High-density properties of liquid-state theories: Physically intuitive meaning for the direct correlation functions

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(Received 25 January 1985)

We prove that the hypernetted-chain and soft-mean-spherical integral-equation theories, together with the variational perturbation theory (based on the Percus-Yevick approximation for the hard-sphere reference system) are all identical in the asymptotic high-density limit: They share the same Madelung energy that constitutes an exact lower bound to the true potential energy of the system. The Percus-Yevick equation for hard spheres is shown to diverge at total packing fraction equal to unity, with a direct correlation function $c(r)$ given by the overlap volume of two spheres with separation r. We present the exact analytic solution of the mean-spherical approximation for any repulsive potential $\phi(r)$ satisfying $\tilde{\phi}(k)\geq 0$ which is a Green's function for an operator of the Sturm-Liouville-type. The corresponding direct correlation function is given by the interaction between the particles when they are "uniformly smeared" inside a sphere. Our results are general, applicable to any number of dimensions and to mixtures. The physically intuitive meaning for the direct correlation functions is offered as a starting point for the statistical thermodynamic analysis of nonspherical hard, and/or charged, objects.

I. INTRODUCTION

Integral-equation theories for fluids occupy a time-honored niche in the modern history of liquid-state theory.[1] Their low-density properties have been studied by graph theoretical methods and partial information regarding their merit may be gleaned from their predictions for the low-order virial coefficients. The validity of these equations for strongly coupled fluids is assessed by comparison with computer simulation results. No general analysis of the properties of these theories at high densities is available. Yet, a great deal about the structure of these theories and the underlying physics can be learned from the study of their behavior in the asymptotic high-density limit (AHDL). As an example for what we have in mind, and to set the stage for the present study, recall that both the Onsager "smearing" idea[2] and the Lieb-Narnhofer[3] "ion-sphere" lower bound for the potential energy of the classical one-component plasma (OCP) are contained[4] in the AHDL result for a mean-spherical approximation (MSA) with continuous direct correlation functions (DCF's) $c(r)$. We proved[4] that in the AHDL (superscript ∞) $c^{\infty}(r)$ for the OCP is given by the electrostatic interaction energy between two uniformly charged spheres of radius equal to a_{WS} (Wigner-Seitz radius) and separation r. This physically intuitive meaning for the DCF's has been already instrumental in the study of the equation of state (EOS) for plasma mixtures[5] and prompted a new approach to the statistical thermodynamics of arbitrary shaped-charged objects.[6]

Another time-honored approach to the statistical thermodynamics of liquids is perturbation theory.[1] This approach finds its widest range of applications when used in the variational form based on the Gibbs-Bogoliubov inequality.[7] It has been recently investigated in light of new developments in the diagrammatic analysis of liquid-state theory—the universality of the bridge functions.[8] In most applications of the variational perturbation theory (VPT), the energy integrals are evaluated by using the Percus-Yevick (PY) pair correlation functions for hard spheres (HS), and may be handled semianalytically in many cases. This particular version of the VPT is denoted "VPY" in short. The AHDL of the VPY has been demonstrated[9] to yield universal features for the equation of state in strong coupling.[10] When applied to the strongly coupled OCP in three dimensions it yields the "ion-sphere" Madelung energy mentioned above—the same result as obtained analytically by the MSA, and close to the result found from the numerical solution of the hypernetted-chain (HNC) equations.[9,10]

The present study was motivated by the contention that these OCP features are general and apply to arbitrary repulsive interactions in strong coupling. Our study of the AHDL behavior of the most widely used integral equation and perturbation theories reveals that they all become identical in high densities, and it enables us to find a general, physically intuitive meaning for the DCF's. In addition to revealing fundamental properties of the theories discussed, and similarly to the case of charged objects,[6] our analysis offers a possible starting point for physically intuitive and accurate statistical thermodynamics of "nonspherical" hard particles.

We start (Sec. II) by gathering relevant information about the integral-equation theories, namely the HNC, MSA, and PY approximations. The thermodynamic functionals of the pair functions are central to the developments to follow, and the results are obtained in a surprisingly simple way once certain observations are made.

The AHDL is formally defined as the limit in which the compressibility tends to zero. For continuous (soft) interactions it is physically equivalent to the limit in which the excess free energy F^{ex}/N and the potential energy U/N are both asymptotically equal to the Madelung energy $u_M(\rho)$.

The PY theory for hard spheres and hard-sphere mixtures of arbitrary dimensionality D is discussed in Sec. III where, in particular, we prove (S1). The AHDL is approached when the total packing fraction, $\eta\equiv$(total volume of sphere/total volume of the system)$=1$. (S2), $c^\infty(r)=\lim_{\eta\to t}(r)$ is proportional to the overlap volume of two spheres of diameter R and separation r. Note that (S3), once proven for hard spheres, (S1) and (S2) are obviously valid for the MSA for an arbitrary potential $\phi(r)$ containing a hard core.

The HNC and soft-MSA (SMSA) theories for continuous potentials that are strongly repulsive at short distances are considered in Sec. IV where, for arbitrary D, we prove (S4). In the AHDL, the HNC and SMSA theories are identical; they share the same DCF's, $c^\infty(r)$, and the same Madelung energy (e.g., $-\frac{9}{10}\Gamma$ for the three-dimensional OCP, $\Gamma=\beta e^2/a_{\rm WS}$). (S5), the AHDL result from the HNC (SMSA) theory constitutes an exact lower bound to the true potential energy of the system; e.g., the HNC Madelung energy is lower than that for the stable high-density lattice. (S6), $g^\infty(r)$, the AHDL pair correlation function, has an "excluded-volume" range corresponding to total packing fraction equal to unity, i.e., $g^\infty(r\le 2a_{\rm WS})=0$. Since the SMSA is a parametric MSA, this result (S6) is actually contained in (S1).

These results lead to a reexamination of the MSA integral equation for a general class of potentials (Sec. V). We find the exact analytic solution of the MSA in any number of dimensions and for mixtures, for any repulsive potential $\phi(r)$ satisfying $\tilde{\phi}(k)\ge 0$ (e.g., Coulomb, Yukawa) which is a Green's function for an operator of the Sturm-Liouville type. The physically intuitive meaning of the DCF's is revealed.

Finally, using (S1)—(S6), we prove (Sec. VI) that the three different theories, namely HNC, SMSA, and VPY become identical in the AHDL. The analytic form of their strong coupling equation of state is discussed. We end (Sec. VII) by discussing the extension of our results to mixtures and their implications to the statistical thermodynamics of "nonspherical" objects.

