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Variational modified hypernetted-chain approximation for multicomponent liquids: Formalism and application to simple-liquid binary mixtures

L. E. Gonzalez and D. J. Gonzalez
Departamento de Fisica Teorica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain

M. Silbert
School of Mathematics and Physics, University of East Anglia, Norwich NR4 7TJ, United Kingdom

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In this paper we extend the variational modified hypernetted-chain theory to multicomponent liquids. Following the hypothesis of universality of the bridge functions we use the additive hard-sphere Percus-Yevick bridge functions. This can be seen as a first step in a bootstrap procedure. The theory is applied to binary mixtures interacting via Lennard-Jones potentials, and its accuracy is assessed by comparing with simulation results. We also compare this theory with others regarded to be of comparable accuracy.

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I. INTRODUCTION

During the last decade several schemes have been put forward on what can be generally defined as a new generation of fairly accurate integral-equation theories of liquids [1–6]. The availability of efficient algorithms that speed up the iterative solution of these integral equations has made possible their use with a relatively modest cost of computing time [7–10]. Despite claims and counterclaims, it would be difficult to set apart the accuracy of the predictions of most of these schemes when the calculations are made for, say, a Lennard-Jones type of liquid. In fact a basic requirement of any new integral equation of liquids is that it should be of, at least, comparable accuracy to those already available when the calculations are carried out for simple liquids.

Nevertheless, different schemes arose as a response to different needs and problems and, alas, there is no theory for the theory of liquids, namely, *a priori* criteria that tell us in advance which theory is more appropriate to use for a given class of liquids. Consequently the interest of adding a new integral-equation theory of liquids to those already in existence is that it satisfies a number of requirements that the others can only partially fulfill.

In our case the systems of primary interest are liquid metals. These are two-component systems comprising positive ions and degenerate conduction (or valence) electrons. However, if we restrict ourselves to simple metallic liquids and their alloys, namely, those where it could be assumed that the electron-ion coupling is weak, a simple picture can be used, based on pseudopotential theory and second-order perturbation theory, of a one-component system composed of a collection of pseudoions interacting via an effective pair potential [11]. There is, however, a price to be paid. First, the effective pair potential is dependent on the thermodynamic state of the system; specifically, in the particular case of local pseudopotentials, it is a function of the electronic density and—through the overall charge neutrality—of the ionic density. Second, the total potential energy includes a volume term, whose contribution, though irrelevant in the calculation of the structure, is very important in the calculation of the thermodynamic properties of the system. Third, the effective pair potential obtained from pseudopotential theory leads to an intrinsic inconsistency, the so-called electronic or Brovman inconsistency [12], when the bulk modulus is evaluated either via the virial or the compressibility route, quite unrelated to the normal inconsistencies which are present in approximate theories of liquids, however accurate these may be. Admittedly the Brovman inconsistency is fairly small for liquid simple metals near the melting point, but it is likely to become important in the expanded liquid and in liquid binary alloys. So far the only successful attempt to solve this inconsistency, while retaining the pairwise additivity of the potential, is due to Rosenfeld and Stott [13] for solid metals. The extension to liquids of this approach is proving difficult to accomplish [13,14]. The major problem is that, whereas in the solid the structure is assumed as given, in the liquid phase it is one of the properties which the theory is expected to predict. Hence we suggest that any scheme which forces the virial-compressibility consistency in the liquid theory should not be used for liquid metals. Finally, there is another problem concerning the effective pair potentials obtained from pseudopotential theory. The potentials of several systems exhibit shoulders (viz., liquid Ga) and/or extended repulsive regions. Some schemes rely on the ability of splitting up the potential into a "reference" potential and a "tail." Yet in these cases the criteria to use in the splitting of the potentials is not clearcut, and the results crucially depend on how this is done. A scheme which does not require such a splitting of the potential offers clear advantages in its application to liquid metals.

Of the several theories available at present we suggest that the variational modified hypernetted-chain (VMHNC) theory, proposed by Rosenfeld [5], is ideally suited for liquid metals. We have already presented the results of calculations for the structure of liquid metals using the VMHNC with excellent results. We have applied it to the study of the structure of expanded liquid rubidium [15] and, more recently, we have compared its predictions with the results of computer simulations for the liquid alkali metals [16].

In this paper we extend the formalism of the VMHNC theory to multicomponent mixtures. Its generalization from the one-component case is not straightforward and requires a new formulation of the VMHNC which is amenable to generalization; this is presented in the next section, which also covers all other aspects of the theory. We have also developed the algorithm for its numerical solution, which we assess by comparing the predictions of the VMHNC with computer simulations for Lennard-Jones binary mixtures; the results are presented in Sec. III. In line with the arguments given above it would have been desirable to present results for liquid binary alloys. However, to our knowledge, the few simulations using realistic potentials probe only structure, but not thermodynamic properties. Direct comparison with experiment is not appropriate for the purposes of this work, for we want to assess the accuracy of the formalism, presented below, unhindered by questions concerning the reliability of the potentials used in the calculations. It is not unknown in the field of liquid binary alloys that potentials predicting accurately the liquid structure are not as good at predicting the thermodynamic properties.

We complete the paper with a brief discussion of our results.

II. THEORY

A. Fundamentals

Consider a system made up of m components with number densities ρ_i and concentrations $x_i=\rho_i/\rho$, where ρ is the total number density and $1\leq i\leq m$. The starting point of most of the integral-equation theories of homogeneous, uniform, liquid mixtures is the Ornstein-Zernike (OZ) equations

$$h_{ij}(r)=c_{ij}(r)+\rho\sum_l x_l\int d\bar{r}'h_{il}(|\bar{r}-\bar{r}'|)c_{lj}(r') \tag{2.1}$$

which basically define the direct correlation functions in terms of the total correlation functions $h_{ij}(r)=g_{ij}(r)-1$, where $g_{ij}(r)$ denote the pair distribution functions.

If we further assume that the intermolecular forces are central and pairwise additive, so that the total structure-dependent potential energy takes the form

$$\Phi_N=\frac{1}{2}\sum_{i,j}\sum_{\substack{l,m\\ l\neq m}}\phi_{ij}(|\bar{r}_l-\bar{r}_m|)\ , \tag{2.2}$$

then an exact second, closure equation may be written as

$$c_{ij}(r)=h_{ij}(r)-\ln[g_{ij}(r)e^{\beta\phi_{ij}(r)-E_{ij}(r)}]\ . \tag{2.3}$$

In Eq. (2.3) $\beta=(k_BT)^{-1}$ is the inverse of the temperature times the Boltzmann constant, and $E_{ij}(r)$ are the so-called elementary correlation functions, which, in the language of graph theory, are defined as the sum of all the diagrams with $h_{ij}(r)$ bonds that have at least triply connected field points. Henceforth, and following the convention introduced by Rosenfeld [5], we shall use the bridge functions $B_{ij}(r)$, defined as $B_{ij}(r)=-E_{ij}(r)$.

