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Analytic example of a free energy functional

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We use the ideas of Percus for the construction of classical density functionals for two model interactions: simple hard spheres and adhesive hard spheres (AHSs). The required input, the properties of the *uniform* fluid, is taken from the analytic mean spherical solution for these two systems. For hard spheres we derive—via a bilinear decomposition of the direct correlation functions—a set of basis functions, which is the same as the one presented by Rosenfeld in his fundamental measure theory framework. For AHSs additional basis functions have to be considered to ensure the bilinear decomposition of the direct correlation functions; we present an expression for the free energy functional for the one-component case.

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I. INTRODUCTION

Classical density functional theory (DFT) is a modern tool to study the structure and thermodynamic properties of nonuniform fluids and related systems (for an excellent overview see, for instance, [1]). The list of applications of classical DFT in this field comprises topics such as freezing phenomena, nucleation, structure and thermodynamics of interfaces and surfaces, or wetting problems [2]. The framework of DFT can be considered as a reformulation of statistical mechanics in the language of generating functionals. Its central issue is a theorem [3], that states that the Helmholtz free energy $F[\rho]$ of any system with a given stable interaction potential, at a given temperature T $(\beta=1/k_{\mathrm{B}}T)$ and external potential $U(\mathbf{r})$, is uniquely minimized by the equilibrium one-particle density $\rho(\mathbf{r})=\rho_0(\mathbf{r})$. Furthermore, with $\beta F[\rho]=\beta\overline{F}[\rho]+\int d\mathbf{r}\rho(r)\beta U(r)$, $\overline{F}[\rho]$ (the intrinsic free energy) is a generating functional for the direct correlation function $c^{(2)}(\mathbf{r},\mathbf{r}')$,

$$\frac{\delta^2\beta\overline{F}}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}=\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})}-c^{(2)}(\mathbf{r},\mathbf{r}'). \tag{1}$$

Of course, in the *uniform limit* [i.e., $\rho(\mathbf{r})\rightarrow\rho$] the properties of the corresponding uniform system have to be recovered.

Practical applications require the explicit form of the corresponding energy functional. However, this information is accessible only in very rare cases (most of them being one-dimensional systems); one therefore has to resort to approximate schemes. Again, it is not possible to present a complete list of approximate approaches that have been proposed in the literature; we therefore refer the reader to [1]. Despite the success of these approaches in a wide range of applications, considerable effort is nonetheless devoted to gaining new insight into the *general* structure of density functionals via exactly or semianalytically solvable systems. Two of these concepts are pointed out in particular: the fundamental measure theory (FMT; proposed by Rosenfeld in [4] and elaborated in many subsequent articles) and an approach followed for a long time by Percus and other authors (for an overview see, for example, [5]). These frameworks have mainly been used for simple systems; already for such systems—although their interactions are rather simple—the formalism turns out to be sometimes ‘‘unduly complicated’’ [6].

The FMT, proposed originally by Rosenfeld [4] and refined in subsequent work (summarized, e.g., in [7,8]) introduced a new concept for the construction of functionals. Instead of using a good knowledge of the bulk properties of the system as an input (as is often done in approximate schemes), the construction of the density functional (DF) is based on the geometric features of the particles. In the original work [4] the concept was applied to a mixture of hard spheres, reproducing, indeed, the analytic expressions of the bulk direct correlation functions of the Percus-Yevick (PY) equation [9,10]. From this functional, thermodynamic and structural properties of the uniform fluid can be derived. Among several hard-core systems (even nonspherical ones, such as cubes [11,12]), there is only one ‘‘soft’’ system where the framework has been applied [13].

The other strategy is (mainly) due to Percus, who has followed this route now for more than 20 years; contributions due to other authors in this direction are quoted in [5]. Essentially, it consists in the development of mathematical models of the free energy of a nonuniform fluid [14,5] with the bulk direct correlation functions as the only specific input, whereas the general structure of the free energy ansatz (called the format) is taken from (mostly) one-dimensional exactly solved model systems [5,15–17]. The hope behind this approach is that these ‘‘exactly solvable model systems . . . might serve as guides’’ [15] for more complex, realistic systems. The mathematical model we are going to define below and illustrate for a system with attractive potentials was proposed in [14,5]. As in the FMT this approach is a weighted-density type DFT: the density profile [one-particle density $\rho(\mathbf{r})$] is smoothed via a convolution with an appropriate set of weight (basis) functions. These weight functions have— as in the FMT framework—a range of half the range of the interaction.

In this contribution we first of all show that for simple hard spheres we can reproduce Rosenfeld's original FMT set of basis functions (which—as in the Percus approach—

represents *only one* possible set of functions) and the corresponding energy density [5]. We then proceed to the most simple (and convenient) extension of hard spheres by including some attraction, leading us to adhesive hard spheres, a system introduced by Baxter [18]. Here, the direct correlation functions are known analytically for both the PY equation and the mean spherical model (MSM). We are able to present a set of basis functions (which we obtain from a decomposition of the direct correlation function in the MSM): with respect to the hard sphere case, additional basis functions have to be included. Further, it is indeed possible—due to a simple density dependence of the correlation functions—to write down a closed expression for the energy density. We have also tried to generalize these results to the *N*-component case: this step fails due to a violation of the integrability condition of the compressibility relation, i.e., some inconsistency of the MSM.

