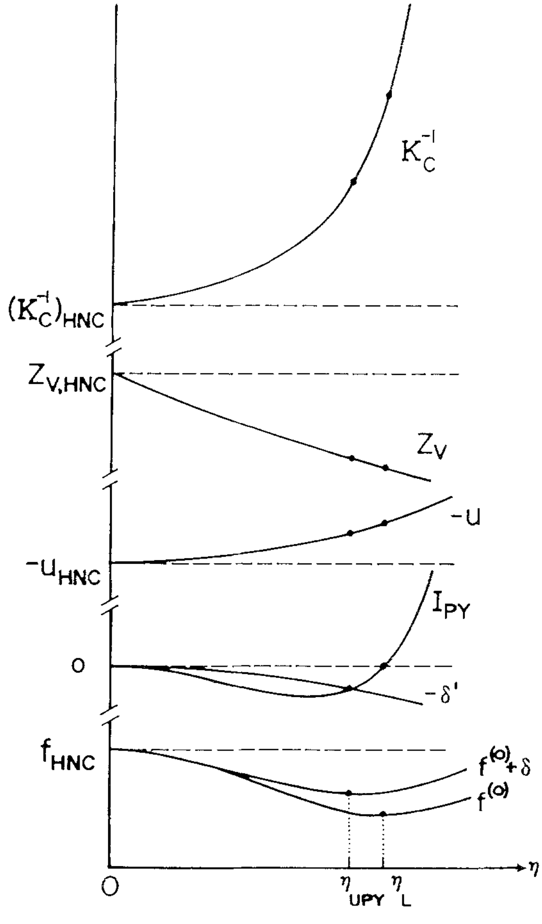

Fig. 1. Thermodynamic functions for a Lennard-Jones-type potential, in the liquid state, obtained by the MHNC theory as functions of the "bridge" parameter η (schematic, see the text). The values at $\eta = 0$ correspond to the results by the HNC approximation.

of the bridge functions as "effectively repulsive potentials," the HNC results for u, Z_v, and f^{VMHNC} overestimate the "true" values, while they underestimate K_c^{-1}. Also as a rule, the function K_c^{-1} varies with η much more strongly than u, Z_v, and f^{VMHNC}. This feature is the basic reason why the UPY virial-compressibility criterion is so important. In turn, this behavior implies that when a correction to the results of Lado is sought, the function $\delta_\phi(\eta)$ should be chosen so as to shift the minimum of f_ϕ^{VMHNC} [i.e., the intersection of I_{PY} and $-\delta'_\phi(\eta)$] toward the value of η appropriate to the "correct" K_c^{-1}. The effect of such a shift on the other thermodynamic functions plotted in Fig. 1 is relatively small. Again as a rule, the results using Lado's approximation yield values of $\eta = \eta_{\text{L}}(\beta, \rho)$ which are larger than those obtained by the UPY procedure, $\eta_{\text{L}}(\beta, \rho) \geqslant \eta_{\text{UPY}}(\beta, \rho)$.

These general trends mean that the function $\delta_\phi(\eta)$ is a smooth monotonically increasing positive function which is relatively small compared with $f_{\text{PYV}}(\eta)$. As an example for the utility of our formulation which lead to the simple "pictorial" analysis we obtain (see Appendix B) an accurate estimate for the fitting function for hard spheres given by the following simple expression:

$$\delta_{\text{HS}}(\eta) \equiv \delta_{\phi = r^{-\infty}}(\eta) \cong f_{\text{CS}}(\eta) - f_{\text{PYV}}(\eta) \tag{40}$$

where f_{CS} is the Carnahan–Starling(28) fit to the hard sphere simulation data. By employing this expression for an arbitrary potential, i.e., $\delta_\phi(\eta) = \delta_{\text{HS}}(\eta)$, we upgrade the results of Lado to the LFA accuracy: our result with $\delta_\phi(\eta) = \delta_{\text{HS}}(\eta)$, given by Eq. (40), represents the needed change in the PY-reference system which will upgrade it to the UPY–HS result, which is, in turn, of the same accuracy as the VWGH fit for the hard spheres. The difference between using (40) and using VWGH (as LFA did) is just the difference between using two equally accurate but alternative fittings to the HS simulation data.