The OZ equations (2.1) coupled with the closure relations (2.3) cannot be solved unless approximations to the latter are introduced. The basic assumption leading to several of the new generation of integral-equation theories of liquids is embodied in the assumption of "universality" of the bridge functions proposed by Rosenfeld and Ashcroft [17]. This means that, except for small differences of detail, the bridge functions for all the systems are the same, the only difference being a relabeling of the parameters defining the bridge functions.

Within the concept of "universality" the choice of the bridge functions is somewhat arbitrary, and is mainly dictated by the availability of analytic expressions or computer-simulation results. There are at present several possible choices available for the bridge functions, ranging from the soft one- or multicomponent plasma and the inverse-power potentials, to the hard-sphere (HS) bridge functions. For the latter we could use computer simulations, the Verlet-Weiss-Henderson-Grundke (VWHG) [18,19] semiempirical relations, or the Percus-Yevick (PY) theory. Following Rosenfeld, and due to the good analytic behavior of the HS-PY bridge functions, we have chosen to use these in our calculations. We note that, once the bridge functions are chosen, the VMHNC has no adjustable parameters. The bridge functions we shall use are

$$B_{ij;\mathrm{PY}}(x,c_l,\eta_n)=y_{ij;\mathrm{PY}}(x,c_l,\eta_n)-1-\ln y_{ij;\mathrm{PY}}(x,c_l,\eta_n) \tag{2.4}$$

where we have introduced the variable $x=\rho^{1/3}r$ and c_l $(l=1,\ldots,m-1)$ are the independent concentrations of each HS species $(c_m=1-\sum_{l=1}^{m-1}c_l)$, and η_n $(n=1,\ldots,m)$ are the packing fractions for each species, $\eta_n=\pi\rho c_n\sigma_n^3/6$, with σ_n denoting the hard-sphere diameter of component n.

Furthermore, within the PY approximation for HS, the functions $y_{ij}(x)=g_{ij}(x)e^{\beta\phi_{ij}(x/\rho^{1/3})}$ are given by

$$y_{ij;\mathrm{PY}}(x)=\begin{cases}g_{ij;\mathrm{PY}}(x), & x>\rho^{1/3}\sigma_{ij}\\ -c_{ij;\mathrm{PY}}(x), & x\leq\rho^{1/3}\sigma_{ij}\end{cases} \tag{2.5}$$

where $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, and

$$\rho^{1/3}\sigma_{ij}=\frac{1}{2}\left[\left[\frac{6\eta_i}{\pi c_i}\right]^{1/3}+\left[\frac{6\eta_j}{\pi c_j}\right]^{1/3}\right]\ . \tag{2.6}$$

We then have the bridge functions parametrized by the $2m-1$ parameters c_l,η_n; and the remaining question is how to determine these parameters as a function of the thermodynamic state of the system, given by β, ρ, and the concentration of each species in the system, x_l. (Note that we denote by x_l the concentrations of the *actual system*, and by c_l the concentration parameters of the HS *bridge functions*. In principle these are not necessarily the same, as the latter enter the definition of the packing fractions.)

The criterion for doing this will be discussed below (see Sec. II C), and is such that the energy route and the virial route for the thermodynamics are consistent with each other, and the inconsistency of these with the compressibility route is made as small as possible, but it is not forced to be exact.

Before presenting the extension to multicomponent mixtures, we shall briefly review the VMHNC for one-component systems, and state an alternative (though equivalent) formalism that will allow a straightforward generalization to the case of mixtures.

B. VMHNC for one-component systems

We start considering the exact expression for the configurational Helmholtz free energy [20] $F'/NkT \equiv f = f^{\mathrm{MHNC}} + f^{(1)}$, where

$$\begin{aligned} f^{\mathrm{MHNC}} = {} & \tfrac{1}{2}\int d\bar{x}\, g(x)[\beta\phi(x/\rho^{1/3}) + B(x)] \\ & -\tfrac{1}{2}\int d\bar{x}\,[\tfrac{1}{2}h^2(x) + h(x) - g(x)\ln g(x)] \\ & -\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\,\{\ln[1+\tilde{h}(k)] - \tilde{h}(k)\} \end{aligned} \tag{2.7}$$

and

$$f^{(1)} = -\tfrac{1}{2}\int_0^1 d\xi \int d\bar{x}\, g_\xi(x)\frac{\partial B_\xi(x)}{\partial \xi} \tag{2.8}$$

where the tilde denotes the Fourier transform, and ξ stands for the Kirkwood charging parameter, with $g_\xi(x)$ and $B_\xi(x)$ defining the radial distribution functions and bridge functions corresponding to the potential $\phi_\xi(x/\rho^{1/3}) = \xi\phi(x/\rho^{1/3})$.

If we now make the assumption of universality of the bridge functions, and take those to be the functions obtained from the HS-PY [that is, $B(x) = B_{\mathrm{PY}}(x,\eta)$], then the MHNC free energy becomes a function of β, ρ, and η. Its partial derivatives are easily calculated as

$$\begin{aligned} \beta\frac{\partial f^{\mathrm{MHNC}}(\beta,\rho,\eta)}{\partial\beta} &= \tfrac{1}{2}\int d\bar{x}\, g(x)\beta\phi(x/\rho^{1/3}) \\ &= u(\beta,\rho,\eta) \equiv \frac{U'}{NkT}\ , \end{aligned} \tag{2.9}$$

$$\begin{aligned} \rho\frac{\partial f^{\mathrm{MHNC}}(\beta,\rho,\eta)}{\partial\rho} &= -\tfrac{1}{6}\int d\bar{x}\, g(x)(x/\rho^{1/3})\beta\phi'(x/\rho^{1/3}) \\ &= z_v(\beta,\rho,\eta)\ , \end{aligned} \tag{2.10}$$

$$\frac{\partial f^{\mathrm{MHNC}}(\beta,\rho,\eta)}{\partial\eta} = \tfrac{1}{2}\int d\bar{x}\, g(x)\frac{\partial B_{\mathrm{PY}}(x,\eta)}{\partial\eta} \tag{2.11}$$

where U'/NkT and z_v represent the configurational parts of the internal energy and the virial-compressibility factor $(P/\rho kT)$, respectively, and $\phi'(r) = \partial\phi/\partial r$.

It should be noted that Eq. (2.11) is obtained by making the implicit assumption that the potential ϕ does not depend on η (as is indeed the case here).