The paper is organized as follows. In the next section we present the mathematical model of the density functional and in Sec. III the decomposition of the direct correlation functions in terms of the basis functions and the reconstruction of the density functional for the two model interactions mentioned above. We then discuss in Sec. IV how this mathematical model of a generating functional can be solved for those systems where analytic solutions of the structure functions are no longer available. The paper is closed with concluding remarks.

II. THE FORMAT

We start from the general ansatz (format) for the intrinsic free energy functional $\overline{F}[\rho]$ [14,5]

$$\beta F[\rho]=\beta\overline{F}[\rho]+\int d\mathbf{r}U\beta(r)\rho(\mathbf{r}),$$

$$\beta\overline{F}[\rho]=\int d\mathbf{r}\rho(\mathbf{r})[\ln\rho(\mathbf{r})-1]+\int d\mathbf{r}\Phi(\{\rho_\alpha\})(\mathbf{r}), \tag{2}$$

where $\rho(\mathbf{r})$ is the nonuniform one-particle density, and the density dependence of the excess free energy density Φ occurs locally via the nonlocal $\rho_\alpha(\mathbf{r})$, α being from a finite set of indices [5]; the $\rho_\alpha(\mathbf{r})$ are given by

$$\rho_\alpha(\mathbf{r})=\int d\mathbf{r}' \quad b_\alpha(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')=[b_\alpha\otimes\rho](\mathbf{r}), \tag{3}$$

and the basis functions $b_\alpha(r)$ have half the range of the interaction [5,14–17]. The basic physical restriction for this format is that the local structure of the DF is valid only for short-range interactions; this restriction stems from results obtained for exactly solvable one-dimensional systems (restriction to nearest-neighbor interactions) [15–17,5].

Following Percus we distinguish two types of basis functions $\{b_\alpha\}=\{b_{\alpha'},\mathbf{b}_{\alpha''}\}$: the scalars, where

$$\int d\mathbf{r}b_{\alpha'}(\mathbf{r})=1 \tag{4}$$

and the vector components with

$$\int d\mathbf{r}\mathbf{b}_{\alpha''}(\mathbf{r})=0. \tag{5}$$

We will now construct the generating functional in a three-step procedure. The first step is the determination of the basis functions. This is most readily done via the bilinear decomposition of the Boltzmann factor $e(r)=\exp[-\beta\Psi(r)]$ [where $\Psi(r)$ is the interaction potential]. This step is motivated by the fact that $e(r)$ represents the low-density limit of the free energy. One should also point out that this step is used in the FMT to fix the basis functions [4].

In the second step the direct correlation function is obtained from the functional $\overline{F}[\rho]$ via a double functional derivative using Eq. (1). Using Eqs. (2) and (3) we find in the uniform limit

$$\begin{aligned}-c^{(2)}(\mathbf{r},\mathbf{r}')&=-c^{(2)}(|\mathbf{r}-\mathbf{r}'|)\\&=\sum_{\alpha\beta}\int d\mathbf{r}''b_\alpha(\mathbf{r}''-\mathbf{r})b_\beta(\mathbf{r}''-\mathbf{r}')\\&\quad\times\Phi_{\alpha,\beta}(\{\rho\})_{\rho(\mathbf{r})=\rho}\end{aligned} \tag{6}$$

which in Fourier space (a caret denotes the Fourier transform) reads

$$-\hat{c}^{(2)}(q)=\sum_{\alpha\beta}\hat{b}_\alpha(q)\hat{b}_\beta(q)\Phi_{\alpha,\beta}(\{\rho\})|_{\rho(\mathbf{r})=\rho}. \tag{7}$$

Here we require knowledge of the direct correlation function and we have to verify that the basis functions chosen in the first step are indeed able to decompose the direct correlation functions for *any* density. There are a few model systems where this function can be determined analytically (which does not guarantee that the generating functional can be written down in a closed analytic expression). In this contribution we restrict ourselves to two such analytically solvable systems: hard spheres (HSs; in the PY equation), and their mathematically simplest extension, adhesive hard spheres (AHSs; in the mean spherical model). In the general case the correlation functions have to be determined via one of the accurate liquid state theories [19,20] known in the literature. The decomposition of $c^{(2)}(\mathbf{r},\mathbf{r}')$ in terms of the basis functions yields the coefficients $\Phi_{\alpha,\beta}$, i.e., the partial derivatives of Φ with respect to ρ_α and ρ_β.

In the third step, Φ and the generating functional $F[\rho]$ are finally obtained via a double integration with respect to the bulk density (and by including some further, nontrivial technical assumptions). The argument dependence of Φ on $\{\rho_\alpha\}$ fixes the local character of this function for any density (uniform or nonuniform).