A consistency check of the perturbatively correct nature of our bootstrap procedure is given by noting that $\delta_{\text{HS}}(\eta) \ll f_{\text{PYV}}(\eta)$ in the entire fluid range ($\eta \lesssim 0.45$).

The demonstrated high accuracy of the LFA results, which are essentially embodied by the first bootstrapping perturbation term [Eq. (40)], indicates that the next order in this systematic bootstrapping within the UPY is indeed much smaller: If we replace the hard sphere reference by a soft reference, i.e., use $\delta_\phi(\eta) = \delta_n(\eta)$ or $\delta_\phi^{(n)}(\eta) = 0$ (with, say, $n \simeq 12$ as proved accurate in the VPT) then we know now from LFA(2) that

$$|\delta_n(\eta) - \delta_{\text{HS}}(\eta)| \ll \delta_{\text{HS}}(\eta) \tag{41}$$

It is interesting to note that the integrand in the expression

$$\delta'_{\mathrm{HS}}(\eta)-\delta'_n(\eta)=\frac{1}{2}\int d\mathbf{x}[g_n(x,\xi_{\mathrm{UPY},n}(\eta),\eta)-g_{\mathrm{HS}}(x,\xi_{\mathrm{UPY},\infty}(\eta),\eta)]\,\frac{\partial B(x,\eta)}{\partial\eta} \tag{42}$$

has the familiar "blip function"$^{(29)}$ form, but with an already optimized η that ensures the relation (41). In fact, rewriting (42) as a k-space integral, and imposing [as implied by (39)]

$$\int d\mathbf{k}[S_n(k,\xi_{\mathrm{UPY},n}(\eta),\eta)-S_{\mathrm{HS}}(k,\xi_{\mathrm{UPY},\infty}(\eta),\eta)]\,\frac{\partial\tilde{B}(k,\eta)}{\partial\eta}=0 \tag{43}$$

it is found that the main contribution to the integral comes from the main peak of the structure factor. This is in accordance with the finding that the matching of peaks in order to obtain the mapping of liquid metals on the hard sphere system proved consistent with the perturbation calculations for these systems$^{(30)}$ (e.g., the freezing rule $\eta\cong 0.45$).

A systematic study of $\delta_n(\eta)$ may be of interest, but it should be noted that at that level of accuracy [i.e., $\delta_\phi(\eta)\simeq\delta_n(\eta)$] the nonuniversal features of the bridge functions need to be taken into account.

6. DIAGRAMMATIC ANALYSIS OF THE PAIR STRUCTURE: VARIATIONAL ITERATION PROCEDURE USING SCALING

At the time when the analysis of the diagrammatic density expansion of the pair correlation functions led to Eqs. (1)–(3), it was immediately realized$^{(14)}$ that a formal iterative solution of these equations generates all the defining diagrams of $g(r)$, $c(r)$, and $B(r)$. The procedure is as follows: start with $B(x,\beta,\rho)=B_0(x)=0$ and solve Eqs. (1), (2) to obtain $h_0(x,\beta,\rho)$ which is the HNC result, $h_0(x,\beta,\rho)=h_{\mathrm{HNC}}(x,\beta,\rho)$. Use Eq. (3) to evaluate $B_1(x,\beta,\rho)=\mathscr{B}\{h_0(x,\beta,\rho)\}$. Solve Eqs. (1), (2) using $B_1(x,\beta,\rho)$ to obtain $h_1(x,\beta,\rho)$. Evaluate $B_2(x,\beta,\rho)=\mathscr{B}\{h_1(x,\beta,\rho)\}$, and so on. The result of the jth iteration, $h_j(x,\beta,\rho)$, in the limit $j\to\infty$, contains all the defining diagrams of $h_{\mathrm{exact}}(x,\beta,\rho)$, and in this sense we have

$$\lim_{j\to\infty} h_j(x,\beta,\rho)=h_{\mathrm{exact}}(x,\beta,\rho) \tag{44}$$

