

Universality of bridge functions and its relation to variational perturbation theory and additivity of equations of state

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Featuring the modified hypernetted-chain (MHNC) scheme as a variational fitting procedure, we demonstrate that the accuracy of the variational perturbation theory (VPT) and of the method based on additivity of equations of state is determined by the excess entropy dependence of the bridge-function parameters [i.e., $\eta(s)$ when the Percus-Yevick hard-sphere bridge functions are employed]. It is found that $\eta(s)$ is nearly universal for all soft (i.e., “physical”) potentials while it is distinctly different for the hard spheres, providing a graphical display of the “jump” in pair-potential space (with respect to accuracy of VPT) from “hard” to “soft” behavior. The universality of $\eta(s)$ provides a local criterion for the MHNC scheme that should be useful for inverting structure-factor data in order to obtain the potential. An alternative local MHNC criterion due to Lado is rederived and extended, and it is also analyzed in light of the plot of $\eta(s)$.

I. INTRODUCTION

The modified hypernetted-chain (MHNC) scheme was originally proposed as a method for parametrizing computer simulation data in terms of fitting bridge functions.¹ It is based on the MHNC equations for the pair (radial) distribution function $g(x)$,

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

and the Ornstein-Zernike (OZ) relation for the direct correlation function $c(x)$,

$$\tilde{c}(k) = \tilde{h}(k) / [1 - \tilde{h}(k)], \quad (2)$$

where $h(x) \equiv g(x) - 1$, $\tilde{h}(k)$ is the Fourier transform, $\phi(r)$ is the pair potential, ρ is the number density, $\beta = (k_B T)^{-1}$ is the inverse temperature, and we use the reduced length $x = r\rho^{1/3}$. $B(x) = B(x, \mu_i)$ is a fitting or an approximating bridge function, with free parameters (μ_i), that serves as input in Eq. (1).

The exact bridge function, $B_{\phi, \text{exact}}(x, \beta, \rho)$, is a functional of the exact pair function, $g_{\phi, \text{exact}}(x, \beta, \rho)$, given by the sum of all elementary graphs with $h(r)$ bonds that have at least triply connected field points, and can be formally written as

$$B_{\phi, \text{exact}}(x, \beta, \rho) = \mathcal{F}[g_{\phi, \text{exact}}(x, \beta, \rho)]. \quad (3)$$

If the evaluation of $\mathcal{F}[g]$ could be managed, then starting from $B=0$ (the HNC approximation), Eqs. (1)–(3) would provide a formal iteration scheme² by which the exact pair function could be obtained. It has been argued and demonstrated that $B_{\phi, \text{exact}}(x)$ should have roughly the same functional form for all potentials¹ (“universality of the bridge functions”). In fact, setting

$$B(x) = B_{\text{PY}}(x; \eta), \quad (4)$$

where $B_{\text{PY}}(x; \eta)$ is obtained from the Percus-Yevick (PY) equation for hard spheres, (HS), and requiring thermo-

dynamic consistency between the equation of state obtained separately from the virial theorem and from the compressibility, excellent agreement with the computer simulation results has been obtained for a wide variety of quite disparate potentials.^{1,3,4} For easy reference below, we denote by UPY that particular MHNC scheme which employs the PY bridge functions (4) as a universal input with the “virial-compressibility” consistency criterion. The practical importance of the UPY fit stems from the fact that by way of construction it constitutes a well-defined and very accurate approximation scheme for all kinds of simple classical fluids.

As a framework for understanding basic properties of simple classical fluids in terms of the pair potential, the MHNC scheme is meant to make progress, systematically, in several intimately related (and finally converging) directions:

(i) Fitting computer data via bridge functions in order to study the nature of relation (3) and in order to obtain information on the correct “closure” for the integral equation (diagrammatic) approach to simple classical fluids. A related problem is the extrapolation of the pair function beyond the “simulation range.”

(ii) *A priori* calculations of the pair structure and thermodynamic properties for given pair potentials.

(iii) Obtaining the pair potential (or effective pair potential) from the given pair function (or from the experimental structure factor data). The UPY scheme answers to some extent the first two of the above aims, and the present work intends to make further progress along these lines. As a fitting procedure the UPY scheme puts emphasis on satisfying the compressibility sum rule. We must keep in mind, though, that a systematic fitting procedure must include parameters that measure deviations from the data to be fitted, and that eventually corrections to “universality” may be sought with trial bridge functions of the type

$$B(x;(\mu_i))=B_{\text{PY}}(x;\eta)+B^{(R)}(x;(\xi_i)) \quad (5)$$

with the number of parameters exceeding the number of thermodynamic consistency conditions that may be imposed. Regarding the third aim above, namely, the possibility of inverting experimental structure-factor data in order to extract potentials, the UPY scheme *as it stands* cannot be applied in view of the *nonlocal* condition that it imposes in order to determine the free parameter of the bridge function. By *nonlocal* we mean that we must solve the MHNC equation self-consistently for an entire isochore even if we are interested in only a single thermodynamic state.

In order to be useful for inverting the pair function data (or experimental structure-factor data) to obtain the potential, the MHNC criteria that determine the free parameters of the bridge function should be *local* and involve the pair structure and the assumed bridge function, but should not explicitly involve the pair potential. In principle (and as will become clearer later on), such a criterion can be constructed only on the basis of some perturbation approximation. In order that the MHNC fitting procedure will enable us to make systematic progress in all three directions above, we have to study its characteristics with regard to various perturbation theories. A fully developed MHNC scheme should be accompanied by an appropriate perturbation theory of comparable accuracy.

In particular, we shall demonstrate that the variational first-order thermodynamic perturbation theory (VPT) is an appropriate perturbation theory to supplement the UPY scheme when applied to soft (i.e., "physical") potentials.

Thermodynamic perturbation methods⁵⁻⁸ should be studied in their own right since, although somewhat less accurate than the UPY scheme, they are considerably simpler to apply and will be preferable for many practical equation-of-state calculations. Perturbation theory finds its widest range of applicability in the variational form based on the Gibbs-Bogoliubov inequality, with the system of hard spheres as the virtually unanimous choice for the reference system. In recent work,⁸ a large body of computer simulation data for simple classical fluids was analyzed in light of various types of applications of perturbation theory. It was realized that a single one-parameter pair function could be employed in the VPT description of the equation of state for a wide range of *soft* potentials, and that by moving over from the hard spheres to a yet-to-be specified soft reference, a substantial improvement in accuracy is achieved. Just by assuming the *existence* of such a universal one-parameter description, a new method for equation of state calculations was derived; it is based on the idea of "additivity," with the excess entropy and the density serving as the independent variables. This potentially powerful method⁹ requires a more careful assessment before large scale applications are attempted.

The analysis in the present work shows how the MHNC scheme provides a natural parametric description for the pair structure and the equation of state. We determine conditions for the bridge functions from which follow a universal one-parameter description of the equation of state and additivity of equations of state. Moreover, we

shall demonstrate that, to the extent that the "soft" VPT is accurate, the UPY consistency condition may be replaced by a *local* condition thus realizing the basic aims of the MHNC scheme as listed above.

This paper is organized as follows: In Sec. II the MHNC scheme is featured as a variational fitting procedure and it is shown that any local MHNC condition is equivalent to an approximate local evaluation of the excess entropy. Variational perturbation theory (VPT) within the MHNC scheme is considered in Sec. III, where it is also investigated under what conditions it may serve as a local MHNC condition. In Sec. IV we display UPY results in the form $\eta(s)$, i.e., the excess-entropy dependence of the bridge parameter, and interpret the picture in light of the VPT results. A modified VPT (MVPT) is proposed in Sec. V, as an interpretation of the plot $\eta(s)$, which provides an explanation for the higher accuracy obtained by employing (in the VPT) the PY-hard-sphere results instead of the "exact" hard-sphere computer data. A local MHNC criterion, originally due to Lado,¹⁰ is rederived and extended in Sec. VI, so that it may be useful for fitting simulation data to obtain the bridge function, and for inverting structure factor data in order to obtain potentials. A brief summary of the results and some of their implications are presented in Sec. VIII. The Appendix is devoted to estimating the relative position, in the plot $\eta(s)$, of the lines representing the hard-sphere potential and the PY approximation for the same potential.