Suppose we already have a criterion to choose η as a function of the thermodynamic state; that is, we have a function $\eta = \eta(\beta,\rho)$. Then we can integrate Eq. (2.9) with respect to temperature, to obtain the "energy"-configurational Helmholtz free energy, and Eq. (2.10) with respect to density, to obtain the "virial"-configurational Helmholtz free energy. For example,

$$f^E = \int_0^\beta \frac{1}{\beta'} u(\beta',\rho,\eta(\beta',\rho))\,d\beta' = \int_0^\beta \frac{\partial f^{\mathrm{MHNC}}}{\partial\beta'}\,d\beta'\ . \tag{2.12}$$

But

$$\frac{df^{\mathrm{MHNC}}(\beta',\rho,\eta(\beta',\rho))}{d\beta'} = \frac{\partial f^{\mathrm{MHNC}}}{\partial\beta'} + \frac{\partial f^{\mathrm{MHNC}}}{\partial\eta'}\frac{\partial\eta}{\partial\beta'} \tag{2.13}$$

and so,

$$\begin{aligned} f^E &= \int_0^\beta \frac{df^{\mathrm{MHNC}}}{d\beta'}\,d\beta' - \int_0^\beta \frac{\partial f^{\mathrm{MHNC}}}{\partial\eta}\frac{\partial\eta}{\partial\beta'}\,d\beta' \\ &= f^{\mathrm{MHNC}} - \int_0^\beta \frac{\partial f^{\mathrm{MHNC}}}{\partial\eta}\frac{\partial\eta}{\partial\beta'}\,d\beta'\ . \end{aligned} \tag{2.14}$$

In the same way it is found that

$$f^V = f^{\mathrm{MHNC}} - \int_0^\rho \frac{\partial f^{\mathrm{MHNC}}}{\partial\eta}\frac{\partial\eta}{\partial\rho'}\,d\rho'\ . \tag{2.15}$$

Now suppose that the function $\eta = \eta(\beta,\rho)$ is obtained from a criterion of the type

$$\frac{\partial f^{\mathrm{MHNC}}(\beta,\rho,\eta)}{\partial\eta} = \frac{d}{d\eta}\Delta^{(0)}(\eta) \tag{2.16}$$

where $\Delta^{(0)}(\eta)$ is an arbitrary function of η only, satisfying $\Delta^{(0)}(\eta=0)=0$. Then

$$\frac{\partial f^{\mathrm{MHNC}}}{\partial\eta}\frac{\partial\eta}{\partial\beta'} = \frac{d\Delta^{(0)}(\eta)}{d\eta}\frac{\partial\eta}{\partial\beta'} = \frac{d\Delta^{(0)}}{d\beta'} \tag{2.17}$$

with a similar relation holding for ρ'. From Eqs. (2.14) and (2.15) we finally obtain

$$\begin{aligned} f^E = f^V &= f^{\mathrm{MHNC}}(\beta,\rho,\eta(\beta,\rho)) - \Delta^{(0)}(\eta(\beta,\rho)) \\ &\equiv f^{\mathrm{VMHNC}}\ . \end{aligned} \tag{2.18}$$

From this we conclude: (1) The virial-energy consistency is guaranteed. (2) Criterion (2.16) can be written in the variational form

$$\frac{\partial f^{\mathrm{VMHNC}}(\beta,\rho,\eta)}{\partial\eta} = 0\ . \tag{2.19}$$

Little has been said about $\Delta^{(0)}(\eta)$, except that it should vanish for $\eta=0$. This condition allows the VMHNC results to include the correct low-density limit, accurately given by the HNC. But otherwise $\Delta^{(0)}(\eta)$ is arbitrary. We then seek the function $\Delta^{(0)}(\eta)$ that optimizes the compressibility-virial consistency without enforcing it. In other words, $\Delta^{(0)}(\eta)$ is a fitting function.

Within the spirit of perturbation theory we expect that $\Delta^{(0)}(\eta)$ can be separated into a relatively large part that is independent of the potential, and a relatively small ϕ-dependent part. Looking at Eqs. (2.16) and (2.11) it seems appropriate to take the ϕ-independent part as

$$\Delta^{(0)}_{\mathrm{PY}}(\eta) = \int_0^\eta d\eta' \left[\tfrac{1}{2}\int d\bar{x}\, g_{\mathrm{PY}}(x,\eta')\frac{\partial B_{\mathrm{PY}}(x,\eta')}{\partial\eta'}\right] \tag{2.20}$$

so

$$\Delta^{(0)}(\eta)=\Delta^{(0)}_{\rm PY}(\eta)-\delta_\phi(\eta)\ . \tag{2.21}$$

According to Rosenfeld, and in view of the results obtained in Ref. [16], a good candidate for $\delta_\phi(\eta)$ is $f_{\rm CS}(\eta)-f_{\rm PYV}(\eta)$, these denoting, respectively, the empirical Carnahan-Starling [21] and the Percus-Yevick-virial free energies for hard spheres of packing fraction η. **It has been argued by Rosenfeld [5] that this particular choice of δ_ϕ is equivalent to using the VWHG bridge functions in the reference hypernetted-chain (RHNC) formalism [2].**

Summing up, the VMHNC criterion to choose $\eta=\eta(\beta,\rho)$ follows: Minimize with respect to variations in η the function

$$f^{\rm VMHNC}(\beta,\rho,\eta)=f^{\rm MHNC}(\beta,\rho,\eta)-\Delta^{(0)}(\eta) \tag{2.22a}$$

where

$$\Delta^{(0)}(\eta)=\Delta^{(0)}_{\rm PY}(\eta)-\delta_\phi(\eta) \tag{2.22b}$$

with

$$\delta_\phi(\eta)=f_{\rm CS}(\eta)-f_{\rm PYV}(\eta) \tag{2.22c}$$

and

$$\frac{d\Delta^{(0)}_{\rm PY}(\eta)}{d\eta}=\tfrac{1}{2}\int d\bar{x}\, g_{\rm PY}(x,\eta)\frac{\partial B_{\rm PY}(x,\eta)}{\partial\eta}\ . \tag{2.22d}$$

Let us now present another, alternative, formulation of the VMHNC theory which will be necessary for the generalization of the theory to multicomponent systems.