Of course, the free energy of the uniform system, *F*, is reproduced when $\rho(\mathbf{r})=\rho$, i.e.,

$$\beta\overline{F}[\rho(\mathbf{r})]|_\rho=\beta F. \tag{8}$$

III. THE SYSTEMS

A. Hard spheres

The simplest model system in three dimensions that can be treated analytically is an N-component mixture of HSs, characterized by diameters $d_{ii}=d_i$, a set of concentrations c_i, and a packing fraction $\eta=(\pi/6)\rho\Sigma_i c_i d_i^3$, $i=1,\ldots,N$; the $\rho_i=\rho c_i$ are the partial densities. Further, $d_{ij}=\frac{1}{2}(d_i+d_j)$, $s_{ij}=\frac{1}{2}(d_i-d_j)$, and we assume that $s_{ji}>0$. For the PY equation (or MSM) closed analytic expressions are available for the direct correlation function $c_{ij}^{(2)}(r)=c_{ij}^{(2)}(|\mathbf{r}'-\mathbf{r}''|)$ [9,10]:

$$-c_{ij}^{(2)}(r)=\chi^{(3)}\Delta V_{ij}(r)+\chi^{(2)}\Delta S_{ij}(r)+\chi^{(1)}\Delta R_{ij}(r)+\chi^{(0)}\Theta(d_{ij}-r). \tag{9}$$

This formulation was proposed by Rosenfeld [21,4] and is a geometric interpretation of the direct correlation function: $\Delta V_{ij}(r)$ and $\Delta S_{ij}(r)$ are the overlap volume and the overlap surface of two spheres separated by a distance r, and $\Delta R_{ij}(r)$ is the mean radius of the spherocone; $\Theta(r)$ is the usual Heaviside step function. For completeness the explicit expressions for the functions $\Delta V_{ij}(r)$, $\Delta S_{ij}(r)$, and $\Delta R_{ij}(r)$ are given:

$$\Delta V_{ij}(r):=\begin{cases} \dfrac{\pi d_i^3}{6}, & r\in(0,s_{ji}) \\ \dfrac{\pi}{6r}\left(-\dfrac{3(d_j^2-d_i^2)^2}{32}+\dfrac{d_j^3+d_i^3}{2}r-\dfrac{3(d_j^2+d_i^2)}{4}r^2+\dfrac{1}{2}r^4\right), & r\in[s_{ji},d_{ij}] \\ 0, & r\in(d_{ij},\infty), \end{cases} \tag{10}$$

$$\Delta S_{ij}(r):=\begin{cases} \pi d_i^2, & r\in(0,s_{ji}) \\ \dfrac{\pi}{r}\left\{-\dfrac{d_i+d_j}{2}\left(\dfrac{d_i-d_j}{2}\right)^2+2\left[\left(\dfrac{d_i}{2}\right)^2+\left(\dfrac{d_j}{2}\right)^2\right]r-\dfrac{d_i+d_j}{2}r^2\right\}, & r\in[s_{ji},d_{ij}] \\ 0, & r\in(d_{ij},\infty), \end{cases} \tag{11}$$

$$\Delta R_{ij}(r):=\begin{cases} \dfrac{d_i}{2}, & r\in(0,s_{ji}) \\ \dfrac{1}{r}\left[-\dfrac{1}{4}\left(\dfrac{d_i-d_j}{2}\right)^2+\dfrac{d_i+d_j}{4}r-\dfrac{1}{4}r^2\right], & r\in[s_{ji},d_{ij}] \\ 0, & r\in(d_{ij},\infty). \end{cases} \tag{12}$$

The three-step procedure outlined in the preceding section can now be applied: decomposition of the Boltzmann factor leads to a set of basis functions (the $\sigma_\alpha^{(d_i)}$ are henceforward the scalar, while the $\boldsymbol{\tau}_\alpha^{(d_i)}$ are the vector basis functions)

$$\sigma_3^{(d_i)}(r)=\Theta\left(\frac{d_i}{2}-r\right),\qquad \boldsymbol{\tau}_2^{(d_i)}(r)=\boldsymbol{\nabla}\sigma_3^{(d_i)}(r),$$

$$\sigma_2^{(d_i)}(r)=|\boldsymbol{\tau}_2^{(d_i)}(r)| \tag{13}$$

and

$$\sigma_1^{(d_i)}(r)=\frac{1}{4\pi d_i/2}\sigma_2^{(d_i)}(r),\qquad \boldsymbol{\tau}_1^{(d_i)}(r)=\frac{1}{4\pi d_i/2}\boldsymbol{\tau}_2^{(d_i)}(r),$$

$$\sigma_0^{(d_i)}(r)=\frac{1}{4\pi(d_i/2)^2}\sigma_2^{(d_i)}(r). \tag{14}$$

Defining the set $\{\rho_\alpha(r)\}=\{\sigma_{\alpha'}(r),\boldsymbol{\tau}_{\alpha''}(r)\}$,

$$\sigma_{\alpha'}(r)=\sum_{i=1}^{N}(\sigma_{\alpha'}^{(d_i)}\otimes\rho_i)(r),\qquad \alpha'=0,\ldots,3,$$

$$\boldsymbol{\tau}_{\alpha''}(r)=\sum_{i=1}^{N}(\boldsymbol{\tau}_{\alpha''}^{(d_i)}\otimes\rho_i)(r),\qquad \alpha''=1,2, \tag{15}$$

we can extract the partial derivatives $\Phi_{\alpha,\beta}$. Φ is then determined via integration of $\Phi_{\alpha,\beta}$ (up to integration constants) and is found to be (see also [4,5])

$$\Phi(\{\rho_\alpha\})=-\sigma_0\ln(1-\sigma_3)+\frac{\sigma_1\sigma_2-\boldsymbol{\tau}_1\cdot\boldsymbol{\tau}_2}{1-\sigma_3}+\frac{(1/8\pi)\sigma_2\left(\frac{1}{3}\sigma_2^2-\boldsymbol{\tau}_2\cdot\boldsymbol{\tau}_2\right)}{(1-\sigma_3)^2}. \tag{16}$$

The basis functions in Eqs. (13) and (14) are exactly those that were proposed by Rosenfeld [4] in his geometrically motivated decomposition of the direct correlation function.