When developing the idea of universality of the bridge functions as a starting approximation in the context of the MHNC scheme, it was argued$^{(3,15,31)}$ that in view of the general high similarity between the HNC results for the pair functions, $h_0(x)$, and the corresponding Monte-Carlo data, $h_{\mathrm{MC}}(x) \cong h_{\mathrm{exact}}(x)$, it is expected that $h_1(x)$ will be very close to $h_\infty(x)$, with the higher iterative corrections being relatively small. The validity of this "one-iteration-approximation" and that of the "universality of the bridge functions" are intimately connected. This possibility inherent within the MHNC approach to gain information regarding the diagrammatic expansion has not yet been pursued. The present analysis of the VMHNC procedure enables us to draw a rather precise conclusion regarding the "one-iteration" statement above, despite the fact that even this one iteration is still not computationally feasible.

We start by noting that our analysis of the VMHNC within the context of the UPY representation of the structure and thermodynamics for various pair potentials should represent, in view of the UPY's demonstrated high accuracy, a valid quantitative analysis for the more general statement given originally by Lado,$^{(1)}$ and which in our formulation reads as follows: Given the exact pair structure and equation of state for a soft potential $g_{\phi 0}(x, \beta, \rho)$, $B_{\phi 0}(x, \beta, \rho)$, $f_{\phi 0}(\beta, \rho)$, solve the MHNC equations (1), (2) for the potential ϕ, employing the reference bridge functions $B_{\phi 0}(x, \beta', \rho')$ and consider the following excess free energy functional:

$$f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \beta', \rho') = f_{\phi 0}(\beta', \rho') + f_\phi^{\mathrm{MHNC}}(\beta, \rho. \beta'. \rho') - f_{\phi 0}^{\mathrm{MHNC}}\ (\beta', \rho') \tag{45}$$

Provided the reference states $\beta'(\beta, \rho)$, $\rho'(\beta, \rho)$ are chosen by solving the variation equations:

$$\frac{\partial f_\phi^{\mathrm{VMHNC}}}{\partial \beta'} = \frac{1}{2} \int d\mathbf{x} [g_\phi(x, \beta, \rho, \beta', \rho') - g_{\phi 0}(x, \beta', \rho')] \frac{\partial B_{\phi 0}(x, \beta', \rho')}{\partial \beta'} = 0 \tag{46a}$$

$$\frac{\partial f_\phi^{\mathrm{VMHNC}}}{\partial \rho'} = \frac{1}{2} \int d\mathbf{x} [g_\phi(x, \beta, \rho, \beta', \rho') - g_{\phi 0}(x, \beta', \rho')] \frac{\partial B_{\phi 0}(x, \beta', \rho')}{\partial \rho'} = 0 \tag{46b}$$

we expect to obtain the structure $g_\phi(x, \beta, \rho) = g_\phi(x, \beta, \rho, \beta'(\beta, \rho), \rho'(\beta, \beta))$ and the consistent excess free energy $f_\phi(\beta, \rho) = f_\phi^{\mathrm{VMHNC}}(\beta, \rho, \beta'(\beta, \rho), \rho'(\beta, \rho))$ for the potential $\phi(r)$, to within less than 1% error (i.e., present day simulation accuracy), corresponding to $\delta_\phi(\eta) = \delta_n(\eta)$ in the UPY representation. With a hard core reference system applied for a soft potential slightly less accurate results are expected, similarly to that obtained by employing $\delta_\phi(\eta) = \delta_{\mathrm{HS}}(\eta)$ (i.e., the LFA results).