Consider a system of hard spheres of packing fraction η and with bridge functions as given by Eq. (2.4) corresponding to the same value of η. Then Eq. (2.3) reduces to the closure relation of the PY theory and Eq. (2.7) for this system (we will call it $f^{\rm MHNC}_{\rm PY}$) only depends on η. Moreover, the potential also depends on η, through σ, so Eq. (2.11) is no longer valid. Instead we obtain after some algebraic manipulation (see Appendix A)

$$\frac{df^{\rm MHNC}_{\rm PY}(\eta)}{d\eta}=\frac{d\Delta^{(0)}_{\rm PY}(\eta)}{d\eta}+4y^*_{\rm PY}\ . \tag{2.23}$$

$y^*_{\rm PY}$ denotes the contact value of y, that is, **$y_{\rm PY}(x=\rho^{1/3}\sigma)$, with $\Delta^{(0)}_{\rm PY}$ defined by Eq. (2.20).**

Integration of (2.23) with respect to η yields

$$f^{\rm MHNC}_{\rm PY}(\eta)=\Delta^{(0)}_{\rm PY}(\eta)+f_{\rm PYV}(\eta)\ . \tag{2.24}$$

Criterion (2.22) can now be written as the following: Minimize with respect to variations in η the function

$$f^{\rm VMHNC}(\beta,\rho,\eta)=f^{\rm MHNC}(\beta,\rho,\eta)-\Delta^{(0)}(\eta) \tag{2.25a}$$

where

$$\Delta^{(0)}(\eta)=f^{\rm MHNC}_{\rm PY}(\eta)-f_{\rm PYV}(\eta)-\delta_\phi(\eta) \tag{2.25b}$$

with

$$\delta_\phi(\eta)=f_{\rm CS}(\eta)-f_{\rm PYV}(\eta)\ . \tag{2.25c}$$

Note that, for a given potential, the value of the parameter of the bridge function to be used—say $\bar\eta$—is calculated via (2.19). Hence the free energy is obtained by substituting this value of $\bar\eta$ in the first of Eqs. (2.25), that is,

$$f=f^{\rm VMHNC}(\beta,\rho,\bar\eta)\ . \tag{2.26}$$

However, when dealing with hard spheres we have chosen $\bar\eta=\eta$, the actual packing fraction of the system. Then the value of the free energy of the HS system is given by

$$\begin{aligned}
f^{\rm HS}=f^{\rm VMHNC}_{\rm PY}(\bar\eta)&=f^{\rm VMHNC}_{\rm PY}(\eta)\\
&=f^{\rm MHNC}_{\rm PY}(\eta)-\Delta^{(0)}(\eta)\\
&=f^{\rm MHNC}_{\rm PY}(\eta)-f^{\rm MHNC}_{\rm PY}(\eta)+f_{\rm PYV}(\eta)+\delta_\phi(\eta)\\
&=f_{\rm PYV}(\eta)+f_{\rm CS}(\eta)-f_{\rm PYV}(\eta)=f_{\rm CS}(\eta)\ .
\end{aligned} \tag{2.27}$$

This is indeed a very good reason to use the $\delta_\phi(\eta)$ proposed by Rosenfeld.

Before turning to the extension of the VMHNC to mixtures, let us point out that Eq. (2.24), along with Eq. (2.20), is not the best way to compute numerically the function $f^{\rm MHNC}_{\rm PY}(\eta)$. The following equation (see Appendix B):

$$f^{\rm MHNC}_{\rm PY}(\eta)=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\{\tfrac{1}{2}\tilde{h}^2_{\rm PY}(k)-\ln[1+\tilde{h}_{\rm PY}(k)]+\tilde{h}_{\rm PY}(k)\} \tag{2.28}$$

is to be preferred to Eqs. (2.20) and (2.24). The reason is that Eq. (2.28) only involves one integration of the function $\tilde{h}_{\rm PY}(k)$, which may be written in closed form for all k; whereas the use of Eqs. (2.20) and (2.24) requires two integrations and one differentiation of piecewise continuous functions of x which, in practice, cannot be written in closed form.

C. VMHNC for multicomponent mixtures

The generalization is now straightforward. The analogs to Eqs. (2.7) and (2.8) are [22]

$$f^{\mathrm{MHNC}}=\tfrac{1}{2}\sum_{i,j}x_ix_j\int d\bar{x}\, g_{ij}(x)[\beta\phi_{ij}(x/\rho^{1/3})+B_{ij}(x)]$$

$$-\tfrac{1}{2}\sum_{i,j}x_ix_j\int d\bar{x}[\tfrac{1}{2}h_{ij}^2(x)+h_{ij}(x)-g_{ij}(x)\ln g_{ij}(x)]-\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\{\ln \mathrm{Det}[\mathbf{I}+\tilde{\mathbf{H}}(k)]-\mathrm{Tr}[\tilde{\mathbf{H}}(k)]\}\ , \quad (2.29)$$

and

$$f^{(1)}=-\tfrac{1}{2}\int_0^1 d\xi\int d\bar{x}\sum_{i,j}g_{ij,\xi}(x)\frac{\partial B_{ij,\xi}(x)}{\partial\xi} \quad (2.30)$$

where Det and Tr denote the matrix determinant and trace, respectively, while the elements of the matrix $\tilde{\mathbf{H}}$ are given by

$$\tilde{\mathbf{H}}_{ij}=(x_ix_j)^{1/2}\tilde{h}_{ij}(k)\ . \quad (2.31)$$

To parametrize the bridge functions we use Eq. (2.4). In principle one could treat the c_l as parameters of B_{ij} to be determined by, say, a variational procedure. We have instead set these c_l equal to the concentrations x_l of the components of the system. This choice is a physically sound one and also saves on computing time.

f^{MHNC} is a function of β, ρ, x_l, and η_n, and its partial derivatives are

$$\beta\frac{\partial f^{\mathrm{MHNC}}}{\partial\beta}=u\ , \quad (2.32)$$

$$\rho\frac{\partial f^{\mathrm{MHNC}}}{\partial\rho}=z_v\ , \quad (2.33)$$

and

$$\frac{\partial f^{\mathrm{MHNC}}}{\partial\eta_k}=\tfrac{1}{2}\sum_{i,j}x_ix_j\int d\bar{x}\, g_{ij}(x)\frac{\partial B_{ij}(x)}{\partial\eta_k}\ . \quad (2.34)$$

If, as before, one chooses the criteria for taking $\eta_k=\eta_k(\beta,\rho,x_l)$ as

$$\frac{\partial f^{\mathrm{MHNC}}}{\partial\eta_k}(\beta,\rho,x_l,\eta_n)=\frac{\partial}{\partial\eta_k}\Delta^{(0)}(x_l,\eta_n)\ , \quad (2.35)$$

then the virial-energy consistency is guaranteed and criteria (2.35) can be rewritten in the variational form

$$\frac{\partial f^{\mathrm{VMHNC}}(\beta,\rho,x_l,\eta_n)}{\partial\eta_k}=0,\quad k=1,\ldots,m \quad (2.36)$$

where

$$f^{\mathrm{VMHNC}}(\beta,\rho,x_1,\eta_n)=f^{\mathrm{MHNC}}(\beta,\rho,x_l,\eta_n)-\Delta^{(0)}(x_l,\eta_n)\ . \quad (2.37)$$

Again $\Delta^{(0)}(x_l,\eta_n)$ is arbitrary, except that it should vanish for $\eta_1=\eta_2=\cdots=\eta_m=0$. Thus we choose it so as to satisfy the virial-compressibility consistency as closely as possible.