II. MHNC SCHEME AS A VARIATIONAL FITTING PROCEDURE

A complete MHNC scheme result for a given pair potential $\phi(r)$ is characterized by a bridge function $B(x;(\mu_i))$ with parameters (μ_i) and specific conditions (denoted by a superscript c , e.g., $c = \text{UPY}$) that determine the value of each parameter as a function of temperature and density, $\mu_{i,\phi}^c(\beta,\rho)$. A solution to Eqs. (1) and (2) for prescribed values for the parameters (μ_i) will be denoted by $g_\phi(x;\beta,\rho,(\mu_i))$. For a complete MHNC scheme result, if the functions $\mu_{i,\phi}^c(\beta,\rho)$ are single valued functions of β , they may be used to eliminate the explicit β dependence of g , and for each isochore the values of ρ and the $\mu_{i,\phi}^c(\beta,\rho)$ completely specify the pair function

$$g_\phi^c(x;\rho, [\mu_{i,\phi}^c(\beta,\rho)]) .$$

In this sense, any MHNC scheme result for a given bridge function but with different ϕ or c defines a different parametric set of pair functions $g_\phi^c(x;\rho,(\mu_i))$.

For inverse power potentials $\phi_n = r^{-n}$ the density and temperature combine into a single independent variable $y_n = \beta^{3/n}\rho$, and for these potentials the parametric sets of pair functions are $g_n^c(x;(\mu_i))$ corresponding to $[\mu_{i,\phi_n}^c(y_n)]$. In particular, the UPY scheme defines a one-parameter set of functions $g_n^{\text{UPY}}(x;\eta)$ for each inverse power potential. If the bridge function employed is the *exact* bridge function for some general potential, $\phi(r;\epsilon,\sigma,(\lambda_i))$, typically containing the energy and distance scales ϵ and σ , as well as other parameters (λ_i) , then the set (μ_i) of the MHNC scheme may consist of any subset of $[\beta^*,\rho^*,(\lambda_i)]$, where $\beta^* = \beta\epsilon$ and $\rho^* = \rho\sigma^3$ are the reduced quantities. Such

bridge functions are denoted by $B_{\phi, \text{exact}}(x; (\mu_i))$. For example, $B_{\phi_n, \text{exact}}(x; y_n)$ may be employed in a MHNC scheme for a potential ϕ to yield the set $g_{\phi}^c(x; \rho, y_n)$, or for another inverse power potential ϕ_m to yield a set $g_{\phi_m}^c(x; y_n)$ which represents another one-parameter set different from $g_{\phi_n, \text{exact}}(x; y_n)$.

Central to the development of the present work is the MHNC excess free energy as obtained via the "energy" equation of state. At any value of ρ , starting from the expression for the potential energy per particle,

$$U/N = \frac{1}{2} \int d\vec{x} g(x) \phi(x/\rho^{1/3}) \quad (6)$$

and integrating the relation

$$U/N = \partial/\partial\beta(\beta F^E/N)$$

while using Eqs. (1) and (2), the excess entropy per particle via the energy equation of state, S^E/Nk_B , is obtained from the relation

$$\begin{aligned} s^{\text{nonlocal}} &\equiv \frac{1}{2} \int d\vec{x} \int_0^{\beta} d\beta' g(x) \frac{dB(x)}{d\beta'} \\ &= \frac{1}{2} \int d\vec{x} \int_0^{\beta} d\beta' g_{\phi}^c(x; \rho, [\mu_{i,\phi}^c(\beta', \rho)]) \sum_i \frac{\partial \mu_{i,\phi}^c(\beta', \rho)}{\partial \beta'} \frac{\partial B(x; (\mu_i))}{\partial \mu_i} \Bigg|_{(\mu_i)=[\mu_{i,\phi}^c(\beta', \rho)]} \end{aligned} \quad (9)$$

where we also defined $s = s^{\text{loc}} + s^{\text{nonloc}}$ (loc is local and nonloc is nonlocal). As for the pair function, for each isochore the function s given by (8) is completely specified by ρ and the $\mu_{i,\phi}^c(\beta; \rho)$, i.e., $s = s_{\phi}^c(\rho, [\mu_{i,\phi}^c(\beta, \rho)])$, and, similarly to the pair functions, this relation defines a parametric set of functions $s_{\phi}^c(\rho, (\mu_i))$.

Using the parametric sets of functions $g_{\phi_1}^c(x; \rho, (\mu_i))$, $s_{\phi_1}^c(\rho, (\mu_i))$ as obtained by a particular MHNC scheme for some general potential ϕ_1 , we define the following energy and free energy parametric expressions (functionals) for any general potential ϕ_2 , by

$$u_{\phi_2}^{\phi_1, c_1}(\rho, (\mu_i)) \equiv \frac{1}{2} \int d\vec{x} g_{\phi_1}^c(x; \rho, (\mu_i)) \phi_2(x/\rho^{1/3}), \quad (10)$$

$$f_{\phi_2}^{\phi_1, c_1}(\beta, \rho, (\mu_i)) \equiv \beta u_{\phi_2}^{\phi_1, c_1}(\rho, (\mu_i)) + s_{\phi_1}^c(\rho, (\mu_i)). \quad (11)$$

We define

$$\bar{u}_{\phi}^{\phi, c}(\beta, \rho) = u_{\phi}^{\phi, c}(\rho, [\mu_{i,\phi}^c(\beta, \rho)]),$$

$$\bar{s}_{\phi}^c(\beta, \rho) = s_{\phi}^c(\rho, [\mu_{i,\phi}^c(\beta, \rho)]),$$

$$\bar{f}_{\phi}^{\phi, c}(\beta, \rho) = f_{\phi}^{\phi, c}(\beta, \rho, [\mu_{i,\phi}^c(\beta, \rho)]).$$

By definition [Eqs. (6)–(9)] we also have

$$\beta \bar{u}_{\phi}^{\phi, c}(\beta, \rho) = \left[\frac{d\bar{f}_{\phi}^{\phi, c}(\beta, \rho)}{d\beta} \right]_{\rho} = \beta u_{\phi}^{\phi, c}(\rho, [\mu_{i,\phi}^c(\beta, \rho)]) + \sum_i \left[\frac{\partial \mu_i}{\partial \beta} \right]_{\rho} \left[\frac{\partial f_{\phi}^{\phi, c}(\beta, \rho, (\mu_i))}{\partial \mu_i} \right]_{\beta, \rho} \Bigg|_{(\mu_i)=[\mu_{i,\phi}^c(\beta, \rho)]} \quad (12)$$

so that the MHNC equation of state has the form of a variational fitting procedure (as discussed in Ref. 8):

$$\bar{f}_{\phi}^{\phi, c}(\beta, \rho) = f_{\phi}^{\phi, c}(\beta, \rho, [\mu_{i,\phi}^c(\beta, \rho)]) \quad (13)$$

with the parameters $\mu_{i,\phi}^c(\beta, \rho)$ satisfying the variation equations,

$$\frac{\partial f_{\phi}^{\phi, c}}{\partial \mu_i}(\beta, \rho, (\mu_i)) = 0, \quad i = 1, 2, \dots \quad (14)$$

$$\beta F^E/N \equiv f = U/N + s, \quad (7)$$

where $s \equiv -S^E/Nk_B \geq 0$ is given by¹¹

$$\begin{aligned} s &= -\frac{1}{2} \int d\vec{x} \left[\frac{1}{2} h^2(x) + h(x) - g(x) \ln g(x) \right] \\ &\quad - \frac{1}{2} \int \frac{d\vec{x}}{(2\Pi)^3} \{ \ln[1 + \tilde{h}(k)] - \tilde{h}(k) \} \\ &\quad - \frac{1}{2} \int d\vec{x} g(x) B(x) + \frac{1}{2} \int d\vec{x} \int_0^{\beta} d\beta' g(x) \frac{dB(x)}{d\beta'}. \end{aligned} \quad (8)$$

We use the short notations

$$g(x) = g_{\phi}^c(x; \rho, (\mu_i)), \quad B(x) = B(x; (\mu_i)),$$

$$\frac{d}{d\beta} = \frac{\partial}{\partial \beta} + \sum_i \frac{\partial \mu_i}{\partial \beta} \frac{\partial}{\partial \mu_i}.$$

Specifically, in fuller notation, the last (and *nonlocal*) term in Eq. (8) reads as follows:

Going backwards it becomes clear that any MHNC scheme for a given potential is fully determined by specifying the bridge function $B(x; (\mu_i))$ and the entropy function $s(\rho, (\mu_i))$. In other words, the set of conditions c leading to $\mu_{i,\phi}^c(\beta, \rho)$ is equivalent to specifying the functions $s_{\phi}^c(\rho, (\mu_i))$. If the function $s_{\phi}^c(\rho, (\mu_i))$ is specified, the calculation of the pair structure and, of course, of the $\mu_{i,\phi}^c(\beta, \rho)$, may be carried out as follows: For any ρ start from $\beta \rightarrow 0$ and solve Eqs. (1) and (2) for each β , varying

the parameters (μ_i) of B until the expression (8) satisfies

$$s(\beta, \rho) = s_\phi^c(\rho, (\mu_i))$$

with $g(x)$ at these β, ρ being evaluated with the same set $\{\mu_i\}$. Such a procedure to obtain $\mu_{i,\phi}^c(\beta, \rho)$ [and thus to obtain $g_\phi^c(x; \rho, [\mu_{i,\phi}^c(\beta, \rho)])$] is manifestly *nonlocal*, in the general case, in view of the last term in Eq. (8).