However, it should be pointed out that Rosenfeld's approach is from the conceptual point of view completely different from the present one: Rosenfeld starts from the decomposition of the Boltzmann factor and determines the functional based on a differential equation, originally proposed for a uniform mixture of hard spheres in [22]; however, the extension to systems with attractive tails is impossible. The direct correlation functions that come out of the formalism are exactly those that are obtained from the PY equation for a mixture of HSs [9]. This idea has lead to the very fruitful concept of fundamental measure theory which has been applied in many fields of liquid state physics (for an overview see, for example, [7,8]). As, for instance, discussed in [5] several equivalent sets of basis functions are possible solutions to the decomposition of the direct correlation functions. A further equivalent set of functions has been proposed by Kierlik and Rosinberg [23]: there, the basis functions are purely scalar ones (this possibility was already predicted by Percus [14,5]), but contain, on the other hand, higher-order derivatives of the δ function. The equivalence of the two parametrizations has been shown explicitly in [24].

B. Adhesive hard spheres

The most simple extension of HSs is to add an attractive potential to the hard core. This can be done most conveniently in terms of an adhesive potential, introduced by Baxter [18] as a special limiting case of a square-well system; we consider an N-component mixture of AHSs, their interaction being given by

$$\beta\Psi_{ij}(r)=\lim_{\epsilon\to 0}\begin{cases}\infty, & r\in[0,d_{ij}) \\ -\Theta(r-d_{ij})\ln\left(\dfrac{\gamma_{ij}d_{ij}}{\epsilon}\right)\Theta(d_{ij}+\epsilon-r), & r\in[d_{ij},\infty).\end{cases} \tag{17}$$

We use the same symbols as in the HS case. The parameters γ_{ij} characterize the stickiness of the spheres. The Ornstein-Zernike (OZ) equations, which relate the direct $[c_{ij}^{(2)}(r)]$ and the total $[h_{ij}^{(2)}(r)]$ correlation functions, are most conveniently solved by a Wiener-Hopf (Wertheim-Baxter) factorization procedure [25,10]. The factor functions $q_{ij}(r)$ that are introduced in this framework are related to the $c_{ij}^{(2)}(r)$ via

$$rc_{ij}^{(2)}(r)=\begin{cases}-q_{ij}'(r)+2\pi\sum_{k=1}^{N}\rho_k\int_0^{\infty}q_{ki}(t)q_{kj}'(r+t)dt, & r\in(0,d_{ij}] \\ 0, & r\in(d_{ij},\infty).\end{cases} \tag{18}$$

One finds for the $q_{ij}(r)$ [26]

$$q_{ij}(r)=\Theta(r-s_{ij})\left(\frac{1}{2}a_i(r^2-d_{ij}^2)+b_i(r-d_{ij})+\lambda_{ij}d_{ij}^2\right)\times\Theta(d_{ij}-r) \tag{19}$$

with yet undetermined λ_{ij} and the following parameters (summations run here and in the following from 1 to N):

$$a_i=\frac{1-12X_i}{1-\zeta_3}+\frac{d_i\zeta_2}{2(1-\zeta_3)^2},\quad \frac{d_i}{1-\zeta_3}=(d_ia_i+2b_i), \tag{20}$$

$$X_i=\frac{\pi}{6}\sum_l\rho_l\Gamma_{il}d_l,\quad \Gamma_{ij}=\gamma_{ij}d_{ij}^2, \tag{21}$$

$$\zeta_0=\sum_l\rho_l,\qquad \zeta_1=\sum_l\rho_l(d_l/2)=\frac{1}{2}\sum_l\rho_ld_l,$$

$$\zeta_2=\sum_l\rho_l[4\pi(d_l/2)^2]=\pi\sum_l\rho_ld_l^2,$$

$$\zeta_3=\sum_l\rho_l[(4\pi/3)(d_l/2)^3]=(\pi/6)\sum_l\rho_ld_l^3. \tag{22}$$

The (factorized) OZ equations have to be solved along with a closure relation. In the PY case we obtain a set of coupled quadratic equations that has to be solved numerically [26]:

$$\lambda_{ij}d_{ij}=\gamma_{ij}\left(a_id_{ij}+b_i+2\pi\sum_k\rho_k\lambda_{kj}d_{kj}^2q_{ik}(s_{ik})\right). \tag{23}$$

The λ_{ij} are explicitly density dependent; for this reason—as will be explained later—we discard in this contribution the

PY solution. The MSM, on the other hand, leads to the very simple and density-independent solution [27]

$$\lambda_{ij}=\gamma_{ij}\,. \tag{24}$$

For the decomposition of the direct correlation functions we use again the $\Delta V_{ij}(r)$, $\Delta S_{ij}(r)$, and $\Delta R_{ij}(r)$ introduced in Sec. III A. Using Eqs. (18)–(22) we find the following expressions for the direct correlation functions (see also [28]):