The concrete generalization we make is that of (2.25), namely: Choose $\eta_k=\eta_k(\beta,\rho,x_l)$ by minimizing the function

$$f^{\mathrm{VMHNC}}(\beta,\rho,x_l,\eta_n)=f^{\mathrm{MHNC}}(\beta,\rho,x_l,\eta_n)-\Delta^{(0)}(x_l,\eta_n) \quad (2.38a)$$

where

$$\Delta^{(0)}(x_l,\eta_n)=f_{\mathrm{PY}}^{\mathrm{MHNC}}(x_l,\eta_n)-f_{\mathrm{PYV}}(x_l,\eta_n)-\delta_\phi(x_l,\eta_n) \quad (2.38b)$$

with

$$\delta_\phi(x_l,\eta_n)=f_{\mathrm{CS}}(x_l,\eta_n)-f_{\mathrm{PYV}}(x_l,\eta_n) \quad (2.38c)$$

where f_{CS} is now the empirical Mansoori-Carnahan-Starling-Leland [23] free energy for a mixture of hard spheres, and $f_{\mathrm{PY}}^{\mathrm{MHNC}}$ is computed by using the generalization of (2.28),

$$f_{\mathrm{PY}}^{\mathrm{MHNC}}(x_l,\eta_n)=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}[\mathrm{Tr}(\tfrac{1}{2}\tilde{\mathbf{H}}^2)-\ln\mathrm{Det}(\mathbf{I}+\tilde{\mathbf{H}})+\mathrm{Tr}(\tilde{\mathbf{H}})]\ . \quad (2.39)$$

Also note that for a mixture of hard spheres f^{VMHNC} reduces to f_{CS}.

The use of the HS-PY bridge functions, together with the specified proposal for the function δ_ϕ constitute the first step in a bootstrap procedure. Further steps would consist of using a δ_ϕ more adequate to soft potentials, or in the use of bridge functions that directly correspond to soft potentials (multicomponent plasmas, inverse-power potentials, etc.).

The remaining question is: Why generalize (2.25) instead of (2.22), that is, why not take $\Delta^{(0)}=\Delta_{\mathrm{PY}}^{(0)}-\delta_\phi$ with

$$F_{(k)}\equiv\frac{\partial\Delta_{\mathrm{PY}}^{(0)}}{\partial\eta_k}=\tfrac{1}{2}\sum_{i,j}x_ix_j\int d\bar{x}\, g_{ij;\mathrm{PY}}(x)\frac{\partial B_{ij;\mathrm{PY}}(x)}{\partial\eta_k}\ ? \quad (2.40)$$

The reason is that the function $\Delta_{\mathrm{PY}}^{(0)}(x_l,\eta_n)$ cannot exist. If it did exist, the following relations should be satisfied:

$$\frac{\partial F_{(k)}}{\partial\eta_p}=\frac{\partial F_{(p)}}{\partial\eta_k}\ , \quad (2.41)$$

namely, the crossed second derivatives of $\Delta_{\mathrm{PY}}^{(0)}$ should be equal. However, it can be shown that relations (2.41) are not satisfied (see Appendix C). This result is the likely reason for the problems encountered in the generalization of the VMHNC to multicomponent systems.

III. RESULTS AND DISCUSSION

We have solved the VMHNC for a number of two-component mixtures of Lennard-Jones (LJ) systems, in order to assess the accuracy of the theory by comparing with simulation results.

The algorithm we have used to solve the integral equations is the extension to mixtures of Gillan's algorithm [7,8], using for the functions a grid of 1024 points. The method we followed to minimize f^{VMHNC} is the standard steepest-descent method [24].

For comparison we have used three sets of simulations; those by Singer and Singer [25], carried out at constant N, V, and T by the Monte Carlo method (MC); by McDonald [26] for the Ar-Kr system, carried out at constant N, P, and T also by MC; and by Gupta [27], carried out in the *NPT* ensemble by molecular dynamics (MD). The values of the parameters of the Lennard-Jones potentials used in these simulations are given in Table I.

The first set was used by Zerah and Hansen to compare with their HMSA [4], namely, an interpolation scheme between the hypernetted-chain approximation and the soft-core mean spherical approximation. In Table II we compare the MC data, the HMSA, and the VMHNC results. The parameters $\lambda=\varepsilon_{11}/\varepsilon_{12}-1$ and $\mu=\sigma_{11}/\sigma_{12}-1$ correspond to different choices of the ratios of the potential parameters. We have chosen those values for which Singer and Singer calculate the thermodynamic properties directly from a simulation run, and not by some interpolation scheme [25].

By inspection of Table II we find that the VMHNC results for the energy are of an accuracy similar to the HMSA, while the results for the virial show a distinct improvement with respect to the HMSA. The deviations of the VMHNC values from the simulation are always less than 0.2% for the energy and 3.5% for the virial (the statistical errors of the MC data are approximately 0.15% for the energy and 5% for the virial).

For the Ar-Kr system [26], the MC simulations were made in the *NPT* ensemble. For each concentration we have varied the density until the calculated pressure approximately matches the simulation pressure within the statistical errors of the latter. In Table III we show the comparison between the MC data and our results. For $x_1=0.5$ the RHNC results of Enciso *et al.* [6] are also listed for comparison.

It can be seen that the agreement between simulation and VMHNC is excellent for every concentration (the discrepancies are of 0.16% for the density and 0.22% for the energy), and that the improvement over the RHNC in the case of $x_1=0.5$ is remarkable.

We have also compared the VMHNC and the RHNC with the molecular-dynamics simulations of Gupta [27], carried out in the *NPT* ensemble (Table IV). Our results show a very good agreement with MD (1.1% for density, 1.6% for energy), although the RHNC results for the thermodynamics are slightly better. For the particular choice of δ_ϕ used in this work, we believe that the VMHNC and the RHNC are of equivalent accuracy. Therefore it is likely that the small discrepancies between our results and those obtained for the RHNC by Enciso *et al.* are due to differences in the algorithms used in carrying out the calculations. However, it should be noticed that Enciso *et al.* used the HS-VWHG parametrized bridge functions, whereas we use the HS-PY ones. The latter have the advantage of avoiding the small, but unphysical, structural deficiencies posed by the analytic behavior of the VWHG bridge functions. As noted by Lado, Foiles, and Ashcroft [2] these are due to the small discontinuities found in the functions $y_{ij;\mathrm{VWHG}}(x)$ at the cores.

In order to show the accuracy of the VMHNC concerning the structural properties, we have plotted in Fig. 1 the radial distribution functions obtained for the system studied by Gupta at $x_1=0.5$. The agreement between the MD $g_{ij}(r)$ and our results is similar to that obtained using the RHNC [6]. In both cases this agreement is excellent.