Any attempt to fit a given pair function from simulations by a MHNC scheme with conditions specified by $s_\phi^c(\rho, (\mu_i))$ calls for some approximation that enables a *local* evaluation of the excess entropy. In the final analysis, a determination or an approximation of the excess entropy just from a given pair function of a given potential may be carried out only by comparison with another pair function for which the excess entropy is known.

III. VARIATIONAL PERTURBATION THEORY (VPT) WITHIN THE MHNC SCHEME: CHARACTERISTICS OF THE VPT CLASSES

Suppose that the structure and equation of state for a pair potential ϕ_0 are fitted to a *high accuracy* by a MHNC scheme that employs $B(x; (\mu_i))$ and $s_{\phi_0}^{c_0}(\rho, (\mu_i))$, and suppose we also know $g_{\phi_0}^{c_0}(x; \rho, (\mu_i))$. Consider the free-energy functions $f_{\phi_j}^{\phi_0, c_0}(\beta, \rho, (\mu_i))$ as defined in Eqs. (10) and (11), for various potentials ϕ_i , and impose the variational conditions

$$\frac{\partial f_{\phi_j}^{\phi_0, c_0}}{\partial \mu_i}(\beta, \rho, (\mu_i)) = 0, \quad i = 1, 2, \dots \quad (15)$$

which determine the parameters as functions of β and ρ for each ϕ_j : $\mu_{i,\phi_j}^{\phi_0, c_0}(\beta, \rho)$. This defines the VPT result for ϕ_j using the MHNC result c_0 for ϕ_0 as the reference. In the special case when

$$g_{\phi_0}^{c_0}(x; \rho, (\mu_i)) = g_{\phi_0, \text{exact}}(x; (\mu_i)),$$

so that

$$s_{\phi_0}^{c_0}(\rho, (\mu_i)) = s_{\phi_0, \text{exact}}(\mu_i),$$

it represents the exact VPT results for the potentials ϕ_j using ϕ_0 as the reference potential. The equations of state are given by the excess free energy

$$\begin{aligned} \bar{f}_{\phi_j}^{\phi_0, c_0}(\beta, \rho) &= \frac{1}{2}\beta \int d\vec{x} g_{\phi_0}^{c_0}(x; \rho, [\mu_{i,\phi_j}^{\phi_0, c_0}(\beta, \rho)]) \\ &\quad \times \phi_j(x/\rho^{1/3}) \\ &\quad + s_{\phi_0}^{c_0}(\rho, [\mu_{i,\phi_j}^{\phi_0, c_0}(\beta, \rho)]), \end{aligned} \quad (16)$$

where, in view of (14), this also holds for $\phi_j = \phi_0$, where

$$\mu_{i,\phi_0}^{\phi_0, c_0}(\beta, \rho) \equiv \mu_{i,\phi_0}^{c_0}(\beta, \rho).$$

Consider now the MHNC scheme C_j for some potential ϕ_j using the above $B(x; (\mu_i))$ and the conditions

$$s_{\phi_j}^{c_j}(\rho, (\mu_i)) = s_{\phi_0}^{c_0}(\rho, (\mu_i)). \quad (17)$$

By the definitions above we may characterize the result by

$$\begin{aligned} f_{\phi_j}^{\phi_j, c_j}(\beta, \rho, (\mu_i)) &= f_{\phi_j}^{\phi_0, c_0}(\beta, \rho, (\mu_i)) \\ &\quad + \beta [u_{\phi_j}^{\phi_j, c_j}(\rho, (\mu_i)) - u_{\phi_j}^{\phi_0, c_0}(\rho, (\mu_i))] \end{aligned} \quad (18)$$

with the variational conditions

$$\begin{aligned} 0 &= \frac{\partial f_{\phi_j}^{\phi_j, c_j}}{\partial \mu_i} \\ &= \frac{\partial f_{\phi_j}^{\phi_0, c_0}}{\partial \mu_i} + \beta \frac{\partial}{\partial \mu_i} [u_{\phi_j}^{\phi_j, c_j}(\rho, (\mu_i)) - u_{\phi_j}^{\phi_0, c_0}(\rho, (\mu_i))]. \end{aligned} \quad (19)$$

In the *special case* when the solution to Eqs. (15) (which is assumed to be known) also satisfies

$$u_{\phi_j}^{\phi_j, c_j}(\rho, (\mu_i)) = u_{\phi_j}^{\phi_0, c_0}(\rho, (\mu_i)) \quad (20)$$

the result is then

$$\mu_{i,\phi_j}^{c_j}(\beta, \rho) = \mu_{i,\phi_j}^{\phi_0, c_0}(\beta, \rho),$$

and the VPT and c_j -MHNC results are identical:

$$\bar{f}_{\phi_j}^{\phi_j, c_j}(\beta, \rho) = \bar{f}_{\phi_j}^{\phi_0, c_0}(\beta, \rho). \quad (21)$$

Since the (c_0, ϕ_0) -MHNC result is assumed to be available, then, in such a *special case* as above, the given functions $\mu_{i,\phi_j}^{\phi_0, c_0}(\beta, \rho)$ provide a *local* criterion for the c_j -MHNC scheme. The local conditions may also be applied via (20); namely, at any given β, ρ vary the parameters (μ_i) until

$$\begin{aligned} \int d\vec{x} [g_{\phi_j}(x; \beta, \rho, (\mu_i)) \\ - g_{\phi_0}^{c_0}(x; \rho, (\mu_i))] \phi_j(x/\rho^{1/3}) = 0. \end{aligned} \quad (22)$$

All MHNC scheme results for potentials ϕ_j that employ the same $B(x; (\mu_i))$, and that obey (17) and (20), are said to belong to the same $(B, s_{\phi_0}^{c_0})$ -VPT class generated by the potential ϕ_0 . The main class property is that the VPT result for any ϕ_j of the class provides a *local* criterion via Eq. (20) and fully determines the equation of state by (21).

Two special types of generating potentials should be especially noted: (1) ϕ_0 is an inverse power potential, and (2) ϕ_0 is the potential for which the employed bridge functions is the exact one, i.e.,

$$B(x; (\mu_i)) = B_{\phi_0, \text{exact}}(x; (\mu_i)).$$

In both of the above cases there is no explicit density dependence in $g_{\phi_0}^{c_0}$ or $s_{\phi_0}^{c_0}$, and the VPT functional for any potential ϕ takes the form

$$\begin{aligned} f_{\phi}^{\phi_0, c_0}(\beta, \rho, (\mu_i)) &= \frac{1}{2}\beta \int d\vec{x} g_{\phi_0}^{c_0}(x; (\mu_i)) \phi(x/\rho^{1/3}) \\ &\quad + s_{\phi_0}^{c_0}(\mu_i). \end{aligned} \quad (23)$$

In view of the variational property

$$\frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial \mu_i} = 0,$$

we find that the pressure for any potential of the class is given by the virial expression with $g_{\phi_0}^{c_0}$:

$$\begin{aligned} \frac{\beta P}{\rho} - 1 &= \left[\frac{df_{\phi}^{\phi_0, c_0}}{d\rho} \right]_{\beta} \\ &= \left[\frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial \rho} \right]_{\beta, \{\mu_i\}} + \sum_i \left[\frac{\partial \mu_i}{\partial \rho} \right]_{\beta} \left[\frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial \mu_i} \right]_{\beta} \\ &= \left[\frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial \rho} \right]_{\beta} \\ &= -\frac{\beta}{6} \int d\bar{x} g_{\phi_0}^{c_0}(x; \{\mu_i\}) \left[\frac{x}{\rho^{1/3}} \right] \phi' \left[\frac{x}{\rho^{1/3}} \right]. \end{aligned} \quad (24)$$