II. INTEGRAL-EQUATION THEORIES AND THERMODYNAMIC FUNCTIONALS OF THE PAIR FUNCTIONS

This section contains a short resume of the most widely used integral-equation theories, namely the HNC, MSA, and PY. These integral equations are obtained from the Ornstein-Zernike (OZ) relation between $c(r)$ and the pair correlation function $g(r)\equiv h(r)+1$,

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

and the "closure" relations are for HNC,

$$c(r)+\beta\phi(r)=g(r)-1-\ln(r)\ge 0\ , \tag{2}$$

for MSA,

$$g(r)=0,\ r<R;\ \ c(r)+\beta\phi(r)=0,\ \ r>R \tag{3}$$

and for PY,

$$c(r)=g(r)-g(r)\exp[\beta\phi(r)]\ , \tag{4}$$

where $\rho=N/V$ is the number density, $\beta=(k_BT)^{-1}$ the inverse temperature, $\phi(r)$ the pair potential, and R is the MSA hard-core diameter.

The HNC theory, which is perhaps the most fundamental of these theories has been extensively discussed recently in connection to the modified HNC (MHNC) scheme that attempts to include the contribution of the "bridge" diagrams.[8,11–13]

The MSA has been originally developed[14] for potentials that contain a hard core, i.e., an excluded-volume regime for which the closure $g(r<R)=0$ is exact. The MSA for continuous potentials with soft repulsion at short distances is obtained[15] by adjusting the MSA hard-core diameter R, $R=R(\beta,\rho)$, until continuity of the pair functions is reached, i.e., $g(r=R+0)=0$. This model, termed SMSA, has been attracting considerable interest in recent years. It has been analyzed[16,17] as a model akin to the more fundamental HNC theory, and was applied successfully to Coulomb plasmas[4,5,18] (including screening effects[19]), liquid metals,[20,21] charged colloidal dispersions,[22] and the isotropic-nematic transition of line charges.[6] We consider the HNC and SMSA theories for soft interactions and the PY theory for hard spheres. For the hard-sphere interaction, $\phi(r>R)=0$ and $\phi(r<R)=\infty$, the MSA and PY equations are identical.

Central to our analysis are the thermodynamic functionals (of the pair functions) from which the integral equations are obtained by variation. Recall that the inverse compressibility $\kappa_T^{-1}\equiv\beta(\partial P/\partial\rho)_T\equiv 1+X[c]$ is given by

$$\kappa_T^{-1}=1-\rho\int c(r)d\mathbf{r}\ , \tag{5}$$

and denote $B[c]=\frac{1}{2}(X[c]+c(r=0))$. Using the 0Z relation we obtain the following identity for the potential energy $u\equiv\beta(U/N)$:

$$u=\frac{\rho}{2}\int g(r)\beta\phi(r)d\mathbf{r}=B[c]+\tfrac{1}{2}+G\ , \tag{6a}$$

with

$$G=\frac{\rho}{2}\int g(r)[c(r)+\beta\phi(r)]d\mathbf{r} \tag{6b}$$

vanishing identically for the MSA. Notice that the HNC and SMSA equations of state as obtained from the energy or from the virial theorem for the pressure are identical. Denote by f_v the "virial" excess free energy, $\beta F^{ex}/N$, and let $Z_v\equiv\beta P/\rho=\rho(\partial f_v/\partial\rho)_T$ while Z_c denotes the corresponding quantity obtained from Eq. (5). The thermodynamic inconsistency of the HNC and SMSA theories is reflected by $Z_v\ne Z_c$. For the PY theory, the "energy," "virial" (pressure), and "compressibility" equations of state are all different in the general case. The functionals f_v,Z_v for HNC and SMSA, and Z_c for PY, are compiled in Ref. 17, all of them containing the crucial random-phase approximation (RPA)-type "logarithmic" term L

$$L[c]=\frac{1}{2\rho}(2\pi)^{-D}\int d\mathbf{k}\ln[1-\rho\tilde{c}(k)]\ , \tag{7}$$

where the tilde denotes Fourier transforms.

Defining the RPA free-energy functional $\mathscr{F}[c]$ by

$$\mathscr{F}[c]=B[c]+L[c]=u-\tfrac{1}{2}-G+L[c] , \tag{8}$$

we quote the following results from Ref. 17, with the understanding that each functional is evaluated subject to the appropriate closure (2)—(4):

(i) HNC

$$\mathscr{F}_{\mathrm{HNC}}=u-\tfrac{1}{2}-G+L ;\quad H=\frac{\rho}{4}\int h^2(r)d\mathbf{r} \tag{9a}$$

$$f_v=\mathscr{F}_{\mathrm{HNC}}+H , \tag{9b}$$

$$Z_v=\tfrac{1}{2}\chi+\tfrac{3}{2}+H-L . \tag{10}$$

(ii) SMSA

$$\mathscr{F}_{\mathrm{MSA}}=u-\tfrac{1}{2}+L , \tag{11a}$$

$$f_v=\mathscr{F}_{\mathrm{MSA}}+\mathscr{F}_0 , \tag{11b}$$

$$Z_v=\tfrac{1}{2}\chi+\tfrac{3}{2}-L , \tag{12}$$

where $\mathscr{F}_0$ is some finite constant corresponding to the value of f_v for the smallest β or ρ for which a solution to the SMSA criterion $[g(r=R+0)=0]$ can be obtained. For potentials having Fourier transform (e.g., Coulomb, Yukawa) $\mathscr{F}_0=0$.

(iii) PY

$$\mathscr{F}_{\mathrm{PYHS}}=B[c]+L[c] , \tag{13a}$$

$$Z_c=2\mathscr{F}_{\mathrm{PYHS}}+1 . \tag{13b}$$

Note that for hard spheres $B[c]+\frac{1}{2}=0$, since $u=0$, so that

$$\chi[c^{\infty}]=-c^{\infty}(r=0)\rightarrow\infty . \tag{14}$$

The key to our analysis is the observation that a necessary and sufficient condition for the logarithmic term $L[c]$ to be real in the asymptotic high-density limit is

$$\tilde{C}^{\infty}(k)\leq 0 . \tag{15}$$

III. THE PY THEORY FOR D-DIMENSIONAL HARD SPHERES

The required information enabling us to obtain the results (S1),(S2) of Sec. I is the recently derived[17] exact result for the PY (MSA) theory for hard spheres (HS) in D dimensions [for which $g(r=R+0)=-c(r=R-0)$],

$$\eta\frac{dZ_c}{d\eta}=2^{D-1}\eta g^2(r=R+0)\equiv\frac{(Z_v-1)^2}{2^{D-1}\eta} . \tag{16}$$

If the AHDL is approached for some $\eta=\overline{\eta}_D$ then $c^{\infty}(r=0)$ diverges at least as fast as $g^2(r=R+0)$ and thus the function $\psi(r)=c^{\infty}(r)/c^{\infty}(r=0)$ is continuous and obeys $\psi(r=0)=1$, $\psi(r\geq R)=0$, and [Eq. (15)] $\tilde{\psi}(k)\geq 0$.