We have also compared the bulk modulus obtained via the compressibility and the virial routes. The latter has been calculated by using the finite-difference derivative of P/kT with respect to the density. The results are shown in Table V. Although the agreement is reasonably good, bearing in mind we are not forcing the virial-compressibility consistency, a few comments on the results presented in Table V are in order. We believe that even at concentrations other than $x_1=0.5$ (Fig. 1) we would find the same level of agreement between our $g_{ij}(r)$ and those obtained by computer simulations. The remarkably good agreement we find for the virial route to the equation of state with computer simulation (Tables

TABLE I. Reduced values of the Lennard-Jones potential parameters defining the different systems studied in this work. Different values of λ and μ are considered (see Table II). Here ε_{ij}^* denotes $\varepsilon_{ij}/\varepsilon$ and $\sigma_{ij}^*=\sigma_{ij}/\sigma$, where ε is the unit of energy and σ the unit of length. Most of the results in this work are given using these reduced units.

	kT/ε	ε_{11}^*	ε_{12}^*	ε_{22}^*	σ_{11}^*	σ_{12}^*	σ_{22}^*
Singer and Singer[a]	0.8764	$1+\lambda$	1	$1/(1+\lambda)$	$1+\mu$	1	$1-\mu$
Ar-Kr[b]	0.9667	1	1.1807	1.3940	1	1.0335	1.0670
Gupta[c]	1	1	1	1	1	1.1250	1.2500

[a] Reference [25].

[b] Reference [26].

[c] Reference [27].

TABLE II. Comparison of results between HMSA, VMHNC, and simulation for LJ mixtures. In terms of the magnitudes defined in the text, $\langle \phi \rangle / NkT = u$ and $\langle \psi \rangle / NkT = -3z_v$. The statistical errors quoted in Ref. [25] are ±0.01 for the energy and ±0.15 for the virial.

		$-\langle \phi \rangle / NkT$			$\langle \psi \rangle / NkT$		
λ	μ	HMSA[a]	MC[b]	VMHNC	HMSA[b]	MC[b]	VMHNC
−0.19	0.0	6.29	6.30	6.325	2.91	3.34	3.199
−0.19	0.12	5.96	6.01	6.024	2.73	3.14	2.925
−0.10	0.0	6.23	6.23	6.257	2.71	2.81	3.043
−0.10	0.12	6.04	6.06	6.053	2.59	3.17	3.009
0.0	0.0	6.21	6.23	6.236	2.65	3.00	3.008
0.0	0.12	6.10	6.18	6.174	2.94	2.97	3.097
0.111	0.03	6.29	6.31	6.318	2.56	2.97	2.889
0.111	0.12	6.33	6.36	6.364	2.74	3.16	3.138
0.235	0.03	6.39	6.39	6.415	2.82	3.21	3.154
0.235	0.12	6.51	6.54	6.548	3.18	3.66	3.615

[a]From Ref. [4].
[b]From Ref. [25].

TABLE III. Comparison of results between VMHNC and simulation for the Ar-Kr system. For $x_1 = 0.5$ the RHNC values are shown in parentheses.

	P (bar)		$\rho\sigma^3$		$-U'/NkT$	
x_1	VMHNC	MC[a]	VMHNC	MC[a]	VMHNC	MC[a]
0.25	−0.1	0.0±0.6	0.7146	0.7158	8.015	8.031
0.40	1.4	1.6±0.7	0.7202	0.7214	7.461	7.484
0.50	1.4	1.1±0.7	0.7249	0.7245	7.111	7.104
	(2.9)[b]		(0.7186)[b]		(7.014)[b]	
0.60	0.3	0.2±0.6	0.7257	0.7258	6.725	6.722
0.75	0.0	0.0±0.7	0.7285	0.7256	6.185	6.157

[a]From Ref. [26].
[b]From Ref. [6].

TABLE IV. Comparison of results between VMHNC and MD simulations by Gupta [27]. RHNC values are in parentheses.

	$P\sigma^3/\varepsilon$		$\rho\sigma^3$		$-U'/NkT$	
x_1	MD[a]	VMHNC	MD[a]	VMHNC	MD[a]	VMHNC
0.25	0.5	0.498	0.4595	0.4649	5.409	5.495
		(0.500)[b]		(0.4602)[b]		(5.401)[b]
0.50	0.5	0.497	0.5302	0.5360	5.356	5.442
		(0.499)[b]		(0.5303)[b]		(5.347)[b]
0.75	0.5	0.508	0.6256	0.6320	5.314	5.398
		(0.502)[b]		(0.6248)[b]		(5.301)[b]

[a]From Ref. [27].
[b]From Ref. [6].

TABLE V. Virial-compressibility consistency check in the VMHNC.

System	MD[a] $x_1 = 0.25$	MD[a] $x_1 = 0.5$	MD[a] $x_1 = 0.75$	MC[b] $x_1 = 0.5$
B_v/B_c	1.60	1.05	1.70	1.62

[a]Reference [27].
[b]Reference [26].

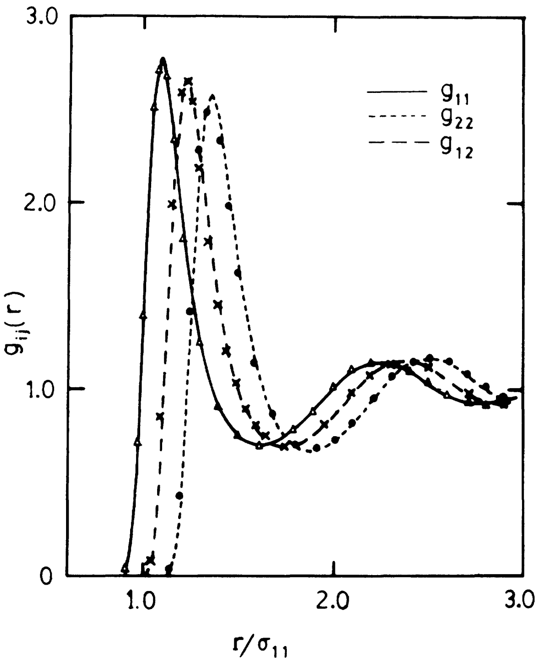

FIG. 1. Pair distribution functions for the equiatomic Lennard-Jones binary mixture. Lines show the theoretical results of this work; the discrete points reproduce the MD results of Gupta [27].

II–IV) is a clear indication that this indeed would be the case. What appears to affect the B_v/B_c ratio is the behavior of the partial structure factors in the long-wavelength limit [or equivalently, the large r behavior of $g_{ij}(r)$; namely, values outside the simulation box], which determine the value of B_c. We suspect that the VMHNC is not as accurate in predicting the isothermal compressibility which, in our view, is the major contribution to the departure from unity of the B_v/B_c ratio shown in Table V. There are, however, at least to our knowledge, no computer simulations for LJ mixtures directly probing density fluctuations to guide us on this point.