Introduce the variable s by the equation

$$s = s_{\phi_0}^{c_0}(\rho, \{\mu_i\}) \quad (25)$$

and use this equation to replace one of the parameters μ_i , for example μ_1 , by s . Denote the set $\{\mu_i | i=2,3,\dots\}$ by $\{\mu_i\}'$. The free-energy functional $f_{\phi}^{\phi_0, c_0}$ takes the form

$$\begin{aligned} f_{\phi}^{\phi_0, c_0}(\beta, \rho, s, \{\mu_i\}') \\ &= \frac{1}{2} \beta \int d\bar{x} g_{\phi_0}^{c_0}(x; \rho, s, \{\mu_i\}') \phi(x/\rho^{1/3}) + s \\ &\equiv \beta u_{\phi}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') + s \end{aligned} \quad (26)$$

while the variational conditions (15) take the form

$$\frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial s} = 0, \quad \frac{\partial f_{\phi}^{\phi_0, c_0}}{\partial \mu_i} = 0, \quad i=2,3,\dots \quad (27)$$

or, in other notation,

$$\beta = - \left[\frac{\partial}{\partial s} u_{\phi}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') \right]^{-1} \equiv \beta_{\phi}(\rho, s, \{\mu_i\}') \quad (28)$$

$$\frac{\partial}{\partial \mu_i} u_{\phi}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') = 0, \quad i=2,3,\dots \quad (29)$$

Equations (29) determine the $\mu_{i,\phi}^{\phi_0, c_0}(\rho, s)$ for $i=2,3,\dots$ that, when inserted in (28), yield

$$\beta = \beta_{\phi}(\rho, s, [\mu_{i,\phi}^{\phi_0, c_0}(\rho, s)]) \equiv \bar{\beta}_{\phi}(\rho, s). \quad (30)$$

The pressure is obtained from

$$\begin{aligned} \frac{\beta P}{\rho} - 1 &= \left[\frac{\partial}{\partial \rho} u_{\phi}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') \right]_{s, \{\mu_i\}'} \\ &\equiv \frac{\beta}{\rho} P_{\phi}^E(\rho, s, \{\mu_i\}'), \end{aligned} \quad (31)$$

so that the excess pressure is given by

$$P^{\text{ex}} = P_{\phi}^E(\rho, s, [\mu_{i,\phi}^{\phi_0, c_0}(\rho, s)]) \equiv \bar{P}_{\phi}^E(\rho, s). \quad (32)$$

Combining Eqs. (30) and (32) we obtain the equation of state $P^{\text{ex}}(\beta, \rho)$. If the potentials ϕ_1, ϕ_2 and a linear combination of the two, $\alpha_1 \phi_1 + \alpha_2 \phi_2$ all belong to the same VPT-class, as above, then by definition

$$\begin{aligned} u_{\alpha_1 \phi_1 + \alpha_2 \phi_2}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') &= \alpha_1 u_{\phi_1}^{\phi_0, c_0}(\rho, s, \{\mu_i\}') \\ &\quad + \alpha_2 u_{\phi_2}^{\phi_0, c_0}(\rho, s, \{\mu_i\}'). \end{aligned} \quad (33)$$

Using Eqs. (26)–(32) we see that, as long as the $\mu_{i,\phi}^{\phi_0, c_0}(\rho, s)$, $i=2,3,\dots$ are independent of ϕ , the equation of state with ρ and s as the independent variables is given in terms of these for ϕ_1 and ϕ_2 by a linear combination:

$$\bar{\beta}_{\alpha_1 \phi_1 + \alpha_2 \phi_2}^{-1}(\rho, s) = \alpha_1 \bar{\beta}_{\phi_1}^{-1}(\rho, s) + \alpha_2 \bar{\beta}_{\phi_2}^{-1}(\rho, s), \quad (34)$$

$$\bar{P}_{\alpha_1 \phi_1 + \alpha_2 \phi_2}^E(\rho, s) = \alpha_1 \bar{P}_{\phi_1}^E(\rho, s) + \alpha_2 \bar{P}_{\phi_2}^E(\rho, s). \quad (35)$$

In the general case we cannot expect the $\mu_{i,\phi}^{\phi_0, c_0}(\rho, s)$ to be independent of ϕ , so that the class property of “additivity of equations of state” [Eqs. (34) and (35)] may be associated with VPT classes for *one-parameter* bridge functions.

We have described above several strong class properties of VPT classes. Yet, in the strict formal sense, a VPT class generated by a potential ϕ_0 with MHNC conditions given by $s_{\phi_0}^{c_0}(\rho, \{\mu_i\})$ may consist of only the potential ϕ_0 itself. We may enlarge, however, the number of members (i.e., potentials) in the class by allowing the following *approximation* [instead of (17)]:

$$|s_{\phi_j}^{c_j}(\rho, \{\mu_i\}) - s_{\phi_0}^{c_0}(\rho, \{\mu_i\})| \leq |\Delta s| \quad (36)$$

with the number and types of potentials in the class depending on ϕ_0 and $|\Delta s|$. Indeed, the main point to be demonstrated in Sec. IV is that with $|\Delta s|$ being the statistical error of present day simulation results, a large body of “physical” potentials are in the same VPT class, appropriate to soft potentials, which may be generated by any member of the class, while the hard spheres are distinctly different in this sense. Bearing in mind the class properties described above, the results of Sec. IV provide the needed *local* conditions mentioned in the introduction.

IV. UPY RESULTS AND VPT CLASSES

As already stated in the Introduction, the UPY approximation provides a very accurate description of the pair structure and thermodynamic properties for a wide class of simple potentials by employing a universal one-parameter bridge function $B_{\text{PY}}(x; \eta)$. The UPY results are within the statistical error of the simulations. Following the discussion of the preceding section, we would like to find out whether the excess-entropy dependence of the UPY parameter for different potentials, namely, $\eta_{\phi}(\rho, s)$, does indeed divide the space of potentials into VPT classes. Present day computer simulation accuracy is generally characterized by

$$|\Delta \eta_{\phi}| / \eta_{\phi} \lesssim 2\%. \quad (37)$$

Analysis of various applications of perturbation theory⁸ as well as direct VPT calculations¹² for various potentials

employing different reference potentials, demonstrated that a single one-parameter set of pair functions, $g_0(x;s)$, may provide by (26) an extremely accurate equation of state for a wide class of *relatively soft* potentials. In fact, for dense fluids one may employ the pair functions $g_{n,\text{exact}}(x;s)$ of the inverse power potentials with results that are nearly independent of $n \leq 12$. Thus, from the equation-of-state point of view, the set of pair functions for the soft potentials $g_\phi(x;\rho,s)$ is nearly independent of ρ and ϕ and may be represented by a single "effective" pair function, for example, $g_I(x;s)$. We emphasize that the hard spheres and similarly harsh potentials are not included in that VPT class. Our calculations do indicate that all soft inverse power potentials ($n \leq 12$) as well as Lennard-Jones states outside the two-phase (liquid-gas) region, belong to the same VPT class that may be generated by each member of the class. Conclusions similar to those for the Lennard-Jones potential are reached for the $\exp-6$ potential $Ae^{-ar} - Br^{-6}$. This variety of potentials found to be in the same VPT class provide a strong indication that, except for a possible two-phase region, the additivity method as demonstrated for the Lennard-Jones system^{8,9} is of general validity.

In Fig. 1 we plot the results of UPY calculations,^{1,3,4} $\eta_\phi(s)$ for the following potentials: r^{-1} (Coulomb), r^{-6} , r^{-12} (soft spheres), $r^{-\infty}$ (hard spheres), and $r^{-12} - r^{-6}$ (Lennard Jones). We see clearly on this plot the universality of $\eta_\phi(s)$ for soft potentials and the "jump" in potential space from the soft line $\eta_{\text{soft}}(s)$ to the hard-sphere line $\eta_{\phi=r^{-\infty}}(s)$ in complete agreement with the picture above regarding the VPT classes. The functions $\eta_\phi(s)$ do indeed divide the space of potentials into VPT classes.