$$\begin{aligned}
-c_{ij}^{(2)}(r)=&\,\Delta V_{ij}(r)\sum_k \rho_k a_k^2+\frac{1}{2}\Delta S_{ij}(r)\sum_k \rho_k a_k(d_k a_k+2b_k)+\pi\Delta R_{ij}(r)\sum_k \rho_k(d_k a_k+2b_k)^2\\
&+\frac{1}{1-\zeta_3}\Theta(d_{ij}-r)-\gamma_{ij}d_{ij}\delta(r-d_{ij})\\
&+\begin{cases}
-\dfrac{12X_i}{1-\zeta_3}-2\pi\displaystyle\sum_k \rho_k a_k\Gamma_{ki}d_i\,, & r\in(0,s_{ji}),\\[2ex]
-\dfrac{6X_i+6X_j}{1-\zeta_3}+\dfrac{6s_{ij}(X_i-X_j)}{1-\zeta_3}\dfrac{1}{r}+\pi\displaystyle\sum_k \rho_k a_k(\Gamma_{ki}+\Gamma_{kj})r & \\[2ex]
-\pi\displaystyle\sum_k \rho_k a_k(\Gamma_{ki}d_i+\Gamma_{kj}d_j)+\pi\sum_k \rho_k a_k d_{ij}s_{ij}(\Gamma_{ki}-\Gamma_{kj})\frac{1}{r} & \\[2ex]
+2\pi\displaystyle\sum_k \rho_k\Gamma_{ki}\Gamma_{kj}\frac{1}{r}, & r\in[s_{ji},d_{ij}],\\[2ex]
0, & r\in(d_{ij},\infty).
\end{cases}
\end{aligned}\tag{25}$$

As in the HS case, the $c_{ij}^{(2)}(r)$ of AHSs of the PY equations and of the MSM are limited to the range of the interaction: for $r\in[0,d_{ij}]$ we recover typical hard core terms, i.e., terms such as those that build up the HS direct correlation functions. In addition, we encounter terms that are caused by the adhesiveness of the interaction and have to be decomposed into convolutions of (eventually new) basis functions: those terms are proportional to r, $1/r$, and $\delta(r-d)$.

Again, we execute the three-step procedure outlined above. The decomposition of the Boltzmann factor leads to a new set of basis functions: indeed, the set of basis functions used for HSs is no longer sufficient. By introducing $\psi_0^{(d_i)}(r)$, $\psi_3^{(d_i)}(r)$, and $\boldsymbol{\tau}_0^{(d_i)}(r)$ we extend the set of basis functions $\{\sigma_{\alpha'}^{(d_i)},\boldsymbol{\tau}_{\alpha''}^{(d_i)}\}$ used for HSs to the following set:

$$\sigma_3^{(d_i)}(r)=\Theta\left(\frac{d_i}{2}-r\right),\qquad \boldsymbol{\tau}_2^{(d_i)}(r)=\boldsymbol{\nabla}\sigma_3^{(d_i)}(r),$$

$$\sigma_2^{(d_i)}(r)=|\boldsymbol{\tau}_2^{(d_i)}(r)|,\qquad \boldsymbol{\tau}_0^{(d_i)}(r)=\frac{1}{4\pi d_i/2}\boldsymbol{\nabla}\sigma_2^{(d_i)}(r),$$

$$\psi_0^{(d_i)}(r)=|\boldsymbol{\tau}_0^{(d_i)}(r)|, \tag{26}$$

and

$$\psi_3^{(d_i)}(r)=\frac{d_i}{6}\sigma_2^{(d_i)}(r),$$

$$\sigma_1^{(d_i)}(r)=\frac{1}{4\pi d_i/2}\sigma_2^{(d_i)}(r),\qquad \boldsymbol{\tau}_1^{(d_i)}(r)=\frac{1}{4\pi d_i/2}\boldsymbol{\tau}_2^{(d_i)}(r).$$

$$\sigma_0^{(d_i)}(r)=\frac{1}{4\pi(d_i/2)^2}\sigma_2^{(d_i)}(r). \tag{27}$$

We can now proceed to the decomposition of the direct correlation functions (6); this task is most readily done in Fourier space. Introducing the Fourier transforms of the basis functions, i.e., $\mathcal{F}[\sigma_3^{(d_i)}](q)=\hat{\sigma}_3^{(d_i)}(q)$, etc., we find the following bilinear decompositions of the r-dependent terms that build up the direct correlation function according to Eq. (25):

$$\mathcal{F}[\Delta V_{ij}](q)=\hat{\sigma}_3^{(d_i)}(q)\hat{\sigma}_3^{(d_j)}(q),$$

$$\mathcal{F}[\Delta S_{ij}](q)=\hat{\sigma}_3^{(d_i)}(q)\hat{\sigma}_2^{(d_j)}(q)+\hat{\sigma}_2^{(d_i)}(q)\hat{\sigma}_3^{(d_j)}(q),$$

$$\begin{aligned}
\mathcal{F}[\Delta R_{ij}](q)=&\,\hat{\sigma}_3^{(d_i)}(q)\hat{\sigma}_1^{(d_j)}(q)+\hat{\sigma}_1^{(d_i)}(q)\hat{\sigma}_3^{(d_j)}(q)\\
&+\frac{1}{4\pi}[\hat{\sigma}_2^{(d_i)}(q)\hat{\sigma}_2^{(d_j)}(q)+\hat{\boldsymbol{\tau}}_2^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_2^{(d_j)}(q)],
\end{aligned}$$