IV. CONCLUSIONS

We have generalized the VMHNC theory to the case of multicomponent systems. We have shown that an alternative formulation of the VMHNC lends itself to a straightforward generalization to the multicomponent case. We have generalized the computer code to solve the VMHNC for binary mixtures and applied it to study Lennard-Jones binary mixtures as a test case. The structural and thermodynamic properties thus obtained are in excellent agreement with the simulation results for these systems.

The theory is based in the hypothesis of universality of the bridge functions, and incorporates the energy-virial consistency, without forcing the consistency with the compressibility route, but trying to make it as close as possible. We have explicitly checked that the virial-compressibility consistency is reasonable, at least for this kind of systems. For ease of presentation, we have assumed in Sec. II the potentials independent of the density and concentrations. However, we have verified that the final expression, Eq. (2.38), and the energy-virial consistency, remain unchanged when this assumption is dropped, although there are some differences in the intermediate steps (the details are available on request). In our view, these features of the VMHNC make this theory very convenient for the study of liquid alloys.

Our proposal for the bridge functions and for the fitting function δ_ϕ can be viewed as the first step in a systematic bootstrap procedure, that can be pursued using functions more adequate to the real soft potentials present for metallic systems. However, in view of the good agreement obtained in this work with simulation results, these further steps in the systematic bootstrapping are likely to have a very small influence on the final results.

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APPENDIX A: DERIVATIVE OF $f_{\rm PY}^{\rm MHNC}(\eta)$ WITH RESPECT TO η

Recalling that $y_{\rm PY}(r)=g_{\rm PY}(r)e^{\beta\phi_{\rm HS}(r)}$ we can rewrite expression (2.7) for the HS-PY system as

$$\begin{aligned} f_{\rm PY}^{\rm MHNC}(\eta)=&\tfrac{1}{2}\int d\bar{x}\, g_{\rm PY}(B_{\rm PY}+\ln y_{\rm PY}) \\ &-\tfrac{1}{2}\int d\bar{x}\,(\tfrac{1}{2}h_{\rm PY}^2+h_{\rm PY}) \\ &-\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\,[\ln(1+\tilde{h}_{\rm PY})-\tilde{h}_{\rm PY}]\ . \end{aligned} \tag{A1}$$

Then,

$$\begin{aligned} \frac{df_{\rm PY}^{\rm MHNC}}{d\eta}=&\tfrac{1}{2}\int d\bar{x}\frac{\partial g_{\rm PY}}{\partial\eta}(B_{\rm PY}+\ln y_{\rm PY})+\tfrac{1}{2}\int d\bar{x}\, g_{\rm PY}\frac{\partial B_{\rm PY}}{\partial\eta} \\ &+\tfrac{1}{2}\int d\bar{x}\frac{g_{\rm PY}}{y_{\rm PY}}\frac{\partial y_{\rm PY}}{\partial\eta}-\tfrac{1}{2}\int d\bar{x}\frac{\partial h_{\rm PY}}{\partial\eta}(h_{\rm PY}+1) \\ &-\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\frac{\partial\tilde{h}_{\rm PY}}{\partial\eta}\left[\frac{1}{1+\tilde{h}_{\rm PY}}-1\right]\ . \end{aligned} \tag{A2}$$

The second term in (A2) is just $d\Delta_{\rm PY}^{(0)}/d\eta$.

The Fourier transform of the OZ equation gives for the last term of (A2)

$$\frac{1}{1+\tilde{h}_{\rm PY}}-1=\frac{-\tilde{h}_{\rm PY}}{1+\tilde{h}_{\rm PY}}=-\tilde{c}_{\rm PY}\ . \tag{A3}$$

Since $h_{\rm PY}=g_{\rm PY}-1$, their derivatives are equal. Rearranging (A2) we find that

$$\frac{df_{\mathrm{PY}}^{\mathrm{MHNC}}}{d\eta}=\frac{d\Delta_{\mathrm{PY}}^{(0)}}{d\eta}+\tfrac{1}{2}\int d\bar{x}\frac{\partial g_{\mathrm{PY}}}{\partial\eta}(B_{\mathrm{PY}}+\ln y_{\mathrm{PY}}-h_{\mathrm{PY}}-1)+\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\frac{\partial\tilde{h}_{\mathrm{PY}}}{\partial\eta}\tilde{c}_{\mathrm{PY}}+\tfrac{1}{2}\int d\bar{x}\frac{g_{\mathrm{PY}}}{y_{\mathrm{PY}}}\frac{\partial y_{\mathrm{PY}}}{\partial\eta}\ . \tag{A4}$$

Using Parseval's theorem the $\bar{k}$ integral can be transformed to an $\bar{x}$ integral,

$$\frac{df_{\mathrm{PY}}^{\mathrm{MHNC}}}{d\eta}=\frac{d\Delta_{\mathrm{PY}}^{(0)}}{d\eta}+\tfrac{1}{2}\int d\bar{x}\frac{\partial g_{\mathrm{PY}}}{\partial\eta}(B_{\mathrm{PY}}+\ln y_{\mathrm{PY}}-h_{\mathrm{PY}}+c_{\mathrm{PY}})-\tfrac{1}{2}\int d\bar{x}\frac{\partial g_{\mathrm{PY}}}{\partial\eta}+\tfrac{1}{2}\int d\bar{x}\frac{g_{\mathrm{PY}}}{y_{\mathrm{PY}}}\frac{\partial y_{\mathrm{PY}}}{\partial\eta}\ . \tag{A5}$$

The term inside parentheses is zero [see Eq. (2.3)].

Since

$$g_{\mathrm{PY}}(x)=y_{\mathrm{PY}}(x)e^{-\beta\phi_{\mathrm{HS}}(x/\rho^{1/3})}=y_{\mathrm{PY}}(x)\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right] \tag{A6}$$

where $\Theta(z)$ is the Heaviside step function, we substitute in the last term of (A5)

$$\frac{g_{\mathrm{PY}}}{y_{\mathrm{PY}}}=\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right] \tag{A7}$$

to obtain

$$\begin{aligned}\frac{\partial g_{\mathrm{PY}}}{\partial\eta}&=\frac{\partial}{\partial\eta}\left[y_{\mathrm{PY}}\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]\right]\\&=\frac{\partial y_{\mathrm{PY}}}{\partial\eta}\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]+y_{\mathrm{PY}}\frac{\partial}{\partial\eta}\left[\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]\right]\ .\end{aligned} \tag{A8}$$