In order to satisfy these properties ψ must be expressible as a convolution of two identical spherical distributions (using $x=r/R$)

$$\psi_D(x)=\int\mu_D(|\mathbf{x}'|)\mu_D(|\mathbf{x}-\mathbf{x}'|)d\mathbf{x}' , \tag{17}$$

with $\mu_D(|\mathbf{x}|>\frac{1}{2})=0$. Inserting this in Eq. (14) and recalling the definition of η we immediately get

$$\left[\int_{|\mathbf{x}|\leq\frac{1}{2}}\mu_D(|\mathbf{x}|)d\mathbf{x}\right]^2=\left[\int_{|\mathbf{x}|\leq\frac{1}{2}}d\mathbf{x}\right]\left[\int_{|\mathbf{x}|\leq\frac{1}{2}}\mu_D^2(|\mathbf{x}|)d\mathbf{x}\right]\frac{1}{\overline{\eta}_D} . \tag{18}$$

A straightforward application of Schwarz's inequality[23] yields $\overline{\eta}_D=1$ and $\mu_D(|\mathbf{x}|)=\mathrm{const}$, which proves (S1) and (S2).

Recalling that the convolution of two uniform spheres of diameter R and separation r is their overlap volume $\Omega_2(r,R)$, we define $\omega(r,R)=\Omega_2(r,R)/\Omega_2(r=0,R)$ to write

$$\psi(r)=\lim_{\eta\rightarrow 1}[c(r)/c(r=0)]=\omega(r,R) . \tag{19}$$

The analytic form of the PY DCF for hard spheres for arbitrary D is contained in the function $\omega(r,R)$ which is an odd-power D-degree polynomial for odd D, and an infinite power series of odd powers for even D. For any odd D the general solution of the PY DCF for hard spheres is given by the odd-power polynomial with $(D+3)/2$ coefficients

$$c(r)=a_0+a_1r+a_3r^3+\cdots+a_0r^D , \tag{20}$$

and using either the method of Percus[24] or that of Gillan *et al.*[25] it is a matter of straightforward (albeit tedious) algebra to obtain the coefficients. The observation that the function $\omega(x,1)$, given in 2D by

$$\frac{2}{\pi}\{\arccos x-x[(1-x^2)^{1/2}]\}=1-\frac{4}{\pi}x+\frac{2}{3\pi}x^3+\frac{1}{10\pi}x^5+\cdots$$

has a rapidly convergent series expansion, suggests a method for obtaining approximate analytic solutions for an even number of dimensions.

For an arbitrary mixture of (additive) hard spheres in any number of dimensions we find that the AHDL is approached for total packing fraction equal unity, with

$$\psi_{ij}(r)=\lim_{\eta\rightarrow 1}[c_{ij}(r)/c_{ij}(r=0)]=\Omega_2(r,R_i,R_j)/\Omega_2(0,R_i,R_j) ,$$

where $\Omega_2(r,R_i,R_j)$ is the overlap volume of two spheres of diameters R_i,R_j and separation r. Thus, for any D, the functions $c_{ii}(r)$ have the same analytic form as for the single component, while $c_{ij}(r)$ for $i\neq j$ is constant for $r\leq(R_i-R_j)/2$. It is easy to check that all available analytic solutions of the PY equations for hard spheres (in $D=1,3,5$) obey our general results.[26]

This newly found "geometric" meaning for the HS DCF's uncovers, for the first time, the general analytic structure of the PY DCF's for hard spheres of arbitrary dimensionality.[27] The overlap volume is a key quantity also in the scaled-particle theory (SPT) for hard particles and our results may uncover the long suspected connection between PY and SPT.[28] The physically intuitive meaning for the DCF's may serve as a starting point for developing accurate approximations in a statistical thermodynamic description of nonspherical hard objects—in analogy with the idea of smearing for charges.[6]

IV. ASYMPTOTIC HIGH-DENSITY LIMIT OF THE HNC AND SMSA THEORIES

Considering the HNC and SMSA functionals in the AHDL we first require $f_v^\infty \to u^\infty$. For the SMSA this leads to [see Eqs. (6),(11),(12)] $Z_v^\infty \to \frac{1}{2}\chi[c^\infty]$. For HNC it means that both L^∞ and H^∞ diverge more weakly than B^∞. Note that L^∞ [in view of (15)], G^∞ [in view of (2)], and H^∞ (by definition) are all positive definite. In turn, a physically acceptable solution must exhibit a negative-definite excess entropy in the AHDL, which means that $f_v^\infty - u^\infty \Longrightarrow L^\infty + H^\infty - G^\infty \geq 0$. Thus, G^∞ must diverge more weakly than $L^\infty + H^\infty$ and, in turn, more weakly than B^∞. We obtain that a physically acceptable solution of the HNC and SMSA theories must have the same AHDL functional forms; namely, for both HNC and SMSA we have

$$f_v^\infty = u^\infty = B[c^\infty] , \tag{21}$$

$$Z_v^\infty = \tfrac{1}{2}\chi[c^\infty] . \tag{22}$$

We outline the remaining part of the proof of (S4) for the special case of the OCP, $\beta\phi(r) = \Gamma/x$ with $x = r/a_{\rm WS}$. In the AHDL ($\Gamma \to \infty$), defined in view of the Madelung behavior, $c_0(x) = \lim_{\Gamma\to\infty}[c(x,\Gamma)/\Gamma]$. From (21) we observe that $c_0(x=0)$ is finite and the continuity of the pair functions implies [see Eq. (2)] that $c_0(x) < 1/x$ for some finite region, $x < x_0$, for which in the limit $\Gamma \to \infty$, $g^\infty(x \leq x_0) = 0$. Considering now (21) and (6) we obtain

$$\lim_{\Gamma\to\infty} (G/\Gamma) = \lim_{\Gamma\to\infty} \int g(x,\Gamma)[c_0(x) + 1/x]d\mathbf{x} = 0 . \tag{23}$$

Since $g(x) \geq 0$ in the HNC theory, the inequality in (2) implies that $c_0(x) + 1/x = 0$ for $x \geq x_0$. Thus, the AHDL-NHC is mapped on the AHDL SMSA, and

$$c^\infty(r) + \beta\phi(r) \geq 0 \tag{24}$$

is valid for both HNC and SMSA. Since the SMSA is a limit of the MSA then in view of S3 (in Sec. I) we get (S4): $x_0 = 2a_{\rm WS}$.