$$\begin{aligned}\mathcal{F}[\Theta(d_{ij}-r)](q)=&\hat{\sigma}_3^{(d_i)}(q)\hat{\sigma}_0^{(d_j)}(q)+\hat{\sigma}_0^{(d_i)}(q)\hat{\sigma}_3^{(d_j)}(q)\\&+\hat{\sigma}_1^{(d_i)}(q)\hat{\sigma}_2^{(d_j)}(q)+\hat{\sigma}_2^{(d_i)}(q)\hat{\sigma}_1^{(d_j)}(q)\\&+\hat{\boldsymbol{\tau}}_1^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_2^{(d_j)}(q)+\hat{\boldsymbol{\tau}}_2^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_1^{(d_j)}(q),\end{aligned}\tag{28}$$

$$\begin{aligned}\mathcal{F}[\delta(r-d_{ij})](q)=&8\pi\hat{\sigma}_1^{(d_i)}(q)\hat{\sigma}_1^{(d_j)}(q)+\hat{\psi}_0^{(d_i)}(q)\hat{\sigma}_2^{(d_j)}(q)\\&+\hat{\sigma}_2^{(d_i)}(q)\hat{\psi}_0^{(d_j)}(q)+\hat{\boldsymbol{\tau}}_0^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_2^{(d_j)}(q)\\&+\hat{\boldsymbol{\tau}}_2^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_0^{(d_j)}(q),\end{aligned}$$

$$\begin{aligned}\mathcal{F}[\Theta(r-s_{ji})r\Theta(d_{ij}-r)](q)=&6[\hat{\psi}_3^{(d_i)}(q)\hat{\sigma}_1^{(d_j)}(q)\\&+\hat{\sigma}_1^{(d_i)}(q)\hat{\psi}_3^{(d_j)}(q)]\\&+\frac{1}{\pi}\hat{\boldsymbol{\tau}}_2^{(d_i)}(q)\cdot\hat{\boldsymbol{\tau}}_2^{(d_j)}(q),\end{aligned}$$

$$\mathcal{F}\left[\Theta(r-s_{ji})\frac{1}{r}\Theta(d_{ij}-r)\right](q)=8\pi\hat{\sigma}_1^{(d_i)}(q)\hat{\sigma}_1^{(d_j)}(q).$$

Now the coefficients $\Phi_{\alpha,\beta}(\{\rho\})$ are determined from Eqs. (25) and (28). The decomposition of the direct correlation functions fixes via Eq. (6) the $\Phi_{\alpha,\beta}$; the determination of Φ can now be done via integration of $\Phi_{\alpha,\beta}$. This integration can be performed in a completely analytic way for the MSM, where the coefficients λ_{ij} are density independent. The situation is somewhat more complicated for the PY equation: here the λ_{ij} are density dependent and Φ can only be determined via a numerical double integration. Since the present contribution seeks only to demonstrate the possibility of the extension of Percus' idea to systems beyond simple HSs we restrict ourselves to the MSM case.

We start with discussion of the one-component case ($N=1$). We are looking for Φ that reproduces in the uniform case the MSM expression for the direct correlation function. Separation of variables (as in the exactly solvable one-dimensional cases [15,16,5,17]) yields Φ *uniquely* up to integration constants which are determined via a lowest-order expansion of the free energy [29]. Φ is then given by

$$\begin{aligned}\Phi(\{\rho_\alpha\})=&-\sigma_0\ln(1-\sigma_3)+\frac{\sigma_1\sigma_2-\boldsymbol{\tau}_1\cdot\boldsymbol{\tau}_2}{1-\sigma_3}+\frac{(1/8\pi)\sigma_2\left(\frac{1}{3}\sigma_2^2-\boldsymbol{\tau}_2\cdot\boldsymbol{\tau}_2\right)}{(1-\sigma_3)^2}-2\gamma\left[\sigma_1\left(4\pi\frac{d}{2}\sigma_1\right)+\frac{d}{2}\psi_0\sigma_2-\frac{d}{2}\boldsymbol{\tau}_0\cdot\boldsymbol{\tau}_2\right]\\&+24\gamma^2\sigma_0\left(\sigma_0\frac{\pi d^3}{6}\right)^2-12\gamma(\sigma_1\sigma_2-\boldsymbol{\tau}_1\cdot\boldsymbol{\tau}_2)\frac{\sigma_3}{1-\sigma_3}-48\gamma\sigma_0\left((1+3\gamma)(\sigma_3+\ln[1-\sigma_3])+\frac{3}{2}\gamma\sigma_3^2\right)\\&+\frac{48\gamma}{\pi d^3/6}\left[(1+6\gamma)\left(-\sigma_3+\frac{1}{2}\sigma_3^2-(1-\sigma_3)\ln(1-\sigma_3)\right)+\gamma\sigma_3^3\right].\end{aligned}\tag{29}$$

The first line is again the expression for the pure HS contribution [cf. Eqs. (15) and (16) with $N=1$]; the other contributions take into account the stickiness. It is straightforward (but tedious) to show that Φ indeed reproduces the direct correlation functions and the free energy.

Of course, it is possible to proceed in a similar way with the PY solution of the direct correlation function. Now the coefficients of the bilinear decomposition of $c^{(2)}(r)$, the $\partial(\partial\Phi/\partial\rho_\beta)\partial\rho_\alpha$, are density dependent; hence Φ has to be determined via a double integration with respect to the bulk density.