The derivative of $\Theta(z)$ with respect to z is the Dirac δ function, so

$$\begin{aligned}\frac{\partial g_{\mathrm{PY}}}{\partial\eta}&=\frac{\partial y_{\mathrm{PY}}}{\partial\eta}\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]+y_{\mathrm{PY}}\,\delta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]\left[-\frac{1}{3}\left[\frac{6\eta}{\pi}\right]^{-2/3}\frac{6}{\pi}\right]\\&=\frac{\partial y_{\mathrm{PY}}}{\partial\eta}\Theta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]-\frac{2}{\pi}\left[\frac{6\eta}{\pi}\right]^{-2/3}y_{\mathrm{PY}}\,\delta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]\ .\end{aligned} \tag{A9}$$

Introducing (2.3), (A7), and (A9) into (A5) we find

$$\begin{aligned}\frac{df_{\mathrm{PY}}^{\mathrm{MHNC}}}{d\eta}&=\frac{d\Delta_{\mathrm{PY}}^{(0)}}{d\eta}+\frac{1}{2}\frac{2}{\pi}\left[\frac{6\eta}{\pi}\right]^{-2/3}\int_0^{\infty}dx\ 4\pi x^2y_{\mathrm{PY}}(x)\delta\left[x-\left[\frac{6\eta}{\pi}\right]^{1/3}\right]\\&=\frac{d\Delta_{\mathrm{PY}}^{(0)}}{d\eta}+4y_{\mathrm{PY}}\left[\left[\frac{6\eta}{\pi}\right]^{1/3}\right]=\frac{d\Delta_{\mathrm{PY}}^{(0)}}{d\eta}+4y_{\mathrm{PY}}^{*}\ .\end{aligned} \tag{A10}$$

APPENDIX B: ALTERNATIVE EXPRESSION FOR $f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta)$

Note that $B_{\mathrm{PY}}=y_{\mathrm{PY}}-1-\ln y_{\mathrm{PY}}$. Using this, the first integral in (A1) becomes

$$I_{1x}=\tfrac{1}{2}\int d\bar{x}\,g_{\mathrm{PY}}(B_{\mathrm{PY}}+\ln y_{\mathrm{PY}})=\tfrac{1}{2}\int_0^{\infty}dx\ 4\pi x^2g_{\mathrm{PY}}(y_{\mathrm{PY}}-1) \tag{B1}$$

and, recalling the properties of g_{PY} and y_{PY}, this results in

$$I_{1x}=\tfrac{1}{2}\int_{(6\eta/\pi)^{1/3}}^{\infty}dx\ 4\pi x^2(h_{\mathrm{PY}}^2+h_{\mathrm{PY}})\ . \tag{B2}$$

The second integral in (A1) is split into two integrals, one ranging from 0 to $(6\eta/\pi)^{1/3}$, where $h_{\mathrm{PY}}=-1$, and the other from $(6\eta/\pi)^{1/3}$ to ∞. Carrying out the explicit integration of the first integral gives

$$I_{2x}=-\tfrac{1}{2}\int d\bar{x}(\tfrac{1}{2}h_{\mathrm{PY}}^2+h_{\mathrm{PY}})=2\eta-\tfrac{1}{2}\int_{(6\eta/\pi)^{1/3}}^{\infty}dx\ 4\pi x^2(\tfrac{1}{2}h_{\mathrm{PY}}^2+h_{\mathrm{PY}})\ . \tag{B3}$$

The sum of the $\bar{x}$ integrals in (A1) yields

$$\begin{aligned}I_{1x}+I_{2x}&=2\eta+\tfrac{1}{2}\int_{(6\eta/\pi)^{1/3}}^{\infty}dx\ 4\pi x^2\tfrac{1}{2}h_{\mathrm{PY}}^2\\&=2\eta+\tfrac{1}{2}\int d\bar{x}\tfrac{1}{2}h_{\mathrm{PY}}^2-\tfrac{1}{2}\int_0^{(6\eta/\pi)^{1/3}}dx\ 4\pi x^2\tfrac{1}{2}h_{\mathrm{PY}}^2\ .\end{aligned} \tag{B4}$$

Substituting h_{PY} in the last integral by -1, the result of the integration is 2η, and, finally,

$$I_{1x}+I_{2x}=\tfrac{1}{2}\int d\bar{x}\tfrac{1}{2}h_{\mathrm{PY}}^2(x)=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}\tfrac{1}{2}\tilde{h}_{\mathrm{PY}}^2(k) \tag{B5}$$

where the last equality results from appealing to Parseval's theorem.

Finally, adding the $\bar{k}$ integral in (A1) to this result gives

$$f_{\mathrm{PY}}^{\mathrm{MHNC}}(\eta)=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\bar{k}[\tfrac{1}{2}\tilde{h}_{\mathrm{PY}}^2-\ln(1+\tilde{h}_{\mathrm{PY}})+\tilde{h}_{\mathrm{PY}}]\ . \tag{B6}$$

APPENDIX C: EXISTENCE OF $\Delta_{\mathrm{PY}}^{(0)}(c_l,\eta_n)$ FOR MULTICOMPONENT MIXTURES

Recalling that the condition for $\Delta_{\mathrm{PY}}^{(0)}(c_l,\eta_n)$ to exist is that the following relations are satisfied:

$$\frac{\partial F_{(k)}}{\partial \eta_l}=\frac{\partial F_{(l)}}{\partial \eta_k}, \quad l,k=1,\ldots,m \tag{C1}$$

with

$$F_{(k)}=\tfrac{1}{2}\sum_{i,j} c_i c_j \int d\bar{x}\, g_{ij;\mathrm{PY}} \frac{\partial B_{ij;\mathrm{PY}}}{\partial \eta_k} . \tag{C2}$$

It is straightforward to show that $F_{(k)}$ may be written as

$$F_{(k)}=\frac{\partial}{\partial \eta_k}\left[\frac{1}{8\pi^2}\sum_{i,j} c_i c_j \int_0^{\infty} dk\, k^2 \tilde{h}^{\,2}_{ij,\mathrm{PY}}(k)\right]+G_{(k)} \tag{C3}$$

where

$$G_{(k)}=\sum_i \left\{\tfrac{1}{2}c_i(h^{*2}_{ik,\mathrm{PY}}-1)\left[1+\left\{\frac{c_k\eta_i}{c_i\eta_k}\right\}^{1/3}\right]^2\right\} . \tag{C4}$$

The asterisk, as before, denotes the contact value of the function.

Then, for (C1) to be satisfied it is necessary and sufficient that the following relations are satisfied:

$$\frac{\partial G_{(k)}}{\partial \eta_l}=\frac{\partial G_{(l)}}{\partial \eta_k}, \quad l,k=1,\ldots,m . \tag{C5}$$

For the contact values, and so for $G_{(k)}$, analytic expressions exist. So one can explicitly check if (C5) are verified. We have done this using a symbolic manipulation program and found that, in fact, these relations are not verified, thus ruling out the existence of $\Delta_{\mathrm{PY}}^{(0)}$ for multicomponent mixtures.

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