The proof of (S5) follows from a general Ewald-type identity for any pair function $g(\mathbf{r}) = h(\mathbf{r}) + 1$ with a structure factor $S(\mathbf{k}) = 1 + \rho\tilde{h}(\mathbf{k})$,

$$\begin{aligned} u &\equiv \frac{\rho}{2} \int g(\mathbf{r})\beta\phi(r)d\mathbf{r} \\ &= B[\Theta] + \frac{\rho}{2} \int g(\mathbf{r})[\Theta(r) + \beta\phi(r)]d\mathbf{r} \\ &\quad - \tfrac{1}{2}(2\pi)^{-D} \int S(\mathbf{k})\tilde{\Theta}(k)d\mathbf{k} , \end{aligned} \tag{25}$$

where $\Theta(r)$ is any (Ewald auxiliary) function for which $\tilde{\Theta}(k)$ exists. Note that Eq. (6) is a special 0Z case of Eq. (25) with $\Theta(r) = c(r)$ and $S(k) = 1/[1 - \rho\tilde{c}(k)]$. Since for any physical distribution $g(\mathbf{r})$, $S(\mathbf{k}) \geq 0$ (by definition), the choice $\Theta(r) = c^\infty(r)$ implies [in view of (15) and (24)]

$$u \geq B[c^\infty] = u^\infty_{\rm HNC\ SMSA} . \tag{26}$$

The variational function giving the best lower bound (26) among functions satisfying (15), (24), and the MSA condition [recall (S6) in Sec. I] $c^\infty(r \geq 2a_{\rm WS}) = -\beta\phi(r)$, is at the same time, the AHDL result of the HNC and SMSA theories. The solution of the "best bound" problem for the Coulomb potential,[4] using the charge-smearing idea[2,3] and elementary electrostatics, led to the OCP results mentioned in the Introduction. The analysis of this best bound problem should lead to better understanding of the nature of the HNC and SMSA approximations. A step in that direction is taken in the next section.

V. SOLUTION OF THE MSA INTEGRAL EQUATION FOR A GENERAL CLASS OF POTENTIALS

Notwithstanding its general interesting properties as a model,[16,17] the SMSA's usefulness stems from the availability of exact analytic solutions, in three dimensions, of the MSA equations for the Coulomb[18,29] and Yukawa[30,31] potentials. The main power of the original methods[32,33] for solving the MSA is their capability to provide the analytic form of the DCF, $c(r)$, inside the core ($r < R$). For a known analytic form, however, the generally complicated set of algebraic equations for the coefficients may be set up also by other methods.[24,25] Partly due to the complexity of the solutions, especially for mixtures, there has not emerged from these methods a general picture of (i) the analytic form of $c(r < R)$, (ii) its dependence on the dimensionality D, (iii) its possible physical interpretation, and (iv) its relation to the potential, $c(r > R) = -\beta\phi(r)$. By means of the "asymptotic" analysis we were able to answer these questions for two important and rather extremely disparate systems, namely Coulomb plasmas (Ref. 4) and hard spheres (Sec. III). In this section we discuss a more general class of potentials.

Consider potentials $\phi(r)$ which are strongly repulsive at short distances [$\phi(r=0) = \infty$, to sustain an excluded volume regime $g(r < R) = 0$] and possess a Fourier transform $\tilde{\phi}(k)$. For such potentials, both the HNC and SMSA theories interpolate between rigorous lower bounds for the exact poential energy of the system: The RPA (or Debye-Hückel) lower bound,[34] which represents the correct low-density (weak coupling) behavior, is an exact feature of the HNC and SMSA theories. Thus, their merit in representing strongly coupled fluids will be determined by the extent to which their high-density behavior (Sec. IV) represents a tight lower bound to the potential energy of the high-density stable lattice. The solution to the best bound problem considered here leads to DCF's which optimize the collective coordinate description for dense classical systems, originated by Percus and Yevick.[35] Interestingly enough, the best bound problem happens to be readily solvable for any potential which is a Green's function for the Sturm-Liouville operator

$$\mathscr{L}\phi(|\mathbf{r}-\mathbf{r}'|) = -\delta(|\mathbf{r}-\mathbf{r}'|) \tag{27}$$

and obeys $\tilde{\phi}(k) \geq 0$. It is interesting to note that the significance of the Green's-function potentials (for the modified Helmholtz operator) has been observed before,[36] in a related context, but without the consequences drawn by the present best bound approach.

We obtain a unified picture, valid for arbitrary dimensionality and for mixtures, of the analytic form of the SMSA (and MSA), DCF, $c(r)$, its physically intuitive meaning and its relation to the Green's-function potential $\phi(r)$. Our results also suggest a method for obtaining approximate solutions for even dimensionalities (e.g., $D=2$), and leads to SMSA-type approximations for the more complicated nonspherical cases (e.g., charged lines[6]). The Coulomb $[\tilde{\phi}(k)=k^{-2},\ \phi_{3D}(r)=r^{-1}]$ and Yukawa $[\tilde{\phi}(k)=(k^2+\lambda^2)^{-1},\ \phi_{3D}(r)=e^{-\lambda r}/r]$ potentials represent the two most important examples corresponding to $\mathscr{L}=\nabla^2,\nabla^2-\lambda^2$, repsectively. It should be noted, however, that even "realistic" potentials for liquid metals (e.g., the "empty core")[37] belong to the general class considered here.

To simplify notations we consider explicitly potentials with a finite $\phi(k=0)$. The treatment of potentials that require a compensating background (like Coulomb, see Ref. 4) needs only minor modifications and leads to the same result [Eq. (35)].

The general SMSA equation can be expressed variationally[17,38] [with continuous $c(r)$] by

$$\delta\mathscr{F}[c]/\delta c(r)=0,\quad r\le R \tag{28}$$

where $\mathscr{F}[c]$ is the RPA free-energy functional [Eq. (8)]. Recall that for potentials having Fourier transform, $\mathscr{F}[c]$ is the SMSA excess free energy as obtained from either the virial pressure or from the potential energy. Consider the SMSA in the AHDL, $\rho\to\infty$, denoted as before by superscript (∞). A physically acceptable behavior in that limit is the Madelung-type equation of state, typical for the static lattice, $\mathscr{F}^\infty=u^\infty\equiv\beta u_M(\rho)$. Defining

$$\psi(r)=-\lim_{\rho\to\infty}[c(r,\beta,\rho)/\beta]=-c^\infty(r)/\beta\ ,$$

we use Eqs. (6) (with $G=0$ for the MSA) to write

$$u_M(\rho)=\tfrac{1}{2}\left[\rho\int\psi(r)d\mathbf{r}-\psi(r=0)\right], \tag{29}$$

with $\psi(r)$ depending only on ρ:$\psi(r,\rho)$. Condition (15) takes the form

$$\tilde{\psi}(k)\ge 0\ . \tag{30}$$

The AHDL of the SMSA variational equation may be thus written as

$$\delta u_M(\rho)/\delta\psi(r)=0,\quad r\le R^\infty \tag{31}$$

for continuous functions $\psi(r)$ that obey (30) and $\psi(r\ge R^\infty)=\phi(r)$. This defines the general asymptotic SMSA variational problem which is now readily solved for any Green's-function potential.