The generalization of this procedure to the N-component case can certainly not be done in the MSM of AHSs. This is due to an inconsistency of the MSM for AHSs (which obviously has not been realized up to now): the partial derivatives of the pressure P with respect to the densities ρ_i, i.e., $\beta(\partial P)/(\partial\rho_i)$, which can be calculated directly from the direct correlation functions [9], do not represent a gradient field, i.e., the equation of state obtained by integration of this quantity is path dependent.

To conclude, two notes have to be made. First, the solution of the OZ equations via the Baxter factorization route is equivalent to the direct solution of the OZ equations only under certain conditions, which have, for instance, been discussed in [10,30]. Second, these conditions lead in the one-component case to the restriction that the MSM for AHSs has no solution for all densities for $\gamma>\gamma_c=(\sqrt{3}+2)/6\sim0.622$ [31].

IV. EXTENSIONS AND APPLICATIONS

We start this section with an outlook on the applicability of this method to other, perhaps more realistic, and complex systems. We are quite sure—although we cannot prove this rigorously—that there is no further three-dimensional system where the density functional can be constructed fully analytically following the framework we have used in this contribution.

However, this should not discourage us from the application of Percus' ideas. We therefore outline a possible application to more realistic systems that we intend to elaborate in the near future. The basis for our optimism is the fact that the direct correlation functions of any ''simple'' liquid can nowadays be determined with arbitrary accuracy using modern concepts of liquid state theory (see, for instance, [19,20]). Again, we proceed in the three-step sequence outlined in the preceding section. First, we determine the set of basis functions $\{b_{\alpha'},\mathbf{b}_{\alpha''}\}$: the fact that for hard core interactions these functions are by now well established (both via Rosenfeld's FMT approach as well as by Percus' concept) suggests that we concentrate on such systems. The additional repulsive (or attractive) tail should then be restricted to simple analytical forms (such as square wells, square shoulders, or related systems) where the decomposition of the Boltzmann factor in terms of additional basis functions is still within reach. Second, we make a bilinear decomposition of the direct correlation functions and determine thus the matrix of coefficients $\partial(\partial\Phi/\partial\rho_\beta)\partial\rho_\alpha$. Finally, third, we calculate Φ via a double integration with respect to density.

Density functionals are not used only to describe properties of nonuniform systems. A third functional derivative of the free energy with respect to density (and taking the limit of a uniform density) gives, for instance, the three-particle direct correlation function $c^{(3)}$ [1]. This fact was, for instance, one of the first applications of Rosenfeld's FMT density functional proposed for HSs and led to quite a satisfactory result in comparison with computer simulation data [32,33]. The fact that we have constructed a density functional for AHSs allows us to present an expression for the three-particle direct correlation functions for such a system. The threefold functional derivative of the functional and the uniform limit can be transformed to threefold partial derivatives of the energy density Φ, and this leads to the following result for the correlation functions in q space, $c^{(3)}(q_1,q_2)$:

$$\begin{aligned}
-\hat{c}^{(3)}(q_1,q_2)={}&4\pi^2d^6\gamma^2\{\hat{\sigma}_0^{(d)}\hat{\sigma}_0^{(d)}\hat{\sigma}_0^{(d)}\}(q_1,q_2)+\frac{1+48\gamma(1+6\gamma\zeta_3-3\gamma\zeta_3^2)}{(1-\zeta_3)^2}\{\hat{\sigma}_0^{(d)}\hat{\sigma}_3^{(d)}\hat{\sigma}_3^{(d)}\}(q_1,q_2)+\frac{1-12\gamma}{(1-\zeta_3)^2}\{(\hat{\sigma}_1^{(d)}\hat{\sigma}_2^{(d)}\\
&-\hat{\boldsymbol{\tau}}_1^{(d)}\cdot\hat{\boldsymbol{\tau}}_2^{(d)})\hat{\sigma}_3^{(d)}\}(q_1,q_2)+\frac{1}{4\pi(1-\zeta_3)^2}\{\hat{\sigma}_2^{(d)}(\hat{\sigma}_2^{(d)}\hat{\sigma}_2^{(d)}-\hat{\boldsymbol{\tau}}_2^{(d)}\cdot\hat{\boldsymbol{\tau}}_2^{(d)})\}(q_1,q_2)+\frac{2\zeta_2(1-12\gamma)}{(1-\zeta_3)^3}\{\hat{\sigma}_1^{(d)}\hat{\sigma}_3^{(d)}\hat{\sigma}_3^{(d)}\}\\
&\times(q_1,q_2)+\frac{\zeta_2}{2\pi(1-\zeta_3)^3}\{(\hat{\sigma}_2^{(d)}\hat{\sigma}_2^{(d)}-\hat{\boldsymbol{\tau}}_2^{(d)}\cdot\hat{\boldsymbol{\tau}}_2^{(d)})\hat{\sigma}_3^{(d)}\}(q_1,q_2)+\left(\frac{3\zeta_2^2}{4\pi(1-\zeta_3)^4}+\frac{2\zeta_1(1-12\gamma)}{(1-\zeta_3)^3}\right)\\
&\times\{\hat{\sigma}_2^{(d)}\hat{\sigma}_3^{(d)}\hat{\sigma}_3^{(d)}\}(q_1,q_2)+\left(\frac{\zeta_2^3}{\pi(1-\zeta_3)^5}+\frac{6\zeta_1\zeta_2(1-12\gamma)}{(1-\zeta_3)^4}+\frac{2\zeta_0[1+48\gamma(1+3\gamma)]}{(1-\zeta_3)^3}\right.\\
&\left.-\frac{288\gamma(1+12\gamma\zeta_3-6\gamma\zeta_3^2)}{\pi d^3(1-\zeta_3)^2}\right)\{\hat{\sigma}_3^{(d)}\hat{\sigma}_3^{(d)}\hat{\sigma}_3^{(d)}\}(q_1,q_2),
\end{aligned}\tag{30}$$