It is a remarkable property of simple classical fluids that the equation of state and the pair structure for such a variety of potentials finally condenses into a universal line:

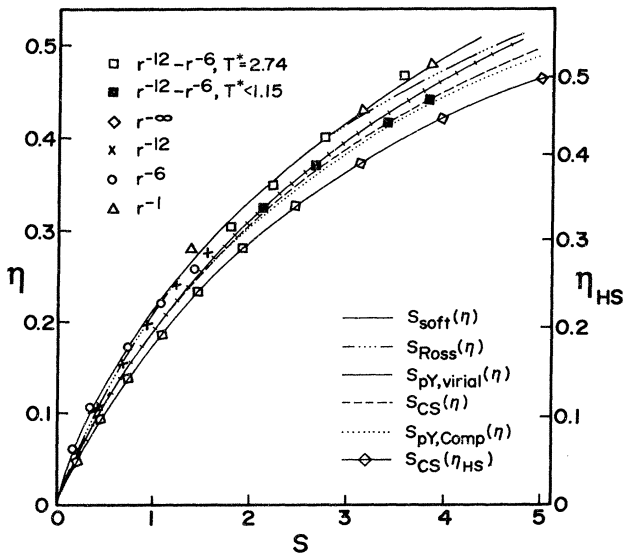


FIG. 1. Percus-Yevick bridge function parameters η as a function of the excess entropy s as obtained by the UPY scheme for different potentials. The scale on the right, η_{HS} , is defined by Eq. (45) such that $s_{\text{CS}}(\eta_{\text{HS}})$ reproduces the line $\eta(s)$ for hard spheres. For the meaning of the different lines see the text.

$$\eta_\phi(\rho,s) \cong \eta_{\text{soft}}(s) \quad (38)$$

corresponding to a universal bridge function

$$B_\phi(x;\rho,s) \cong B_{\text{PY}}(x;\eta_{\text{soft}}(s)) . \quad (39)$$

We may summarize these findings by the statement that the approximation

$$B_\phi(x;\rho,s) = B_{\phi_0}(x,\rho,s) , \quad (40)$$

where ϕ_0 is a reference soft potential, yields essentially the VPT equation of state with ϕ_0 as reference; when employed in the MHNC scheme as a *local* criterion it also yields a very accurate pair function that satisfies to a good accuracy the compressibility sum rule.

This result also offers a better understanding of the difference between the application of the MHNC scheme and the RHNC method originally proposed by Lado.¹¹ In RHNC one would separate $\phi(r) = \phi_0(r) + \phi_1(r)$ and the (assumed known) bridge function of the reference system will be employed in Eqs. (1) and (2) at the same β, ρ :

$$B_{\phi, \text{RHNC}}(x;\beta, \rho) = B_{\phi_0}(x;\beta, \rho) \quad (41)$$

which differs from (40) in complete analogy to the difference between ordinary first-order perturbation theory and variational (i.e., optimized) first-order perturbation theory.

Another interesting feature that follows directly from Fig. 1 is the "bridge" freezing criterion:¹³

$$\eta_\phi^{\text{freezing}}(s) = 0.47 \pm 2\% , \quad (42)$$

which holds for both the hard spheres *and* the soft potentials. For hard spheres $s_{\text{freezing}} \simeq 5$ while for soft potentials $s_{\text{freezing}} \simeq 4$. It is very interesting that the criterion (42) does apply over 25% changes in excess entropy at freezing.

V. MODIFIED VPT AND THE CHOICE OF THE ENTROPY FUNCTIONAL

From the analysis of preceding sections it should be clear that the energy functional

$$u_\phi^{\phi_0, \text{UPY}}(\rho, \eta) = \frac{1}{2} \int d\vec{x} g_{\phi_0}^{\text{UPY}}(x;\rho, \eta) \phi(x/\rho^{1/3})$$

is rather insensitive to ϕ_0 , with the insensitivity being measured by the differences in the corresponding functions $\eta_{\phi_0}(s)$. Let ϕ be a soft potential and let ϕ_0 be any potential. Consider a modified-VPT (MVPT) approximation with the free-energy functional

$$f_{\phi, \text{MVPT}}^{\phi_0, \text{UPY}} = \beta u_\phi^{\phi_0, \text{UPY}}(\rho, \eta) + s_{\text{MVPT}}(\eta) , \quad (43)$$

where instead of $s_\phi^{\text{UPY}}(\eta)$ we may now use any entropy function $s_{\text{MVPT}}(\eta)$. If our interpretation of the lines $\eta_\phi(s)$ is correct, we then expect, in general, that the MVPT approximation gives better results the closer $s_{\phi_0}^{\text{UPY}}(\eta)$ is to $s_\phi^{\text{UPY}}(\eta)$ and, *independently*, the closer $s_{\text{MVPT}}(\eta)$ is to $s_\phi^{\text{UPY}}(\eta)$. The following results clearly favor this interpretation.

The "canonical" VPT calculations in the literature¹⁴ employ Eq. (43), using the PY pair functions, $g_{\text{PY}}(x;\eta)$ and the Carnahan-Starling (CS) expression for the entropy

$$s_{CS}(\eta) = \frac{4\eta - 3\eta^3}{(1-\eta)^2}. \quad (44)$$

Note that throughout this paper η is the parameter name for the UPY bridge parameter. As shown in the Appendix,

$$g_{PY}(x; \eta) \cong g_{PY}^{UPY}(x; \eta), \quad s_{CS}(\eta) \cong s_{PY}^{UPY}(\eta),$$

so that the canonical VPT calculations above essentially represent VPT calculations with a ‘‘PY’’ reference system. These results generally improve upon VPT calculations that employ $s_{CS}(\xi)$ with $g_{HS}(x; \xi)$, namely, the hard spheres of packing fraction $\xi = (\Pi/6)\rho d^3$ as the reference. This result is in agreement with our MVPT interpretation of the hierarchy

$$\eta_{soft}(s) > \eta_{CS}(s) > \eta_{r-\infty}(s).$$

Note that the UPY results for hard sphere as obtained by Tsai⁴ yield

$$\frac{\eta_{r-\infty}(s)}{\eta_{CS}(s)} = [0.982913 - 0.02271\eta_{CS}^{(s)} + 0.02449\eta_{CS}^{(s)2}]^3. \quad (45)$$

Moreover, one finds that, in practice, using $g_{PY}(x; \eta)$ in (43) together with the ‘‘virial’’ expression for the entropy,

$$s_{virial}(\eta) = 6 \left[\frac{1}{1-\eta} - 1 \right] + 2 \ln(1-\eta) \quad (46)$$

one improves^{15,16} upon the results using $s_{CS}(\eta)$ in agreement with

$$\eta_{soft}(s) \geq \eta_{virial}(s) \geq \eta_{CS}(s).$$

Finally, Ross⁵ has fitted the Monte Carlo data for the r^{-12} potential by a VPT functional that employs $g_{PY}(x, \eta)$ together with

$$s_{Ross}(\eta) = s_{CS}(\eta) - \left[\frac{\eta}{2} + \eta^2 + \frac{\eta^4}{2} \right] \quad (47)$$

and, using (47) and $g_{PY}(x, \eta)$ in (43), he also obtained excellent results for other soft potentials. Again, in agreement with our MVPT interpretation of Fig. 1, we see that $s_{Ross}(\eta)$ fits $s_{soft}(\eta)$ to within the simulation accuracy. In view of the Appendix we may thus interpret the bootstrapping approach of Ross as the optimized MVPT with the ‘‘PY’’ potential as reference.

VI. A LOCAL MHNC CRITERION BASED ON ‘‘VIRIAL-ENERGY’’ CONSISTENCY

So far we considered rather general characteristics of the MHNC scheme, and discussed in particular the UPY results. The UPY criterion (i.e., virial-compressibility consistency) is nonlocal, but the demonstrated relation between the universality of $\eta(s)$ and the VPT classes enables us to use a *local* criterion once the UPY results for one soft potential are available. The VPT local criterion, namely, Eq. (22), is based on comparison of ‘‘energy’’ integrals. By this method the entropy functional is obtained

locally only to within the VPT accuracy for ϕ using ϕ_0 as reference, which is a high accuracy if both are soft potentials. In view of (24) and since in most cases both $\phi(r)$ and $r\phi'(r)$ are in the same VPT class, we expect the virial-energy consistency to be obeyed for MHNC calculations with the VPT local criterion.

It is possible, however, to obtain local MHNC criteria, by imposing the virial-energy consistency, that allow a local evaluation of the entropy function without further approximations.