In view of (27) $\psi(r)$ obeys the equation[23] $\mathscr{L}\psi(|\mathbf{r}|)=-f(|\mathbf{r}|)$, with $f(r\ge R^\infty)=0$, and may be represented by the convolution

$$\psi(r)=\int\phi(|\mathbf{r}-\mathbf{r}'|)f(|\mathbf{r}'|)d\mathbf{r}'\ . \tag{32}$$

Since $\tilde{\psi}(k)=\tilde{f}(k)\tilde{\phi}(k)\ge 0$ [Eq. (30)], and we required $\tilde{\phi}(k)\ge 0$, we have $\tilde{f}(k)\ge 0$ or $\tilde{f}(k)=\tilde{q}^{\,2}(k)$ so that $f(r)$ must be expressible as a convolution of two identical functions $q(r>R^\infty/2)=0$:

$$f(r)=\int q(|\mathbf{r}-\mathbf{r}'|)q(|\mathbf{r}'|)d\mathbf{r}'\ . \tag{33}$$

Inserting (32) and (33) into (29), Eq. (31) takes the form $\delta u_M(\rho)/\delta q(r)=0$ by which it is readily solved to give

$$q(r<R^\infty)=\text{const},\quad \rho\int_{|\mathbf{r}|\le R^\infty/2}d\mathbf{r}=1\ . \tag{34}$$

This identifies $R^\infty=2a_{\rm WS}$ and ensures that $\psi(r)\le\phi(r)$, in agreement with the general analysis in Sec. IV.

$\psi(r)$ has a well-defined physical meaning; it is the interaction between the particles when they are "smeared out" uniformly inside a D-dimensional sphere of radius $a_{\rm W}$. For the Coulomb potential this amounts to replacing each point charge by a uniform charge distribution within a hypersphere,[4] and it is equivalent to the charge smearing process of Onsager,[2] with $u_M(\rho)$ corresponding to the "ion-sphere" bound of Lieb and Narnhofer.[3] Using the overlap-volume function $\omega(r,R)$ defined in Sec. III we write our main result in the form

$$\psi(r,\rho)=A(a_{\rm WS})\int\phi(|\mathbf{r}-\mathbf{r}'|)\omega(|\mathbf{r}'|,2a_{\rm WS})d\mathbf{r}\ , \tag{35}$$

where $A(a_{\rm WS})$ is determined from the boundary condition

$$\psi(r=2a_{\rm WS})=\phi(r=2a_{\rm WS})\ .$$

The analytic form of the SMSA DCF is contained in the corresponding hard-sphere (HS) function $\psi_{\rm HS}(r)=\omega(r,R)$ which is an odd-power polynomial for odd D, and an infinite odd-power series for even D. For any density, for odd D, the SMSA DCF has the same analytic form as the function

$$c(r)=\int\phi(|\mathbf{r}-\mathbf{r}'|)\bar{\omega}(r',R)d\mathbf{r}'\ , \tag{36}$$

where $\bar{\omega}(r>R)=0$ is an odd-power polynomial of degree D containing $(D+3)/2$ coefficients like $c_{\rm HS}(r)$ of Eq. (20). The results (35) and (36) agree[39] with available analytic solutions for the Coulomb and Yukawa potentials in 3D, providing at the same time the exact solution for (e.g.) the $\tilde{\phi}(k)=k^{-1}$, $(k^2+\lambda^2)^{-1}$ potentials for arbitrary D together with its physical intuitive meaning. Again, as applies for hard spheres, the observation that the function $\omega(x,1)$ has a fastly convergent series expansion, suggests that an approximate solution employing a low degree odd-power polynomial may be reasonably accurate for an even number of dimensions.

Finally, it is interesting to note that our results (35) and (36) for the SMSA also provide the solution for the MSA. This is so because the discontinuity at $r=R$ is specifically associated[16,40] with the linear (in r) term of $c(r<R)$.

IV. UNIVERSAL STRONG COUPLING EQUATION OF STATE FOR THE HNC, SMSA, AND VPY THEORIES

A. Variational statement of the theories

Most applications of the VPT have been carried out in the VPY mode in which the energy integral is evaluated with the PY hard-sphere (PYHS) pair function

$$u_{\mathrm{VPY}}(\beta,\rho,\eta)=\tfrac{1}{2}\beta\rho\int g_{\mathrm{PYHS}}\left[\frac{r}{d},\eta\right]\phi(r)d\mathbf{r}\;, \tag{37}$$

where $d[=(6\eta/\pi\rho)^{1/3}$ in 3D] is the hard-core diameter. The VPY excess free-energy functional, $f=\beta F^{FX}/N$,

$$f_{\mathrm{VPY}}=u_{\mathrm{VPY}}(\beta,\rho,\eta)+S_{\mathrm{VPY}}(\eta)\;, \tag{38}$$

contains also the parametric (minus-) excess entropy, $S_{\mathrm{VPY}}(\eta)$, that determines $\eta(\beta,\rho)$ by the variational condition

$$\partial f_{\mathrm{VPY}}/\partial\eta=0\;. \tag{39}$$

The optimization of the entropy function, $S_{\mathrm{VPY}}(\eta)$, which plays the role of a "fitting function," has been discussed recently[8,13] in light of the MHNC theory based on the universality of the bridge functions. In particular, it has been demonstrated that a single choice of $S_{\mathrm{VPY}}(\eta)$, independent of the pair potential and reasonably well represented by the PY virial entropy [see (c) below], yields highly accurate thermodynamics for a large class of physically conceivable potentials.

Recall that the SMSA is obtained from the MSA free energy by imposing[17]

$$\partial f_v^{\mathrm{MSA}}/\partial\eta=\frac{\partial\mathcal{F}_{\mathrm{MSA}}}{\partial\eta}=0\;, \tag{40}$$

a requirement equivalent to $g(r=R+0)=0$. Since the AHDL HNC is mapped on the AHDL SMSA (Sec. IV), it can also be written in the variational form

$$\partial f_v^{\mathrm{HNC}}/\partial\eta=0,\quad \eta\simeq1\;. \tag{41}$$

Given the η dependence of the potential energy, $u(\beta,\rho,\eta)$, the analytic form of the first correction to the (leading) Madelung energy term is determined by the relations (40) and (41) from the behavior of the entropy $S(\beta,\rho,\eta)$ as function of η near $\eta=1$ (see examples in Refs. 9, 10, and 17).