Returning now to the iteration procedure above that leads to Eq. (44), consider the following possibility to enhance its convergence rate: Instead of performing all the iteration stages for a single given pair β, ρ, let us consider instead at each iteration stage the solution $h_j(x, \beta, \rho)$ for all β, ρ. At each iteration stage define the following quantities:

$$\Delta^{\mathrm{E}}_{(j)}(\beta', \rho') = \frac{1}{2}\int_0^{\rho'} d\rho'' \int d\mathbf{x}\, g_{j-1}(x, \beta', \rho'')\, \frac{\partial B_j(x, \rho', \rho'')}{\partial \rho''} \tag{47a}$$

$$\Delta^{\mathrm{V}}_{(j)}(\beta', \rho') = \frac{1}{2}\int_0^{\beta'} d\beta'' \int d\mathbf{x}\, g_{j-1}(x, \beta'', \rho')\, \frac{\partial B_j(x, \beta'', \rho')}{\partial \beta''} \tag{47b}$$

(of course $\Delta^{\mathrm{E}}_{(j)} = \Delta^{\mathrm{V}}_{(j)}$ for inverse power potentials), and form the free energy functionals by using $B_j(x, \beta', \rho')$

$$f^{\mathrm{E}}_{(j)}(\beta, \rho, \beta', \rho') = f^{\mathrm{MHNC}}_{(j)}(\beta, \rho, \beta', \rho') - \Delta^{\mathrm{E}}_{(j)}(\beta', \rho') \tag{48a}$$

$$f^{\mathrm{V}}_{(j)}(\beta, \rho, \beta', \rho') = f^{\mathrm{MHNC}}_{(j)}(\beta, \rho, \beta', \rho') - \Delta^{\mathrm{V}}_{(j)}(\beta', \rho') \tag{48b}$$

The iteration is optimized by requiring

$$\frac{\partial f^{\mathrm{E}}_{(j)}}{\partial \beta'} = \frac{1}{2}\int d\mathbf{x}\,[h_j(x, \beta, \rho, \beta', \rho') - h_{j-1}(x, \beta', \rho')]\, \frac{\partial B_j(x, \beta', \rho')}{\partial \beta'} = 0 \tag{49a}$$

$$\frac{\partial f^{\mathrm{V}}_{(j)}}{\partial \rho'} = \frac{1}{2}\int d\mathbf{x}\,[h_j(x, \beta, \rho, \beta', \rho') - h_{j-1}(x, \beta', \rho')]\, \frac{\partial B_j(x, \beta', \rho')}{\partial \rho'} = 0 \tag{49b}$$

In the limit $j \to \infty$, the exact result will satisfy

$$\Delta^{\mathrm{E}}_{(\infty)}(\beta, \rho) = \Delta^{\mathrm{V}}_{(\infty)}(\beta, \rho) = \Delta_{(\infty)}(\beta, \rho) \tag{50a}$$

$$f^{\mathrm{V}}_{(\infty)}(\beta, \rho) = f^{\mathrm{E}}_{(\infty)}(\beta, \rho) = f^{\mathrm{MHNC}}_{(\infty)}(\beta, \rho) - \Delta_{(\infty)}(\beta, \rho) = f_{\mathrm{exact}}(\beta, \rho) \tag{50b}$$

It is obvious that in this iteration procedure we perform at each stage a VMHNC approximation in order to optimize the choice of the bridge function obtained from the previous stage.