Consider again the general MHNC free-energy functional [Eqs. (6)–(9)]. The variation of f due to general variations of the structural properties g and B is given by

$$\begin{aligned} \delta f = & \frac{1}{2} \int d\vec{x} [\phi(x/\rho^{1/3}) - h(x) + \ln g(x)] \delta g(x) \\ & - \frac{1}{2} \int \frac{d\vec{k}}{(2\pi)^3} \frac{\tilde{h}(k)}{1 + \tilde{h}(k)} \delta \tilde{h}(k) - \frac{1}{2} \int d\vec{x} B(x) \delta g(x) \\ & - \frac{1}{2} \int d\vec{x} g(x) \delta B(x) \\ & + \frac{1}{2} \int_0^\beta d\beta' \int d\vec{x} \left[\delta g(x) \frac{dB(x)}{d\beta'} + g \delta \frac{dB(x)}{d\beta'} \right]. \quad (48) \end{aligned}$$

Using Eq. (2) and Parcival’s theorem, the second term in (48) becomes

$$- \frac{1}{2} \int d\vec{x} c(x) \delta g(x),$$

so that in view of Eq. (1) the sum of the first three terms in (48) vanishes, to yield

$$\delta f = \frac{1}{2} \int d\vec{x} \left[\int_0^\beta d\beta' \left[\delta g \frac{dB}{d\beta'} + g \frac{d\delta B}{d\beta'} \right] - g \delta B \right]. \quad (49)$$

Integrating by parts the second term in the square parentheses in (49) we obtain

$$\delta f = \frac{1}{2} \int d\vec{x} \int_0^\beta d\beta' \left[\delta g \frac{dB}{d\beta'} - \delta B \frac{dg}{d\beta'} \right]. \quad (50)$$

The pressure as obtained from f by the usual thermodynamic relation,

$$\frac{\beta P}{\rho} - 1 = \rho \left[\frac{df}{d\rho} \right]_\beta,$$

which is the MHNC energy equation of state, reads [from (7)]

$$\begin{aligned} \rho \left[\frac{df}{d\rho} \right]_\beta = & \rho \left[\left[\frac{\delta f}{\delta \phi} \right]_{\beta, g, B} \frac{d\phi}{d\rho} + \left[\frac{\delta f}{\delta g} \right]_{\beta, \phi, B} \left[\frac{dg}{d\rho} \right]_\beta \right. \\ & \left. + \left[\frac{\delta f}{\delta B} \right]_{\beta, \phi, g} \left[\frac{dB}{d\rho} \right]_\beta \right]. \quad (51) \end{aligned}$$

Using (50) we finally get

$$\frac{\beta P}{\rho} - 1 = - \frac{\beta}{6} \int d\vec{x} g(x) \left[\frac{x}{\rho^{1/3}} \right] \phi' \left[\frac{x}{\rho^{1/3}} \right] + \delta P_{v,E}, \quad (52)$$

where the first term on the right-hand side of (52) is the

virial expression for the pressure, and $\delta P_{v,E}$ represents the deviations from the virial-energy consistency, given by

$$\delta P_{v,E} = \frac{1}{2} \int_0^\beta d\beta' \int d\vec{x} \left[\frac{dg}{d\rho} \frac{dB}{d\beta'} - \frac{dB}{d\rho} \frac{dg}{d\beta'} \right]. \quad (53)$$

The exact bridge function is a functional of the exact pair function [Eq. (3)] so that

$$\delta B \frac{dg}{d\beta'} = \frac{\delta B}{\delta g} \delta g \frac{dg}{d\beta'} = \delta g \frac{\delta B}{\delta g} \frac{dg}{d\beta'} = \delta g \frac{dB}{d\beta'} \quad (54)$$

and the integrands in the expressions for ϕf and $\delta P_{v,E}$ vanish identically:

$$(\delta f)_{\phi, \text{exact}} = 0, \quad (\delta P_{v,E})_{\phi, \text{exact}} = 0. \quad (55)$$

Ultimately, if we push the MHNC parametrization effort to such an extent that we are close to the exact result, then we expect that relation (3) will be closely obeyed in the sense

$$B(x; \{\mu_i\}) \cong \mathcal{F}[g(x; \rho, \{\mu_i\})], \quad (56)$$

and one possible way to take this relation into consideration is by imposing $\delta f = 0$, $\delta P_{v,E} = 0$ for variations in g and B caused by changes in the values of the fitting parameters $\{\mu_i\}$ in B . Expression (49) with $B(x, \{\mu_i\})$ and with g replaced by *any* functional of B , $G[B(x, \{\mu_i\})]$, vanishes identically [e.g., (55)]. Thus, we may rewrite the variation of f due to variations in the μ_i , $\delta f_{\{\mu_i\}}$, in the form

$$\begin{aligned} \delta f_{\{\mu_i\}} &= \frac{1}{2} \int_0^\beta d\beta' \delta \left[\int d\vec{x} (g - G) \frac{dB}{d\beta'} \right] \\ &\quad - \frac{1}{2} \int d\vec{x} (g - G) \delta B. \end{aligned} \quad (57)$$

The corresponding result for $(\delta P_{v,E})_{\{\mu_i\}}$ reads:

$$\begin{aligned} (\delta P_{v,E})_{\{\mu_i\}} &= \frac{1}{2} \int_0^\beta d\beta' \left[\frac{\partial g(x; \rho, \{\mu_i\})}{\partial \rho} \right]_{\{\mu_i\}} \frac{dB(x; \{\mu_i\})}{d\beta'} \\ &\quad + \rho \left[\frac{\delta f_{\{\mu_i\}}}{d\rho} \right]_{\beta}. \end{aligned} \quad (58)$$

If G is a functional of B , with no explicit density dependence, then the general criterion for (57) and (58) to vanish is

$$\int d\vec{x} (g_\phi(x; \beta, \rho, \{\mu_i\}) - G[B(x; \{\mu_i\})]) \delta B(x; \{\mu_i\}) = 0 \quad (59)$$

or equivalently

$$\begin{aligned} \int d\vec{x} (g_\phi(x; \beta, \rho, \{\mu_i\}) \\ - G[B(x; \{\mu_i\})]) \frac{\partial B(x; \{\mu_i\})}{\partial \mu_j} = 0, \\ j = 1, 2, 3, \dots \end{aligned} \quad (60)$$

In particular, G may be any MHNC scheme result for an inverse power potential, $G = g_n^c(x, \{\mu_i\})$, or the exact pair function corresponding to the given bridge function,

$$G = g_{\phi_0, \text{exact}}(x, \{\mu_i\}),$$

where $B = B_{\phi_0, \text{exact}}(x, \{\mu_i\})$.

Since no exact 2D or 3D bridge function is available at present for any potential, a special role is played in this context by the UPY results for the inverse power potentials and the ‘‘PY’’ system (as defined in the Appendix):

$$\int [g_\phi(x; \beta, \rho, \eta) - g_{\phi_{\text{ref}}}^{\text{UPY}}(x; \eta)] \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} d\vec{x} = 0. \quad (61)$$

Obviously, the more similar ϕ is to ϕ_{ref} the better will be the results obtained by the conditions (61), since then $g_{\phi_{\text{ref}}}^{\text{UPY}}(x, \eta)$ provides a better choice of a ‘‘bias’’ function. The criterion (61) may be applied in fitting simulation data and (in a perturbative context) as a local criterion in the MHNC scheme.

For example, if the UPY result for a given inverse power potential is available, $g_n^{\text{UPY}}(x, \eta)$, then when employing $B_{\text{PY}}(x, \eta)$ for a potential ϕ we use (61) with

$$g_{\phi_{\text{ref}}}(x, \eta) = g_n^{\text{UPY}}(x, \eta).$$

Note, however, that in view of (61) the last (and local) term in (8) [given in (9)] takes the form

$$\begin{aligned} \frac{1}{2} \int_0^\beta d\beta' \frac{\partial \eta}{\partial \beta'} \int d\vec{x} g_\phi^c(x; \rho, \eta) \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} \\ = \frac{1}{2} \int_0^\beta d\beta' \frac{\partial \eta}{\partial \beta'} \int d\vec{x} g_n^{\text{UPY}}(x; \eta) \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} \\ = \frac{1}{2} \int_0^\eta d\eta' \int d\vec{x} g_n^{\text{UPY}}(x; \eta') \frac{\partial B_{\text{PY}}(x; \eta')}{\partial \eta'}, \end{aligned}$$

that is,

$$s_\phi^{\text{nonlocal}}(\rho, \eta) = s_n^{\text{UPY}}(\eta) - s_n^{\text{UPY, local}}(\eta). \quad (62)$$

In other words, once we use (61) to obtain $\eta_\phi(\beta, \rho)$, we may obtain the excess entropy for this type of MHNC scheme by a local calculation. For a many-parameter bridge function the analogues of (61) and (62) are

$$\begin{aligned} \int d\vec{x} [g_\phi(x, \beta, \rho, \{\mu_i\}) - g_n^c(x; \{\mu_i\})] \frac{\partial B(x; \{\mu_i\})}{\partial \mu_i} = 0, \\ i = 1, 2, 3, \dots \end{aligned} \quad (63)$$

$$s_\phi^{\text{nonlocal}}(\rho, \{\mu_i\}) = s_n^c(\{\mu_i\}) - s_n^{c, \text{local}}(\{\mu_i\}). \quad (64)$$

When fitting a given pair function obtained by a simulation, $g_{\phi, \text{sim}}(x, \beta, \rho)$, this same function provides a self-consistent choice for a bias function, and the local condition (61) takes the form

$$\begin{aligned} J_i = \int d\vec{x} [g_\phi(x; \beta, \rho, \{\mu_i\}) - g_{\phi, \text{sim}}(x; \beta, \rho)] \\ \times \frac{\partial B(x; \{\mu_i\})}{\partial \mu_i} = 0, \quad i = 1, 2, \dots \end{aligned} \quad (65)$$