B. Potential-energy functionals

Let $g^{\infty}(r),c^{\infty}(r)$ (i.e., nonsubscripted quantities) denote the AHDL results for the HNC (SMSA) theory for the potential $\phi(r)$, and let

$$u_{\mathrm{VPY}}^{\infty}=\lim_{\eta\to1}u_{\mathrm{VPY}}(\beta,\rho,\eta)\;,$$

$$g_{\mathrm{PHYS}}^{\infty}(r)=\lim_{\eta\to1}g_{\mathrm{PHYS}}(r)\;.$$

Consider the difference

$$\Delta\equiv u_{\mathrm{HNC,SMSA}}^{\infty}-u_{\mathrm{VPY}}^{\infty}$$
$$=\tfrac{1}{2}\beta\rho\int g^{\infty}(r)\phi(r)d\mathbf{r}-\tfrac{1}{2}\beta\rho\int g_{\mathrm{PHYS}}^{\infty}(r)\phi(r)d\mathbf{r}\;. \tag{42}$$

Using (6a) and $G=0$ for the first (MSA) integral, and identity (25) with $\theta(r)=c^{\infty}(r)$ for the second (PY) integral in (42), noting that

$$\int g_{\mathrm{PYHS}}^{\infty}(r)(C^{\infty}(r)+\beta\phi(r))d\mathbf{r}=0\;,$$

we obtain

$$\Delta\to\tfrac{1}{2}(2\pi)^{-D}\int S_{\mathrm{HS}}(k)\tilde{C}^{\infty}(k)d\mathbf{k}$$
$$=\tfrac{1}{2}(2\pi)^{-D}\int \tilde{h}_{\mathrm{PYHS}}^{\infty}(k)[\tilde{C}^{\infty}(k)/\tilde{C}_{\mathrm{PYHS}}^{\infty}(k)]d\mathbf{k}\;. \tag{43}$$

Recall that (Sec. III)

$$\tilde{C}_{\mathrm{PYHS}}^{\infty}(k)=C_{\mathrm{PYHS}}^{\infty}(r=0)\tilde{\omega}(k)$$

and that for a Green's-function potential (GFP) (Sec. V) we have

$$\tilde{C}^{\infty}(k)=-\beta A(a_{\mathrm{WS}})\tilde{\omega}(k)\tilde{\phi}(k)$$

to get

$$\Delta_{\mathrm{GFP}}\Longrightarrow\left[-\tfrac{1}{2}\beta(2\pi)^{-D}\int\tilde{h}_{\mathrm{PYHS}}^{\infty}(k)\tilde{\phi}(k)d\mathbf{k}\right]\times\frac{A(a_{\mathrm{WS}})}{C_{\mathrm{PYHS}}^{\infty}(r=0)}\;. \tag{44}$$

For an inverse-power potential (IPP), r^{-n}, with $\Gamma\propto\beta\rho^{n/D}$ denoting the usual coupling constant, we obtain

$$\Delta_{\mathrm{IPP}}\Longrightarrow\left[\tfrac{1}{2}(2\pi)^{-D}\int\tilde{h}_{\mathrm{PYHS}}^{\infty}(k)\frac{\tilde{C}^{\infty}(k)/\Gamma}{\tilde{\omega}(k)}d\mathbf{k}\right]\times\frac{\Gamma}{C_{\mathrm{PYHS}}^{\infty}(r=0)}\;, \tag{45}$$

where the integral is a finite constant. In general we obtain

$$\Delta\Longrightarrow\beta U_2(\rho)/C_{\mathrm{PYHS}}^{\infty}(r=0)\to0\quad\text{as }\eta\to1 \tag{46}$$

with $U_2(\rho)$ some function of the density.

Thus, all three seemingly different theories, the HNC, SMSA, and VPY share the same Madelung energy

$$u_{\mathrm{HNC}}^{\infty}=u_{\mathrm{SMSA}}^{\infty}=u_{\mathrm{VPY}}^{\infty}=\beta u_M(\rho) \tag{47}$$

(e.g., $-\frac{9}{10}\Gamma$ for the OCP) which is an exact lower bound for the true potential energy of the system considered.

Considering the leading correction to this universal behavior it is instructive to deal first with the $D=3$ case. Denoting $\epsilon=1-\eta$ we use the Wertheim-Thiele solution[26] of the PYHS equation in $3D$ to find

$$Z_c^{\infty}\sim\epsilon^{-3},\;f_c^{\infty}\sim\epsilon^{-2},\;Z_v^{\infty}\sim\epsilon^{-2},\;f_v^{\infty}\sim\epsilon^{-1}\;,$$
$$C_{\mathrm{PYHS}}^{\infty}(r=0)\sim\epsilon^{-4}\;. \tag{48}$$

In view of (48) and (46) the leading term in Δ is of order ϵ^4, i.e., $\Gamma\epsilon^4$ for the inverse-power potentials. The leading correction to the VPY Madelung energy term is of order[g] ϵ^3, and thus dominates Δ. The net result is that the asymptotic high-density energy functional, to first and second order, is identical for all three theories (HNC, SMSA, VPY) and is of the following general form:

$$\frac{1}{\beta}u_{D=3}(\rho,\epsilon)=u_M^{(D=3)}(\rho)+u_1^{(D=3)}(\rho)\epsilon^3+\cdots\;. \tag{49}$$

The explicit expressions for $u_M(\rho)$ and $u_1(\rho)$ are given by Eq. (15) of Ref. 9(c)—in which the VPY theory for $D=3$ has been considered in some detail.

The general D-dimensional result is expected to be of the form[41]

$$\frac{1}{\beta}u_D(\rho,\epsilon)=u_m^{(D)}(\rho)+u_1^{(D)}(\rho)\epsilon^{(D+3)/2}+\cdots \quad (50)$$

$u_M^{(D)}(\rho)$ can be evaluated by using the results of Sec. III without resort to the full solution of the PYHS equation, while in order to calculate $u_1^{(D)}(\rho)$ a more detailed solution is required. Fuller discussion of this feature will be given elsewhere.