By its structure the HNC equation for some potential $\phi(r)$ provides the exact pair structure for another potential, $\phi_{\mathrm{HNC}}(r) = \phi(r) - (1/\beta)\, B_{\mathrm{HNC}}(r)$, where $B_{\mathrm{HNC}}(r) = \mathscr{B}\{h_{\mathrm{HNC}}(r)\}$. In particular, for the first iteration stage $B_1(r) = B_{\mathrm{HNC}}(r)$. The first variational iteration stage is exactly the VMHNC result according to Eqs. (43), (44) for the potential $\phi(r)$ using $\phi_{\mathrm{HNC}}(r) = \phi(r) - (1/\beta)\, B_1(r)$ as the reference potential. But we know already from the accumulated information regarding the bridge functions that this $\phi_{\mathrm{HNC}}(r)$ should provide an excellent reference system, at least better than $\phi_{\mathrm{HS}}()$. Thus, the first variational iteration approximation should be more accurate than the LFA results. We find that the theory of simple classical fluids is essentially a "one-iteration theory" provided that this iteration is properly optimized.

Note that the relation between the usual first iteration stage and the optimized (variational) one, is similar to the relation between the RHNC approximation(32) and the MHNC(3) approach which optimizes the bridge functions.

7. CONCLUSION

The UPY results represent a first-order accurate description of the available simulation data for the static pair structure and the thermodynamics of simple classical fluids, based on the universality of the bridge functions. Within the framework of the UPY, i.e., with the PYHS bridge functions, we constructed a whole family of energy-virial consistent local free energy functionals, by which both the structure and the equation of state are calculated via a variational principle. Starting at the level of the approximation used by Lado [$\delta_\phi(\eta) = 0$ in our notations], we formulated a bootstrap perturbation expansion for the corrections to the free energy functional, $\delta_\phi(\eta)$. The first-order correction to the zero-order Lado's PY reference potential is obtained by employing the hard-sphere reference (i.e., LFA) which is equivalent to the aproximation $\delta_\phi(\eta) = \delta_{\mathrm{HS}}(\eta)$. An accurate, simple analytic expression for $\delta_{\mathrm{HS}}(\eta)$ [Eq. (39)] was obtained. The demonstrated high accuracy of the LFA results clearly justifies the chosen cascade of approximations embodied by the relations

$$|\delta_\phi(\eta) - \delta_{\mathrm{HS}}(\eta)| \ll \delta_{\mathrm{HS}}(\eta) \ll f_{\mathrm{PYV}}(\eta) \tag{51}$$

As discussed in Ref. 4, the possibility to obtain such an accurate universal expression for δ_ϕ, namely, $\delta_\phi(\eta) \cong f_{\mathrm{CS}}(\eta) - f_{\mathrm{PYV}}(\eta)$, is related to the fact that to first order the bridge functions are universal locally [without any additional scaling to determine $\eta(\beta, \rho)$] provided we use the excess entropy as the independent variable

$$B_\phi(x, s, \rho) \cong B_{\mathrm{HS}}(x, s) \cong B_{\mathrm{PY}}(x, s) \tag{52}$$

The results of LFA (i.e., $\delta_\phi = \delta_{\mathrm{HS}}$) improve those of Lado ($\delta_\phi = 0$) only because $f_{\mathrm{PYV}}(\eta)$ does not represent the excess free energy for the PY potential. Thus (52) provides the correct framework by which we may appreciate the nature of the "requirement of consistency" as the reason given by LFA for their improvement over the results given by Lado.

Our formulation of the VMHNC enabled a direct interpretation of the results by LFA in terms of the accuracy of the first-order variational iterative diagrammatic expansion.

Finally, using the simple expression for δ_{HS} we now summarize the corresponding recipe for calculating and inverting pair structures:

(a) Given the pair potential $\phi(r)$, the temperature β, and the density ρ.

(i) Solve Eqs. (1) and (2) using the bridge functions (4)–(6) for various values of the parameter η.

(ii) Calculate the function $f_{\phi}^{\mathrm{VMHNC}}(\beta, \rho, \eta)$ as given by Eq. (25) using the expression (40) for $\delta_{\phi}(\eta) = \delta_{\mathrm{HS}}(\eta)$.