Equation (65) may also be derived from the following considerations. Applying the Gibbs-Bogoliubov inequality to

two MHNC solutions for a given potential, the following approximate inequality is obtained:¹

$$0 \lesssim \int d\vec{x} [g_{\phi}^{c_1}(x; \rho, \mu_{i,\phi}^1(\beta, \rho)) - g_{\phi}^{c_2}(x; \rho, \mu_{i,\phi}^2(\beta, \rho))] \times [B(x; \mu_{i,\phi}^2(\beta, \rho)) - B(x; \mu_{i,\phi}^1(\beta, \rho))] . \quad (66)$$

Taking the view that $g_{\phi, \text{sim}}$ is well represented by $B(x, \{\mu_i\})$ we expect our fit to give, at its worst, only slightly displaced values of the “correct” fitting parameters. Thus, we replace $g_{\phi}^{c_2}$ in (66) by $g_{\phi, \text{sim}}$, while the difference in the bridge functions is expanded to first order:

$$B(x; \{\mu_{i,\phi}^{c_2}\}) - B(x; \{\mu_{i,\phi}^{c_1}\}) \simeq \sum_i \left[\frac{\partial B}{\partial \mu_i} \right]_{\mu_{i,\phi}}^{c_2} \delta \mu_i . \quad (67)$$

The criterion (65) just minimizes the right-hand side of (66) for these first-order variations in the μ_i .

The criterion (61) has been originally derived by Lado¹⁰ in a purely perturbative context, which in our notations proceeds as follows. Assume that a reference system is known exactly, that is, for ϕ_0 we have both $g_{\phi_0, \text{exact}}(x; \{\mu_i\})$ and $B_{\phi_0, \text{exact}}(x, \{\mu_i\})$, and thus also $S_{\phi_0, \text{exact}}(\{\mu_i\})$. Assume next that

$$B_{\phi_0, \text{exact}}(x, \{\mu_i\}) = B_{\phi_0, \text{exact}}(x, \{\mu_i\})$$

(i.e., universality of the bridge functions¹), and thus employ $B_{\phi_0, \text{exact}}(x, \{\mu_i\})$ in a MHNC scheme for the potential ϕ . Consider the MHNC free-energy functional (7) [using (6) and (8)], and make the second approximation so that the last (nonlocal) term in (8) may be replaced by the corresponding term for ϕ_0 , i.e.,

$$s_{\phi}^{\text{nonlocal}} = s_{\phi_0}^{\text{nonlocal}} \quad (68)$$

[which should be compared with (64)]. Minimizing the functional with respect to the μ_i 's, taking into account (68), Lado obtains Eq. (68) with $g_{\phi_0, \text{exact}}(x, \{\mu_i\})$ replacing our $g_{\phi, \text{ref}}(x, \{\mu_i\})$.

Lado considered only exact bridge functions, and did not mention at all the application of (61) in the fitting context (namely, for inverting structure factor data to obtain potentials). Indeed, his application of the method to the Coulomb potential is made using $g_{\text{PY}}(x, \eta)$ and $B_{\text{PY}}(x, \eta)$ which should be properly interpreted in the context of our derivation of Eq. (61). Lado's results for the Coulomb potential, using essentially the UPY result for the “PY” potential as reference, represents a special type of a variational perturbation theory, and the expected accuracy of the results for other systems may be inferred from our Fig. 1 and Sec. V. In view of the accurate results that Lado obtained with the “PY” reference, we may expect the corresponding results with $g_n^{\text{UPY}}(x, \eta)$, $n \leq 12$, to yield essentially the exact UPY result for any soft (i.e., “realistic”) potential.

VII. SUMMARY AND IMPLICATIONS OF THE PRESENT WORK

Featuring the MHNC scheme as a variational fitting procedure we considered the characteristics of the VPT classes. We observed that to within the accuracy of present day simulation studies, all soft (i.e., “physical”) potentials and, in particular, the relatively soft inverse power potentials are in the same class, a picture that agrees with the universality of the line $\eta(s)$ as found for the UPY MHNC results. “Additivity of equations of state” and accurate local evaluation of the excess entropies [i.e., local evaluation of η in view of the universality of $\eta(s)$] then follow as class properties. An alternative local condition for the MHNC scheme, originally due to Lado,¹⁰ has been rederived and extended and, when considered in view of the MVPT and Fig. 1, is expected to provide an accurate local MHNC condition especially if UPY results for a soft potential are employed as reference. The jump in potential space from “hard” to “soft” behavior is graphically demonstrated by the lines $\eta_{\phi=r-\infty}(s)$ and $\eta_{\text{soft}}(s)$ in Fig. 1.

The existence of accurate local MHNC conditions as described above enables us to solve the “inverse” problem (namely, of obtaining the pair potential from the given pair function) with the same accuracy as obtained for the “direct” problem (namely, of obtaining the pair structure from the given pair potential), both under the assumption of universality of the bridge functions. In principle, the procedure is as follows: Let $g_{\text{expt}}(r)$ be the pair function at given β, ρ for the (yet unknown) pair potential $\phi_{\text{expt}}(r)$. (i) Use Eqs. (1) and (2) to obtain the sum

$$\phi_{\text{HNC}}(x) = \phi_{\text{expt}}(x) + B_{\text{PY}}(x, \eta_0) ,$$

where now η_0 becomes the required quantity. (ii) Calculate the moments

$$\langle x^{-l} \rangle = \frac{1}{2} \int g_{\text{expt}}(x) x^{-l} d\vec{x} ,$$

and for each l use the known equation of state for the corresponding inverse power potential to solve for s the equations

$$\int [g_{\text{expt}}(x) - g_l(x, s)] x^{-l} d\vec{x} = 0 .$$

(iii) Choose the maximum value for s thus obtained, $s = s_m$ corresponding to $l = m$. It is expected that s will be nearly independent of l . (iv) At this stage there are two possibilities of comparable accuracy to obtain η_0 : (a) Use the line $\eta_{\text{soft}}(s)$ of Fig. 1 to calculate $\eta_0 = \eta_{\text{soft}}(s_m)$. (b) Use the UPY representation for the potential r^{-m} and find η_0 as the solution to the equation

$$\int [g_{\text{expt}}(x) - g_m(x; \eta)] \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} d\vec{x} = 0 . \quad (69)$$

The practical application of these procedures which encounters the usual difficulty of having $g_{\text{expt}}(r)$ (in the case of simulation study) or $s_{\text{expt}}(k)$ (in the case of experimental structure factor data) only over a limited region in r or in k , thus involving the problem of the tail $r > r_{\text{max}}$ or $k > k_{\text{max}}$, and the small k region, will be discussed elsewhere.

In analogy to the MVPT approach of Sec. V one may wish to use the analytic PY hard-sphere results and instead of (62) make the approximation

$$s_{\phi}^{\text{nonlocal}}(\rho, \eta) = \frac{1}{2} \int_0^{\eta} d\eta' \int d\vec{x} g_{\text{PY}}(x; \eta') \frac{\partial B_{\text{PY}}(x, \eta')}{\partial \eta'} + \int_0^{\eta} \Delta(\eta') d\eta', \quad (70)$$

where the function $\Delta(\eta)$ is analogous to the Ross⁵ correction. The variational condition now becomes

$$\frac{1}{2} \int [g_{\phi}(x; \beta, \rho, \eta) - g_{\text{PY}}(x; \eta)] \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} d\vec{x} + \Delta(\eta) = 0, \quad (71)$$

where $\Delta(\eta)$ is universal for the *soft* potentials and a choice that fits well the UPY results is given by

$$\Delta_{\text{UPY}}^{\text{soft}}(\eta) = \eta \left[\left[\frac{\beta P}{\rho} \right]_{\text{comp}} - \left[\frac{\beta P}{\rho} \right]_{\text{virial}} \right] \geq 0 \quad (72)$$

[see (A8) and (A9)]. The details of the analysis leading to this result will be given separately. In the context of the “inverse” problem above it leads to a simple alternative to (69), namely,

$$\frac{1}{2} \int [g_{\text{expt}}(x) - g_{\text{PY}}(x; \eta)] \frac{\partial B_{\text{PY}}(x; \eta)}{\partial \eta} d\vec{x} + \Delta_{\text{UPY}}(\eta) = 0, \quad (73)$$

with a small jump from the soft [Eq. (72)] to the hard-sphere (HS) behavior, given by

$$\Delta_{\text{UPY}}^{\text{HS}}(\eta) \simeq \eta \left[\left[\frac{\beta P}{\rho} \right]_{\text{CS}} - \left[\frac{\beta P}{\rho} \right]_{\text{virial}} \right] \geq 0. \quad (74)$$

Use of the Verlet-Weiss¹⁷ and Henderson-Grundke⁴⁸ parametrizations for the hard-sphere structure functions with a MHNC criterion

$$\frac{1}{2} \int [g_{\phi}(x; \beta, \rho, \eta) - g_{\text{HS}}(x; \eta)] \frac{\partial B_{\text{HS}}(x; \eta)}{\partial \eta} d\vec{x} = 0 \quad (75)$$

is essentially equivalent to the use of (71) with Δ given by (74). It thus improves¹⁹ upon results¹⁰ based on (71) with $\Delta=0$, by “going” part of the way along (71) and (72). Systematic UPY calculations for a reasonably wide “basis” set of pair potentials, needed for constructing equations of state for real materials, will provide the basic set of data needed in order to take full advantage of the methods discussed in this paper, and, at the same time, by comparing the functions $\eta_{\phi}(s)$, direct assessment of their accuracy will be further possible.