C. Analytic form of the strong coupling equation of state for inverse-power potentials

The analytic form of the strong coupling EOS is determined (by the variational condition) from the excess entropy functional $S(\epsilon)$. To be specific consider the inverse-power potentials, r^{-n}, with the coupling constant $\Gamma\propto\beta\rho^{n/D}$, and let us begin with the VPY theory employing the PY-viral excess entropy $S_0(\epsilon)$:

$$f_{\rm VPY}=\Gamma(A_0+A_1\epsilon^{(D+3)/2}+\cdots)+S_0(\epsilon)\ , \quad (51)$$

where

$$S_0(\epsilon)=\begin{cases}B_0\epsilon^{-(D-1)/2}+\cdots\ , & D\neq 1 \quad (52a)\\ B_0\ln\epsilon+\cdots\ , & D=1 \quad (52b)\end{cases}$$

with the constants $A_0,A_1,\ldots,B_0,B_1,\ldots$, depending on the dimensionality D and on the power n. Note that (51)—(52) represent a generalization for arbitrary D of the discussion in Refs. 9 and 10. The generalization of (48) for arbitrary D is[41]

$$Z_c^\infty\sim\epsilon^{-D},\ f_c^\infty\sim\epsilon^{-(D-1)}\ (D\neq1),\ \ln\epsilon\ (D=1)\ , \quad (53a)$$

$$Z_v^\infty\sim\epsilon^{-(D+1)/2},\ f_v^\infty\sim\epsilon^{-(D-1)/2}\ (D\neq1),\ \ln\epsilon\ (D=1)\ , \quad (53b)$$

$$C_{\rm PYHS}^\infty(r=0)\sim\epsilon^{-(D+1)}\ . \quad (53c)$$

Recall (from Ref. 17 and Sec. III) that the following relations hold for the PYHS theory in the AHDL.

$$g_{\rm PYHS}^\infty(r=R,\epsilon)\sim Z_v^\infty\ , \quad (54a)$$

$$\partial f_v^\infty/\partial\epsilon\sim g_{\rm PYHS}^\infty(r=R,\epsilon)\ , \quad (54b)$$

$$C_{\rm PYHS}^\infty(r=0)\sim[g_{\rm PYHS}^\infty(r=R)]^2\sim(Z_v^\infty)^2\ . \quad (54c)$$

In analogy to (54b) we define $g_0(\epsilon)=\partial S_0(\epsilon)/\partial\epsilon$ and use (39) and (51) to obtain the AHDL result

$$\Gamma\sim g_{\rm PYHS}^\infty(r=R)g_0(\epsilon)\ . \quad (55a)$$

Expression (52) yields $g_0(\epsilon)=g_{\rm PYHS}^\infty(r=R)$ and thus

$$\Gamma_{[{\rm Eq.}(52)]}\sim[g_{\rm PYHS}^\infty(r=R)]^2\ , \quad (55b)$$

so that the AHDL expression for the potential energy takes the following form:

$$U_{\rm VPY}^\infty\sim A_0\Gamma+\Gamma O(\epsilon^{(D+3)/2})\sim A_0\Gamma+O(\Gamma^{(D-1)/2(D+1)})\ . \quad (56)$$

For $D=3$ we retrieve the $\Gamma^{1/4}$-type correction[9,10] to the Madelung term.

In one dimension ($D=1$) the PYHS $c(r)$, $g(r)$, and thus the "viral" and "compressibility" equations of state are exact, so that the VPY free energy represents an exact lower bound to the free energy for any density and temperature. In the AHDL it gives the exact harmonic behavior $A_0\Gamma+\frac{1}{2}$ with the Madelung energy of the linear equally spaced lattice.

The leading AHDL behavior of the SMSA and HNC entropy is given by the logarithmic term L which contains, as a Γ-independent term, the result for the PY theory for hard spheres, for which $Z_c^\infty\sim L_{\rm HS}^\infty\sim\epsilon^{-D}$. The AHDL free-energy functional for the SMSA and HNC has a form similar to that for VPY, $S_0(\epsilon)\sim\epsilon^{-D}+\Delta S_0(\Gamma,\epsilon)$. The variational condition now yields $\Gamma\sim\epsilon^{-(3/2)(D+1)}$ with an energy of the form

$$U^\infty\sim A_0\Gamma+O(\Gamma^{2D/3(D+1)})\ . \quad (57)$$

This gives a $\Gamma^{1/2}$ correction to the leading Madelung energy in three dimensions—in agreement with the analytic and numeric (SMSA and HNC, respectively) results for the OCP. The Madelung coefficient A_0 is the same for VPY, HNC, and SMSA. The coefficient of the correction term $\Gamma^{2D/3(D+1)}$ may be different for HNC and SMSA because of possibly different contributions from $\Delta S_0(\Gamma,\epsilon)$. An example for the contribution of $\Delta S_0(\Gamma,\epsilon)$ in the SMSA for the 3D OCP is given by MacGowan.[42]

Finally note that if the MSA hard-core diameter R is fixed by imposing thermodynamic consistency between the virial and compressibility equations of state (the TC-MSA model) we must obtain $g_0(\epsilon)\sim g_{\rm PYHS}^\infty(r=R)$, so that an expansion of the type (56), as for the VPY, is obtained. In analogy to this result for the MSA, the modified-HNC (MHNC) theory with the PYHS bridge functions will feature the same type of an expansion if thermodynamic consistency is imposed to determine the parameter R (the bridge parameter, this time). This result can be immediately checked for $D=1$ in which all the theories considered in this section give the exact AHDL result. In $D=1$ the exact AHDL bridge function for any potential is given by that for the PY theory for hard rods.

VIII. SUMMARY AND IMPLICATIONS

In this work we considered the asymptotic high-density properties of the most widely used theories for classical fluids. The HNC, SMSA, and VPY, along some of their variants (MHNC, TC-MSA), have been considered as models for purely soft interactions (without hard core). The PY theory and the MSA have been considered as models for hard core and hard core containing interactions, respectively.

For soft interactions we find that all theories discussed lead to the same Madelung energy which constitutes an exact lower bound to the true potential energy of the system. This Madelung energy can be evaluated either by solving a boundary value problem or by employing the PYHS pair functions. In the AHDL all theories discussed feature the generally unphysical property of a space-filling excluded volume regime [namely $g^\infty(r\le 2a_{\rm WS})=0$] corresponding to $\eta=1$—which is, however, the exact result in one dimensional ($D=1$). In turn, we found that the asymptotic analysis also leads to a well-defined meaning for the direct correlation functions for both hard-core potentials (via the PY=MSA equation for hard spheres) and soft, Coulomblike, interactions (via the charge-smearing idea and the SMSA). In addition to uncovering these basic features of the theories—with various implications to be discussed below—our novel analysis of the AHDL sheds new light on the mathematical problem of solving the MSA integral equations and on the resulting analytic structure of the solutions. Thus we were able to find, for the first time, the general analytic form of the PY-DCF's for hard spheres in any number of dimensions and to present a general solution of the MSA for any Green's-function potential. Our results have numerous implications, some of which are listed below. We hope to discuss these in greater detail in the future.