where we have used the following shorthand notation for permutations

$$\begin{aligned}
\{\sigma_1\sigma_2\sigma_3\}(x_1,x_2)={}&\sigma_1(x_1)\sigma_2(x_2)\sigma_3(-x_1-x_2)+\sigma_1(-x_1-x_2)\sigma_2(x_1)\sigma_3(x_2)+\sigma_1(x_2)\sigma_2(-x_1-x_2)\sigma_3(x_1)\\
&+\sigma_1(-x_1-x_2)\sigma_2(x_2)\sigma_3(x_1)+\sigma_1(x_1)\sigma_2(-x_1-x_2)\sigma_3(x_2)+\sigma_1(x_2)\sigma_2(x_1)\sigma_3(-x_1-x_2).
\end{aligned}\tag{31}$$

V. CONCLUSIONS

Based on investigations of one-dimensional, exactly solvable problems that were performed during recent decades, Percus and co-workers have proposed a general mathematical model of density functionals that may be solved from knowledge of the uniform direct correlation functions of the system considered. To demonstrate its applicability for systems other than hard spheres we have treated the mean spherical model for adhesive hard spheres. We have shown that it is indeed possible to construct from the uniform direct correlation functions a closed analytic form for the generating functional, that reproduces—as requested—the structural and thermodynamic properties of the uniform system. To this end the set of basis functions (that are used in this weighted-density type functional) has to be extended with respect to the case of simple hard spheres. The basic relations of classical density functional theory allow us to write down a closed expression for the three-particle direct correlation function. We conclude by giving an outline of how this mathematical model can be solved for more realistic systems.

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[1] R. Evans, Adv. Phys. **28**, 143 (1979); in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), Chap. 3.

[2] R. Evans and M. Chan, Phys. World **9**, 48 (1996).

[3] N.D. Mermin, Phys. Rev. A **137**, 1441 (1965); J.T. Chayes, L. Chayes, and E.H. Lieb, Commun. Math. Phys. **93**, 57 (1984); J.T. Chayes and L. Chayes, J. Stat. Phys. **36**, 471 (1984).

[4] Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).

[5] J. K. Percus, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).

[6] J. K. Percus (private communication).

[7] P. Tarazona and Y. Rosenfeld, in *New Approaches to Problems in Liquid State Theory*, edited by C. Caccamo, J.-P. Hansen, and G. Stell, NATO Advanced Study Institute Series C529 (Kluwer, Dordrecht, 1999).

[8] Y. Rosenfeld, in *New Approaches to Problems in Liquid State Theory* (Ref. [7]).

[9] J.L. Lebowitz, Phys. Rev. A **133**, 895 (1964).

[10] R.J. Baxter, J. Chem. Phys. **52**, 4559 (1970).

[11] J.A. Cuesta, Phys. Rev. Lett. **76**, 3742 (1996); J.A. Cuesta and Y. Martínez-Ratón, *ibid.* **78**, 3681 (1997).

[12] Y. Martínez-Ratón and J.A. Cuesta, Phys. Rev. E **58**, R4080 (1998).

[13] M. Schmidt, Phys. Rev. E **60**, R6291 (1999).

[14] J.K. Percus, J. Stat. Phys. **52**, 1157 (1988).

[15] J.K. Percus, J. Stat. Phys. **15**, 505 (1976).

[16] J.K. Percus, J. Stat. Phys. **28**, 67 (1982).

[17] G.R. Brannock and J.K. Percus, J. Chem. Phys. **105**, 614 (1996).

[18] R.J. Baxter, J. Chem. Phys. **49**, 2270 (1968).

[19] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).

[20] C. Caccamo, Phys. Rep. **274**, 1 (1996).

[21] Y. Rosenfeld, J. Chem. Phys. **89**, 4272 (1988).

[22] H. Reis, H. Frisch, and J.L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

[23] E. Kierlik and M.-L. Rosinberg, Phys. Rev. A **42**, 3382 (1990).

[24] S. Phan, E. Kierlik, M.-L. Rosinberg, B. Bildstein, and G. Kahl, Phys. Rev. E **48**, 618 (1993).

[25] M. S. Wertheim, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

[26] J.W. Perram and E.R. Smith, Chem. Phys. Lett. **35**, 138 (1975).

[27] C. Tutschka and G. Kahl, J. Chem. Phys. **108**, 9498 (1998).

[28] B. Barboy and R. Tenne, Chem. Phys. **38**, 369 (1979).

[29] G. Stell, in *Graph Theory and Theoretical Physics*, edited by F. Harary (Academic, London, 1967), p. 281.

[30] G. Pastore, Mol. Phys. **63**, 731 (1988).

[31] L. Mier y Terán, E. Corvera, and A.E. González, Phys. Rev. A **39**, 371 (1989).

[32] Y. Rosenfeld, D. Levesque, and J.-J. Weis, J. Chem. Phys. **92**, 6818 (1990).

[33] B. Bildstein and G. Kahl, Phys. Rev. E **47**, 1712 (1993).