Finally, ideas and formalisms employed here may be generalized to mixtures, e.g., in the spirit of the MVPT one expects to obtain improved results for mixtures by employing the PY pair functions with the corresponding virial excess entropy, $s_{\text{PY, virial}}^{\text{mix}}$ to first order the entropy functional may be further corrected via

$$s^{\text{mix}} = S_{\text{PY, virial}}^{\text{mix}} + S_{\text{Ross}}(\eta) - S_{\text{PY, virial}}(\eta),$$

by adjusting to $S_{\text{Ross}}(\eta)$ in the one-component limit. The mixture problem will be considered separately.

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APPENDIX A: MHNC INTERPRETATION OF THE PERCUS-YEVICK APPROXIMATION FOR HARD SPHERES

The MHNC equations [Eq. (1) and (2)] for the pair potential $\phi(r)$ are equivalent to the HNC equations for an effective potential

$$\phi(r) + \frac{1}{\beta} B(x, \{\mu_i\}),$$

where B is the bridge function. The PY equation for hard spheres is equivalent to the HNC equation for the potential

$$\phi_{\text{HS}}(x) + \frac{1}{\beta} B_{\text{PY}}(x, \xi),$$

where

$$\xi = \frac{\Pi}{6} \rho d^3$$

is the packing fraction for hard spheres of diameters d at density ρ . The solution to that equation is $g_{\text{PY}}(x, \xi)$, usually considered as a good approximation to the exact hard-sphere pair function $g_{\text{HS, exact}}(x, \xi)$. The UPY approximation for the hard-sphere potential is obtained by the solution of the HNC equation for the potential

$$\phi_{\text{HS}}(x) + \frac{1}{\beta} B_{\text{PY}}(x, \eta(\xi)),$$

where⁴

$$\eta_{\infty}(\xi)/\xi = (0.982913 - 0.02271\xi + 0.02449\xi^2)^3.$$

Regarding the solution to the PY equation for hard spheres as the exact UPY result for some potential (denoted the “PY” potential) $u_{\text{PY}}(r)$ with a corresponding bridge function $B_{\text{PY}}(x, \eta_{\text{PY}}(\xi))$, we have the following equation:

$$u_{\text{PY}}(r) + \frac{1}{\beta} B_{\text{PY}}(x; \eta_{\text{PY}}(\xi)) = u_{\text{HS}}(r) + \frac{1}{\beta} B_{\text{PY}}(x; \xi), \quad (\text{A1})$$

where $\eta_{\text{PY}}(\xi)$ is the bridge parameter for the PY potential. Denoting

$$b(x; \xi) = B_{\text{PY}}(x; \xi) - B_{\text{PY}}(x; \eta_{\text{PY}}(\xi)) \quad (\text{A2})$$

we see that the PY potential is explicitly a density and temperature-dependent potential:

$$u_{\text{PY}}(x; \xi) = U_{\text{HS}}(x) + \frac{1}{\beta} b(x; \xi). \quad (\text{A3})$$

The PY excess free energy is given by

$$f_{\text{PY}} = s_{\text{PY}} + \frac{1}{2} \int g_{\text{PY}}(x; \xi) b(x; \xi) d\vec{x}, \quad (\text{A4})$$

where s_{PY} is the excess entropy.

Using the Gibbs-Bogoliubov inequality we have

$$0 \leq s_{PY} - s_{HS}(\xi) \leq \frac{1}{2} \int [g_{HS}(x; \xi) - g_{PY}(x; \xi)] b(x; \xi) d\vec{x}. \quad (A5)$$

Specifying the density, i.e., the parameter ξ in $b(x, \xi)$, the pressure of the PY potential is given by the virial

$$\left[\frac{\beta P}{\rho} \right]_{\text{comp}} + \xi \frac{\partial}{\partial \xi} \left[\frac{\beta P}{\rho} \right]_{\text{comp}} = \left[\frac{\beta P}{\rho} \right]_{\text{virial}} + \xi \frac{\partial}{\partial \xi} \left[\frac{\beta P}{\rho} \right]_{\text{virial}} - \frac{1}{6} \int g_{PY}(x; \xi) x \frac{\partial b(x; \xi)}{\partial x} d\vec{x} - \frac{1}{6} \int \xi \frac{\partial g_{PY}(x; \xi)}{\partial \xi} x \frac{\partial b(x; \xi)}{\partial x} d\vec{x}, \quad (A7)$$

where

$$\left[\frac{\beta P}{\rho} \right]_{\text{virial}} = \frac{1 + 2\xi + 3\xi^2}{(1 - \xi)^2} \quad (A8)$$

and

$$\left[\frac{\beta P}{\rho} \right]_{\text{comp}} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3}. \quad (A9)$$

Instead of exactly solving Eq. (17) we note that to a good approximation the right-hand side of (17) is equal to

$$\left[\frac{\beta P}{\rho} \right]_{PY} + \xi \frac{\partial}{\partial \xi} \left[\left[\frac{\beta P}{\rho} \right]_{PY} \right],$$

where $(\beta P/\rho)_{PY}$ is the expression (A6). This approximation yields

$$\left[\frac{\beta P}{\rho} \right] \cong \left[\frac{\beta P}{\rho} \right]_{\text{comp}} \quad (A10)$$

so that

$$f_{PY} \cong s_{\text{comp}}(\xi) = \frac{3}{2} \left[\frac{1}{(1 - \xi)^2} - 1 \right] - \ln(1 - \xi). \quad (A11)$$

Representing the hard-sphere entropy by the Carnahan-Starling expression,

$$\left[\frac{\beta P}{\rho} \right]_{PY} = \left[\frac{\beta P}{\rho} \right]_{\text{virial}} - \frac{1}{6} \int g_{PY}(x; \xi) x \frac{\partial b(x; \xi)}{\partial x} d\vec{x}. \quad (A6)$$

But the compressibility as obtained from the PY approximation for hard spheres via $c(r)$ corresponds to the case where the potential $b(x, \xi)$ is density independent. The UPY consistency thus takes the form

$$s_{HS}(\xi) \cong s_{CS}(\xi) = \frac{4\xi - 3\xi^2}{(1 - \xi)^2}, \quad (A12)$$

we obtain from (A5) the following:

$$\frac{1}{2} \int g_{PY}(x; \xi) b(x; \xi) \leq s_{\text{comp}}(\xi) - s_{CS}(\xi) \geq \frac{1}{2} \int g_{HS}(x; \xi) b(x; \xi) d\vec{x}. \quad (A13)$$

Estimates of $\eta_{PY}(\xi)$ based on (A13) agree with those based on (A7) and yield

$$\xi - \eta_{PY}(\xi) \ll \xi - \eta_{\infty}(\xi).$$

From (A13) and (A4) we also have

$$s_{PY}(\xi) \cong s_{CS}(\xi). \quad (A14)$$

Thus, the VPT calculation employing $g_{PY}(x, \xi)$ and $s_{CS}(\xi)$, which is usually considered as representing an approximate VPT calculation with the hard spheres as reference, is in fact much closer to representing a "PY" potential as reference. In view of this, the reason for employing $s_{\text{virial}}(\xi)$ instead of $s_{CS}(\xi)$ in order to improve the VPT results cannot be explained by consistency considerations,¹⁶ but may be interpreted by the MVPT (Sec. V), namely, by the finding that

$$s_{\text{soft}}(\eta) \lesssim s_{PY}(\eta) \lesssim s_{r-\infty}(\eta).$$

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