A. Equation of state for mixtures

The generalization of our AHDL analysis to mixtures is straightforward, with the results (19) and (25) carrying over their physical-geometrical meaning. The main technical points to note are the following: The functional L is generalized to

$$L=1/2\rho(2\pi)^{-D}\int d\mathbf{k}\ln\det(\overset{\square}{1}-\overset{\square}{C}) , \tag{58}$$

where $\overset{\square}{1}$ is the unit matrix and the elements of $\overset{\square}{C}$ are $\rho(x_i x_j)^{1/2}\widetilde{C}_{ij}(k)$ while x_i denotes the mole fractions. The condition (15) is generalized to

$$[\widetilde{C}^{\infty}_{ij}(k)]^2=\widetilde{C}^{\infty}_{ii}(k)\widetilde{C}^{\infty}_{jj}(k),\quad \widetilde{C}^{\infty}_{ii}(k)\le 0 \tag{59}$$

while (16) is replaced by a set of equations given in Ref. 17. In the AHDL the total excluded volume is equal to the total volume, i.e., total packing fraction equal to unity for the effective hard cores

$$\eta=\sum_i x_i\eta_i\equiv\sum_i x_i\rho\int_{r\le R_{ii}/2}d\mathbf{r}=1 . \tag{60}$$

This leads to the following types of "one-fluid" equations of state for the mixture (in the AHDL) depending on the type of the interaction.

(i) Volume additivity for non-Coulombic soft potentials (without background): ($\vartheta=\rho^{-1}$)

$$\vartheta(\rho,\tau)=\sum_i x_i\vartheta_i(\rho,\tau) . \tag{61}$$

(ii) Ion-sphere model for multicomponent plasmas:

$$\vartheta_i=\left[Q_i\Big/\sum_i x_iQ_i\right]\vartheta , \tag{62}$$

$$\rho\vartheta=\sum_i x_iP_i(\vartheta,T)\vartheta_i . \tag{63}$$

(iii) van der Waals—like one-fluid model for the hard-spheres mixture in the PY approximation:

$$Z_i\to(1-\eta)^{-D}\ \text{as}\ \eta\to 1\ \text{with}\ \eta=\sum_i x_i\eta_i . \tag{64}$$

B. Statistical thermodynamics of charged objects

For the Green's-function potentials the functional $\mathscr{F}[c]$ which depends only on the relatively structureless DCF is a good approximation of the free energy and yields accurate structures upon functional differentiation (i.e., the MSA integral equation). In analogy to calculating ground-state energies for an Hamiltonian using physically suggestive parameterized trial-wave functions, the smearing idea provides a physically intuitive trial DCF ("wave function") for the functional $\mathscr{F}$ (the "Hamiltonian"). The simplest trial DCF is of the form

$$\overline{C}(r)=-\beta A(R)\int\phi(|\mathbf{r}-\mathbf{r}'|)\omega(r',R)d\mathbf{r}' . \tag{65}$$

With $\mathscr{F}[\overline{c}]$ representing the excess free energy, we fix $A(R)$ by $\overline{C}(r=R)=-\beta\phi(r=R)$, while the optimization $\partial\mathscr{F}[\overline{c}]/\partial R=0$ determines the "smearing" diameter $R(\beta,\rho)$. This procedure yields $R(\beta,\rho=0)=0$, $R(\beta,\rho\to\infty)=2a_{\mathrm{WS}}$, so that the energy $U=\beta(\partial\mathscr{F}[\overline{c}]/\partial\beta)_R$, interpolates (very effectively) between the exact low-density (RPA) and high-density ("particle smearing") lower bounds. This approximation has been fruitfully applied to plasma mixtures.[5] It forms the basis for the treatment of the isotropic-nematic transition of line charges.[6] Being physically intuitive, relatively simple, and of expected reasonably high accuracy, this novel approach may serve as a starting point for a statistical thermodynamic treatment of nonspherical-charged objects [e.g., micelles, viruses, and DNA (deoxyribose nuclei acid) fragments in aqueous solutions]. By increasing the number of free parameters the model can be upgraded—providing eventually the exact solution of the SMSA.

C. Statistical thermodynamics of nonspherical hard particles

The basic physical meaning of the PYHS DCF's as overlap volumes between two particles as function of their distance (and relative orientation if they are axially symmetric) may serve for hard particles the role of the smearing for charges. For a collection of (e.g.) hard ellipsoids, consider a discrete representation in which a fraction x_i of the particles point to the $\hat{i}$ direction relative to some fixed direction in space. In the PY approximation we have

$$Z_c=1/\rho(2\pi)^{-D}\int d\mathbf{k}\ln\det(\overset{\square}{1}-\overset{\square}{C}) , \tag{66}$$

where the elements of $\overset{\square}{C}$ are $\rho(x_ix_j)^{1/2}\widetilde{C}_{ij}(\mathbf{k})$. Instead of solving the full structural problem by variation

$$\delta Z_c/\delta C_{ij}(\mathbf{r})=0,\quad \mathbf{r}<\mathbf{R}_{ij} \tag{67}$$

where $\mathbf{R}_{ij}$ is the vector of closest approach of two objects with given $\hat{i}$ and $\hat{j}$, we may parametrize the functions $C_{ij}(\mathbf{r})$ taking into account their basic geometric meaning. The result (S1) namely that the PY hard-core equation of state diverges a total packing fraction equal to unity is general for any system of hard convex molecules.[43] It is noteworthy that many proposed equations of state for such systems, based on scaled-particle theory or Y expansion,[44] do incorporate such a feature. The geometric meaning of the DCF's should be useful also in the context of the interaction-site models.[45]

Note, finally, that because the SMSA, on the hand, and the PY theory on the other hand provide reasonably good approximating functionals for the free energy of soft interactions and the pressure of hard-core interactions, respectively, by means of the *same* functional $\mathcal{F}$, it is much more difficult to deal with charged hard particles in the regime where the steric hard core is comparable to the smearing length (the charge-effective hard core).

ACKNOWLEDGMENTS

Parts of this work have been done during my sabbatical at University of California, Los Angeles (UCLA). I thank Professor W. M. Gelbart for his warm hospitality, constant encouragement, and valuable discussions. I am grateful to Professor H. Reiss and Dr. H. E. DeWitt for stimulating discussions, and to Professor G. Stell for sending valuable material. This work was supported in part by National Science Foundation Grant No. CHE-80-24270.

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where $\epsilon(k)$ is the dielectric function and R_c is the "core" parameter.

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$$c(r)=c(0)+[2\pi\rho\tfrac{1}{2}R^2g(r=R)\Delta C(r=R)]r+\cdots$$

where ΔC is the jump discontinuity of $c(r)$ at $r=R$.

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