(iii) Monitor the value of η until the ("minimum") condition Eq. (26) is satisfied for some value $\eta = \bar{\eta}$.

(iv) The excess free energy of the system is given by $f_{\phi}^{\mathrm{VMHNC}}(\beta, \rho, \bar{\eta})$ and the pair function is $g_{\phi}(x, \beta, \rho, \bar{\eta})$.

(b) Given the pair structure, $g_{\mathrm{expt}}(x, \beta, \rho)$, or the structure factor $S(k, \beta, \rho)$.

(i) Using the bridge functions Eqs. (4)–(6) and the PY pair function for hard spheres $g_{\mathrm{PY}}(x, \eta)$, solve either

$$\frac{1}{2}\int d\mathbf{x}[g_{\mathrm{expt}}(x, \beta, \rho) - g_{\mathrm{PY}}(x, \eta)]\frac{\partial B(x, \eta)}{\partial \eta} + \delta'_{\mathrm{HS}}(\eta) = 0 \tag{53}$$

or

$$\frac{1}{2}\int d\mathbf{x}[S(k, \beta, \rho) - S_{\mathrm{PY}}(k, \eta)]\frac{\partial \tilde{B}(k, \eta)}{\partial \eta} + \delta'_{\mathrm{HS}}(\eta) = 0 \tag{54}$$

where $S_{\mathrm{PY}}(k, \eta) = 1 + \tilde{h}_{\mathrm{PY}}(k, \eta)$ (recall that we use reduced units $x = r\rho^{1/3}$) and $\tilde{B}(k, \eta)$ is the Fourier transform of $B(x, \eta)$.

(ii) Using either (53) or (54) to find $\bar{\eta}$, solve Eqs. (1)–(2) with $B(x, \eta)$ to find $\phi(r)$.

(iii) Evaluating f_{ϕ}^{MHNC} of Eq. (6) using the above $B(x, \eta)$ and $\phi(r)$, while employing $g_{\mathrm{expt}}(x)$ or $S(k)$, we obtain the free energy from Eq. (25) by using $\delta_{\phi} = \delta_{\mathrm{HS}}$.

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APPENDIX A: RELATION BETWEEN TWO PERTURBATIVE REPRESENTATIONS FOR THE FITTING FUNCTIONS $\Delta_{\Phi}^{(0)}(\eta)$

Using Eq. (28)

$$f_n^{\mathrm{VMHNC}}(\eta) - f_n^{\mathrm{MHNC}}(\eta) = -\Delta_n(\eta)$$

and employing Eq. (25) we get

$$f_n^{\mathrm{VMHNC}}(\eta) - f_n^{\mathrm{MHNC}}(\eta) = f_{\mathrm{PYV}}(\eta) - f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta) + \delta_n(\eta)$$

so that Eq. (30) becomes identical to Eq. (25) provided $\delta_\phi(\eta) = \delta_n(\eta)$.

In turn, writing Eq. (26) for the inverse nth power potential we get

$$\delta_n'(\eta) + \frac{1}{2}\int d\mathbf{x}[g_n(x, \xi_n, \eta) - g_{\mathrm{PY}}(x, \eta)]\,\frac{\partial B(x, \eta)}{\partial \eta} = 0$$

Taking $\delta_\phi^{(n)} = 0$, Eq. (31) becomes

$$\delta_n'(\eta) + \frac{1}{2}\int d\mathbf{x}[g_\phi(x, \beta, \rho, \eta) - g_{\mathrm{PY}}(x, \eta)]\,\frac{\partial B(x, \eta)}{\partial \eta} = 0$$

which is precisely Eq. (26) with $\delta_\phi'(\eta) = \delta_n'(\eta)$, provided we use the UPY representation for the inverse nth power structure.

APPENDIX B: ESTIMATE OF $\delta_{\mathrm{HS}}(\eta) = \delta_{\Phi=r^{-\infty}}(\eta)$

Denoting

$$f_{\text{“fit”}}(\eta) = f_{\mathrm{PYV}}(\eta) + \delta_{\mathrm{HS}}(\eta) \tag{B1}$$

then the functionals Eqs. (34) and (36) as applied to the hard spheres at packing fraction ξ take the form

$$f_{\mathrm{HS}}^{(0)}(\xi, \eta) = f_{\mathrm{PYV}}(\eta) + f_{\mathrm{HS}}^{\mathrm{MHNC}}(\xi, \eta) - f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta) \tag{B2}$$

$$f_{\mathrm{HS}}^{\mathrm{VMHNC}}(\xi, \eta) = f_{\text{“fit”}}(\eta) + f_{\mathrm{HS}}^{\mathrm{MHNC}}(\xi, \eta) - f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta) \tag{B3}$$

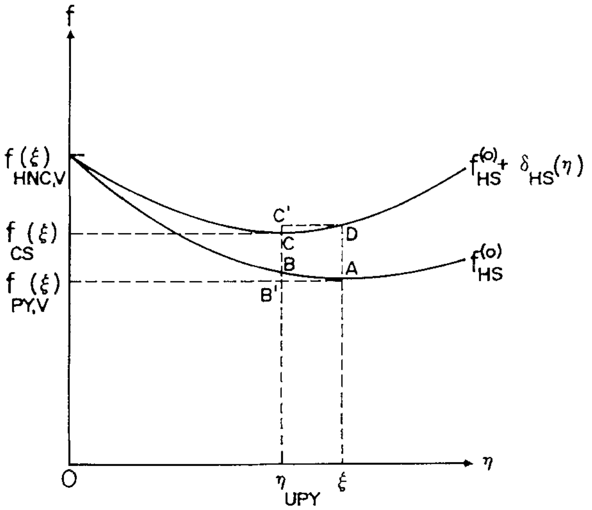

Fig. 2. Modified-HNC excess free energy functionals for the system of hard spheres at packing fraction ξ as functions of the "bridge" parameter η (schematic, see the text). $f_{\mathrm{HNC,V}}(\xi)$ represents the HNC-"virial" results.

By definition they have the following properties (see Fig. 2)

$$f^{(0)}_{\mathrm{HS}}(\xi, \eta=\xi) = f_{\mathrm{PYV}}(\xi) \tag{B4}$$

$$f^{\mathrm{VMHNC}}_{\mathrm{HS}}(\xi, \eta=\xi) = f_{\text{“fit”}}(\xi) \tag{B5}$$

$$f^{\mathrm{VMHNC}}_{\mathrm{HS}}(\xi, \eta_{\mathrm{UPY}}(\xi)) \cong f_{\mathrm{CS}}(\xi) \tag{B6}$$

while

$$\eta_{\mathrm{UPY}}(\xi) \leqslant \xi, \qquad |\eta_{\mathrm{UPY}}(\xi) - \xi|/\xi \ll 1 \tag{B7}$$

The minima (with respect to η) of the functionals (B2) and (B3) occur at $\eta = \xi$ and $\eta = \eta_{\mathrm{UPY}}$, respectively.

To first order, the area of the trapezoid *ABCD* is equal to the area of the rectangle *AB′C′D* (see Fig. 2) and thus we write [using (B6)]

$$\frac{1}{2}\,[\delta_{\mathrm{HS}}(\xi) + \delta_{\mathrm{HS}}(\eta_{\mathrm{UPY}})] \lesssim f_{\mathrm{CS}}(\xi) - f_{\mathrm{PYV}}(\xi) \tag{B8}$$

Recalling (B7) the final first-order result is

$$\delta_{\mathrm{HS}}(\eta) \cong f_{\mathrm{CS}}(\eta) - f_{\mathrm{PYV}}(\eta) \tag{B9}$$

and we quote

$$f_{\mathrm{CS}}(\eta) = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{B10}$$

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